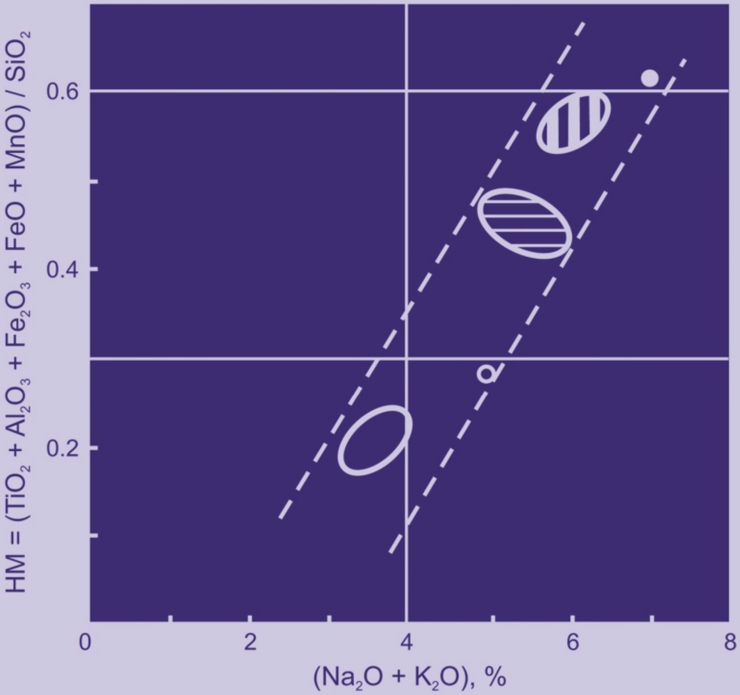
Ya. E. Yudovich, M. P. Ketris

FUNDAMENTALS OF LITHOCHEMISTRY



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Ya. E. Yudovich, M. P. Ketris

FUNDAMENTALS OF LITHOCHEMISTRY

Executive editor
Dr. habil of Geology and Minerology Sciences,
Full Professor L. V. Makhlaev

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Reviewers:

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Yudovich Ya. E., Ketris M. P.
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Lithochemistry is a branch of sedimentary rock geochemistry. The subject of lithochemistry is the distribution of rock-forming chemical elements.

Based on the development of a data bank of about 35 thousand carefully verified silicate analyses, the theoretical foundations of lithochemistry are outlined, its main empirical regularities are formulated, examples of solving actual global problems of lithochemistry are shown, practical recommendations on computer processing of analytical data are given, promising areas of further research are outlined.

The book «FUNDAMENTALS OF LITHOCHEMISTRY», published in Russia in 2000 is very popular in Russia (it has a high impact factor). Unfortunately, it is still unknown to the Western reader.

This book contains a huge factual material on Russia and the former USSR (136 tables and 102 figures), completely unknown to the Western reader, a new chemical classifica-tion of rocks, as well as an original method of computer pro-cessing of chemical analyses; all this is also unknown in the West. The publication of the translation of this book will make all this factual and theoretical wealth available to the Western reader.

The book is necessary for specialists dealing with geochemistry and ore genesis of sedimentary rocks and their analogues.

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РОССИЙСКАЯ АКАДЕМИЯ НАУК
Уральское отделение
Коми научный центр
Институт геологии

Я. Э. Юдович, М. П. Кетрис

ОСНОВЫ ЛИТОХИМИИ

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Рецензенты:
В. Н. Шванов, доктор геолого-минералогических наук, профессор;
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Ю. А. Ткачев, доктор геолого-минералогических наук, профессор

Юдович Я. Э., Кетрис М. П.
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Литохимия - раздел геохимии осадочных пород. Предметом литохимии является распределение породообразующих химических элементов. На основе разработки банка данных, насчитывающего около 35 тыс. тщательно выверенных силикатных анализов, излагаются теоретические основы литохимии, формулируются ее главные эмпирические закономерности, показываются примеры решения актуальных глобальных проблем литохимии, даются практические рекомендации по компьютерной обработке аналитических данных, намечается область перспективных исследований.

Книга необходима специалистам, имеющим дело с геохимией и рудогенезом осадочных горных пород и их аналогов.

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Dedicated
to the 275th anniversary
of the Russian Academy of Sciences

FOREWORD

The term “lithochemistry” is just as legitimate as the term “petrochemistry” since the Greek words “petra” and “lithos” mean the same thing – “stone”. However, the geological tradition classifies “stones” (i.e., earth materials, rocks) generated by endogenous high-temperature processes as *petrology*, and “stones” formed near the Earth's surface as *lithology*. According to the N. M. Strakhov’s testimony [250], such a division of sciences emerged in 1916–1922, when universities began to teach independent courses in petrography of sedimentary rocks, and subsequently courses in lithology (which is called *sedimentology* in the West).

Following this tradition, ***we call lithochemistry (by analogy with petrochemistry) the part of geochemistry that deals with the issues of the gross chemical composition of sedimentary rocks and their analogues[1].*** As a sister (possibly illegitimate!) of petrochemistry, lithochemistry occupies the same borderline position in geological sciences - between lithology and geochemistry.

The subject of lithochemistry lies in distributing rock-forming chemical components of sedimentary rocks and their analogues. As is well known, such components are determined in a complete silicate analysis: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, CaO, Na_2O, K_2O, P_2O_5, CO_2, H_2O, S, and LOI (loss on ignition). Sometimes Cl, F, B, Ba and some other rarer components are added to this list.

For a quarter of a century since the beginning of systematic lithochemical studies (approximately since 1975), we have collected more than 30 thousand silicate analyzes (with careful verification of analytical sums and rejection of low-quality analyzes). This number also includes several thousand of our analyzes performed over 30 years (1967-1997) during the regional research project implementation of the Institute of Geology, the Komi Scientific Center, the Ural Branch of the Russian Academy of Sciences (earlier - the Komi branch of the USSR Academy of Sciences). As an *independent research project*, lithochemical research was formed at the Institute of Geology only in 1994, and it matured in the depths of regional geochemical research before.

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[1] Analogues of sedimentary rocks, in accordance with the newest "Systematics ..." [238], we will call modern unconsolidated sediments and parametamorphites.

The rapid development of physical methods for the analysis of matter led to the fact that already in the 1960s in the USSR (and in the West - a decade earlier), silicate analysis of sedimentary rock became available to any geologist: it became an ordinary method used in geological survey not only for large, but also for medium scale. At this time in the regional geochemical research practice of the Pechora Urals [295], the methods of petrochemical analysis of sedimentary rocks began to be widely used, which required an easy-to-use and formally correct *chemical classification of sedimentary rocks.*

The first version of this classification was published in 1986 [302]. By this time, the classification had already passed a fairly significant practical test on the Paleozoic strata material of the Elets (paleoshelf) structural-formational zone of the North of the Urals. Subsequently, the boundaries of individual taxa changed somewhat, and the terminology was refined and improved. However, these changes were not fundamental: the classification turned out to be quite viable. This circumstance served as an “internal criterion of truth” for us and prompted a wider application of the lithochemical technique for processing not only regional, but also global data.

The first, according to the general opinion, quite successful experience of such processing was the monograph "Geochemistry of Black Shales" [300], where the total composition of all black shales in the world (including their metamorphic equivalents) was first considered on a single methodological basis – in terms and boundaries of chemical classification. This approach made it possible to correctly compare the chemical composition of the black shales of the Earth in the geological age range from the Catarchean to the Holocene. At the same time, practice has shown that chemical taxa do not have a full-fledged "mineralogical" replacement. Further we will see that taxa which are presented as mineralogical [261], in fact, remain chemical.

In 1977–1985 lithochemical studies have already become an important part of regional geochemical works within the research projects: "Sedimentary formations of the Pai-Khoi and the prospects for their ore potential" (1977–1981) and "Sedimentary formations of the Lemva zone of the North of the Urals and the prospects for their ore content" (1982–1985). In these studies, one of the main problems was the petrochemical diagnostics of volcanic admixtures in sedimentary rocks, generated both by surface explosions (Carboniferous strata) and underwater exhalations (typical for manganese-bearing Upper Devonian strata).

The results of petrochemical diagnostics of volcanic material [71, 74, 206, 297] aroused considerable interest of geologists, which can be judged by the "resonance" in the references [62–67, 108, 114, 118, 119, 170, 190–192, 237, 256]. In particular, the efficiency of the *module diagrams* use has been confirmed, i.e., graphs, whose coordinates are proposed by us (and by our predecessors), the ratios of oxides – petrochemical modules.

In 1986—1993, lithochemical problems were further developed within the framework of the scientific theme "Geochemistry of black shale formations in the North of the Urals and Timan" — based on the material of ancient metamorphic strata of the Polar, Subpolar Urals and Timan[2]. Here we encountered not only the traditional problem of diagnosing the primary (premetamorphic) substrate of metamorphites [75, 111, 177, 310, 315], but also with the need to identify the phenomenon of *allochemical metamorphism*, which can greatly complicate the diagnosis of the substrate. It was unexpectedly found that among the metamorphic strata of the Subpolar Urals, alkaline metasomatites are widespread - rocks contrastingly enriched in potassium or sodium [309].

Finally, in 1994–1998, as already mentioned, lithochemical research has for the first time become a priority and is developed in two blocks: global and regional.

In the regional block, the old problem of *convergent hydrolysates diagnostics* unexpectedly came to the fore, once sharply raised in the remarkable book by V.N. Razumova [220]. The essence of the problem lies in the significant similarity between the products of leaching and hydrolysis of two different genetic types – exogenous (metamorphosed weathering crusts) and endogenous (hydrothermal-metasomatic formations – argyllizites and secondary quartzites).

In the Subpolar Urals, in the zone of interformational contact "uralides/ preuralids", rocks-hydrolysates have the form of various metamorphic slates: sericite, paragonite, pyrophyllite, chloritoid, hematite and diaspore slates. However, the genesis of hydrolysates is not clear due to convergence: they can also be metamorphosed formations of the ancient (Cambrian) weathering crust on the substrate of the preuralides complex, and various Paleozoic metasomatites. The extreme urgency of this "academic" problem is given by the fact that all the manifestations of gold, palladium, diamonds, rare and rare-earth elements, manganese, metamorphosed bauxites and iron ores discovered here in recent years are confined to the zone of intraformational contact [111, 186–188]. The methods of lithochemistry should play a primary role in solving the problem of the metal-bearing hydrolysates genesis [111, 304, 308].

So, to date, lithochemical problems have already found reflection in a whole series of our works: preprint brochures [178, 301, 302], articles [71, 130, 132, 206, 288, 298, 299, 301, 304, 308- 310, 312, 315, 317] and monographs [74, 111, 295, 297, 300). The wide interest of geologists in lithochemistry (for example, [114, 192, etc.]) prompted us to hold an All-Russian School of Lithochemistry in Syktyvkar in 1997.

Thus, there is a need to generalize everything that has been done in the theory and practice of lithochemistry, to which this book is devoted. It outlines the general theoretical foundations of lithochemistry (part 1)

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[2] The work on Timan was performed by our graduate student L.I. Oparenkova.

and briefly highlights some of its global problems (part 2). We propose to devote special works to a more detailed elaboration of these and other problems [301, p. 22–25].

The proposed book may be of interest to two categories of readers. For some (for example, geochemists), only theoretical questions and generalizations will probably seem important, while factual material may seem superfluous and even difficult to read. For others (for example, lithologists), specific examples of interpretation of a very abundant factual material may turn out to be interesting. To satisfy the interests of both readers' groups, part of the text is printed in small print: the former can skip it when reading without compromising understanding, while the latter, on the contrary, may find useful information in these fragments.

LIST OF ABBREVIATIONS

Act – actinolite
Anat – anatase
Bt – biotite
Chl – chlorite
Hem – hematite
Hsl – hydromica
Mont – montmorillonite
Ser – sericite
Shm – shamosite
Qu – quartz

INTRODUCTION

FROM THE HISTORY OF LITHOCHEMISTRY: CHEMICAL CLASSIFICATIONS

The impetus for the lithochemistry development in the 1960s of the twentieth century was intensive research in the field of the metamorphic rocks' primary (pre-metamorphic) substrate reconstruction [183, 184, 211, 212, 222, 223, 246, 352]. This work stimulated the chemical composition research of unmetamorphosed sedimentary rocks. For the reconstruction purposes, "metamorphic" geologists needed some template – the chemical compositions of the main lithotypes. And it immediately became clear that since the appearance of the first report by F. Clarke, the geochemistry of the rock-forming components of sedimentary rocks has made very little progress: there was surprisingly little reliable data. In addition, there are many unmetamorphosed sedimentary rocks, the correct diagnosis of which is very difficult without chemical analysis. Such, for example, are very many "black shales", crypto-grained phosphate rocks, etc. Thus, by the end of the 60s it became clear that in the field of classical lithology, chemical analysis is an important and often a decisive tool in the hands of a geologist.

However, the processing of chemical analysis data requires the use of some sort of classification grids. Having obtained, for example, an analysis of a sandstone containing SiO_2 66%, Al_2O_3 11% and K_2O 3%, the geologist must *interpret* it by comparison with known template. This requires a *chemical classification*, which may not coincide (or partially match with) with traditional lithological systematics.

Chemical classifications appeared in the works of the geochemistry's classics; later, geochemists, petrologists and lithologists worked on them [302, p. 4–7]. We can subdivide these classifications into complete (the entire set of sedimentary rocks is classified) and incomplete (only part of the set is classified).

V.M. Goldschmidt's classification. According to the predominance of rock-forming elements, five groups of sedimentary rocks were distinguished:

1) siliceous (more precisely - silicacerous) - Si; 2) clay - Al, Si, K; 3) ferrous - Fe; 4) carbonatic Ca, (Mg); 5) evaporitic - (Ca), Na, (K, Mg).

Classification of Finnish geochemists K. Rankama and T. Sahama. It differs from the Goldschmidt's classification taken as a basis only in that one more group is added – carbonaceous "black shales", often enriched in pyrite, sometimes also with an increased content of manganese[1].

B. Mason's classification. It forms the basis for an extensive compilation of 2,842 chemical analyzes of sedimentary rocks by the US Geological Survey for the Western states: Colorado, Kansas, Montana, Nebraska, South and North Dakota, and Wyoming [333]. The classification is based on four characteristics, of which the first three are normative: 1) clay — $R_2O_3 \cdot 3SiO_2 \cdot nH_2O$; 2) free SiO 2; 3) carbonates ($CaCO_3$+ $MgCO_3$); 4) all other components.

According to the number of the first three normative components, the rocks are divided into three large categories: a) normal (more than 90 %), b) mixed (90–50 %) and c) specialized (less than 50 %). The author emphasizes the conventionality of the "specialized" rocks border. These rocks often fall into the category of mixed breeds. Normal rocks are additionally subdivided on a triangular plot, where the contents of more than 75 % of each component correspond to the groups of clay, siliceous and carbonate rocks, and the three fields in the middle of the triangle correspond to three groups of such mixed rocks, in which two components exceed the third in content, but do not reach 75 %.

Thus, the "normal" rocks prevailing in the sedimentary shell are divided into six groups. In addition, two subgroups are distinguished in the group of carbonates according to the 90 % content of the normative carbonate.

The "specialized" category includes all sedimentary ores. According to the predominance of the leading components, it is divided into 8 groups.

H-group (aluminous rocks) with a module (in wt. %) SiO_2/Al_2O_3 from 3.00 to 0.00, with a more fractional division into three subgroups:

H_K (kaolinite clays) – 3.00–1.766; H_a (high-alumina clays) – 1.768–0.371; H_b (bauxite and bauxite clays) — 0.371—0.0.

A group (stone salt) – more than 50 % NaCl.

C-group (gypsum) – more than 50 % of gypsum $CaSO_4 \cdot 2H_2O$ or anhydrite $CaSO_4$.

S-group (sulfate, sulfate-carbonate and nitrate rocks) – more than 50 % of Na and Mg salts.

P-group (phosphorites) – more than 21.1 % P_2O_5, which corresponds to 50 % fluorapatite $9CaO \cdot 3P_2O_5 \cdot CaF_2$.

Fe-group (ferrous rocks) – more than 50 % Fe_2O_3 or FeO.

Mn-group (manganese rocks) – more than 50 % MnO.

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[1] In fact, black shales with only noticeable carbonate content can be manganese [300, p. 208; 303, p. 263].

M-group (mixed) are those of the "specialized" rocks in which none of the "special" components reaches 50 %[2].

B. Mason's classification attracts scientists because it draws attention to sedimentary ores, i.e., sedimentites of contrasting composition – sharply enriched in one component. As is known, the presence of such formations is a specific feature of the sedimentary shell – the generation of the Earth's biosphere [51].

At the same time, there is no logic in the fact that some contrasting rocks, such as carbonate or siliceous (containing, for example, more than 90 % $CaCO_3$ or SiO_2), fell into one group, while others, no less contrasting (with MnO, Al_2O_3, Fe_2O_3) - to another group, only because the latter are less common. This means that, *implicitly*, B. Mason used another basis in the classification – the relative abundance of sedimentary rocks. Of course, such a pragmatic approach is rather convenient, but it is hardly correct. Note also that we do not know any other examples of using B. Mason's classification, except in the status report by T. Hill and others more than thirty years ago [333]. This may indirectly indicate that the classification did not take root, remaining "the subject of a one-time use".[3]

Classification by H. De La Roche and M. Roubaud. The authors built it on two parameters, in which the contents of only three components were used: (Al/3 – K) and (Al/3 – Na). The graph with these coordinates shows the points of the compositions of both sedimentary and volcanic rocks, forming fields with very indefinite boundaries. It is not surprising that this classification has not become widespread.

A.A. Marakushev's classification [168]. It is also built on two parameters using three components, but instead of aluminum, the author used SiO_2

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[2] A good example of such rocks is the phosphate-bearing black shales of the Permian Phosphorium formation, consisting of three "normal" (siliceous, carbonate, clay) and two "specialized" (phosphate and carbonaceous) components [300, p. 111].

[3] This is the fate of many flawlessly logical classifications, which nevertheless must be completely rejected by practice. For example, the classification of nodules proposed by us [287], as far as we know, has never been used by anyone. From it, only one term has penetrated the scientific literature – *concrezoids* (for example, [153]). The reasons for the adoption or rejection of the classification innovations are completely irrational – as well as any innovations in the language. For example, as pointed out by Korney Chukovsky ("Alive as Life" – M.: Molodaya gvardiya, 1962) in the 1920s, three words appeared in the youth jargon: razdevalka (instead of "dressing room"), stolovka (instead of "dining room") and chitalka (instead of "reading room.") The first word firmly entered the literary language (now no one would think to pronounce or write "dressing room"), and the other two were rejected, and remained jargon. Nobody can explain the reasons for this.

and (Na_2O+K_2O). As you know, both parameters are basic for petrology as they reflect two fundamental features of rocks - silica acidity and alkalinity. The classification is intended for the taxonomy of igneous and metamorphic rocks. Since there are many primary sedimentary rocks among the latter, the classification could also be used for sedimentary rocks. However, the SiO_2 content should not be used without normalization; it is better to use a normalized value like silicon-aluminum, femic or hydrolysate modules.[4] While retaining the value of silica acidity, such modules allow to consider the contents of other important sedimentary rock components.

A. Simonen's classification [352]. It was intended for the primary substrate diagnostics of metamorphic rocks. It is a graph plotting the composition points of the metamorphic rocks of the Svecofennian complex in Southwest Finland. Two parameters (without a special name) are depicted along the axes of the graph – simple (abscissa axis) and complex (ordinate axis): *simple parameter* – Niggli's numerical characteristic S; *complex parameter* – a combination of Niggli's numbers: (al – fm) – (c + alk).[5] On the diagram, in these coordinates, the fields of primary compositions of metamorphic rocks were distinguished: carbonate (I), volcanic (II), clay (III) and sandy (IV).

The A. Simonen's research was of great importance, and not so much scientific as "psychological": it showed that diagnostics of the metamorphites' primary substrate is quite possible if we selected such petrochemical parameters that would reflect the essence of the sedimentary differentiation processes. Thus, E. Peltola followed the example of his colleague. In his work on black shales of the Outokumpu region (for the composition of these rocks, see [300, p. 42], he used A. Simonen's diagram, but instead of (al – fm) used only fm [347]. According to A. A. Predovsky, this innovation corrects "*some of the disadvantages of the A. Simonen's method*" [211, p. 8].

A. A. Predovsky's classification. Also intended for the primary substrate diagnostics of metamorphic rocks. Its author was inspired by the success of A. Simonen, believing that "*A. Simonen's diagram has a certain degree of resolution, conditioned by the purposeful choice of parameters, reflecting to a certain extent the essence of sedimentary differentiation. At the same time, the combination of the parameters al and fm ... leads to a significant overlap*

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[4] See chap. 3 for these modules.

[5] Let us remind the reader that P. Niggli's "numbers" represent some functions of the molecular quantities of the components, –namely: $al = Al_2O_3 \cdot 100/\Sigma$; $fm = [(FeO' + MgO + MnO)/\Sigma] \cdot 100$; $FeO' = Fe_2O_3 + FeO$; $c – CaO \cdot 100/\Sigma$; $alk = \{[0.5 \cdot (Na_2O + K_2O)] \cdot 100)/\Sigma$; $S = SiO_2 \cdot 100/\Sigma$; $\Sigma = Al_2O_3 + 2Fe_2O_3 + FeO + MgO + MnO + CaO + Na_2O + K_2O$.

of sediments and igneous rock fields... and, consequently, to uncertainty in the chemical composition interpretation in this zone" [211, p. 8].

A. A. Predovsky's classification is based on three petrochemical modules, for the calculation of which (as in A. Simonen's case) a preliminary conversion of weight percentages into molecular quantities is required: ***F*** (femicity) = ($FeO + Fe_2O_3 + MgO$) / SiO_2; ***A*** (partial alumina content) = = $Al_2O_3 - (K_2O + Na_2O + CaO^*)$; ***K*** ("*alkali ratio*") = $K_2O - Na_2O$, where CaO^* means the molecular amount of gross CaO, reduced by the value $CaO = CO_2$. Thus, the CaO^* value expresses the "non-carbonate" CaO. The parameter ***F*** resembles the value of fm in P. Niggli (the same numerator), differing in normalization: when calculating fm, the normalization is performed by the sum of all components without SiO_2, and when calculating ***F***, on the contrary, only according to SiO_2.

The graph depicts each composition at the same time by two dots: to the left in ***K-F*** coordinates, to the right in ***A-F*** coordinates. Based on the status report of a significant analyzes number, these plots have contoured fields of typical compositions, which allows to use the diagram for diagnostic purposes.

There was a period (1970–1980s) when A. A. Predovsky's diagram, despite its obvious flaws, was very popular. Now this popularity has greatly diminished: the fact is that A. A. Predovsky's diagram (as well as the diagram of his predecessor A. Simonen!) is characterized by a strong overlapping of fields. So, referring to the diagnostic capabilities of the graph's right field (*A–F*), the Leningrad lithologist V. N. Shvanov wrote [276, p. 133–134]: "*insurmountable difficulties arise when trying to separate the chemical composition of feldspar, feldspar-quartz sandstones, mica sandstones and tuff rocks of acid composition from acid and intermediate magmatic rocks: granites, plagiogranites, diorites and their effusive analogs, since the fields of the latter completely cover the fields of the corresponding sandy rocks*".

Such a situation, on the one hand, reflects the great similarity of the compositions indicated by V. N. Shvanov, but on the other hand, characterizes not entirely successful design of the parameters.

First, the excellent invention of A. A. Predovsky– *the parameter **F** is not universal.* It is good only for petrogenic and pyrogenic rocks, such as basic tuffs and volcanomictic greywackes with an abundance of hydromica-chlorite matrix, and for basic tuffoids with high femicity. In other cases (very numerous), the absence of alumina in the parameter has affect.

Secondly, the attempt to reflect the alkalinity and alumina content of rocks through differences, and not through relationships, is conceptually flawed. It takes us away from the normalized values to a certain number of atoms, the information content of which is often highly questionable.

For example, we get the same value of ***K*** and at K_2O = 3 %, Na_2O = 1 % (***K*** = 64 – 32 = 32) and at K_2O = 6 %, Na_2O = 3 % (***K*** = 128 – 96 = 32). In both cases, the atomic units of potassium are per 32 more than the atomic units of sodium. But the compositions of these rocks are completely different! The first one may correspond to some normal pelitoid (clay rock). The second one is an exotic chemotype – *alkalite* – and can correspond to alkaline tuff or even alkaline metasomatite. At the same time, it is quite possible that the rocks will not show any special differences in the parameter ***F***, which will lead to getting figurative points on the ***K–F*** graph in a close area.

Thirdly (and this is typical for all other classifications with CaO as a parameter), any attempt to construct parameters including CaO inevitably requires normative recalculation. In parameter ***A*** ("partial alumina content"), it is necessary to calculate non-carbonate CaO*. However, following this logic, in rocks with dolomite, magnesite, ankerite, siderite, it would be necessary to calculate the values of MgO*, FeO*, but this is not done (and rightly so). **Below we will see that CaO, as the most important hydrogenic component of sedimentary rocks, is simply contraindicated in their chemical classification**. It should be built in such a way that, immediately separating the "sheep from the goats", i.e., carbonate rocks (CO_2> 20 %) from non-carbonate ones, it can operate with components that do not include CaO. The same attitude (in a milder form) also applies to MgO.[6]

A.N. Neyelov's classification [183]. Like A. A. Predovsky's classification, it is intended to diagnose the primary nature of metamorphic rocks, both primary sedimentary and volcanogenic. It is built on nine parameters, which are functions of the components' contents, expressed in molecular amounts: ***s*** = SiO_2/Σ, ***a*** = Al_20_3/SiO_2, ***b*** = FeO + Fe_2O_3 + MnO + MgO + + CaO, ***m*** = MgO/(MgO + CaO), ***f*** = (FeO + Fe_2O_3)/b, ***t*** = TiO_2/Al_2O_3, ***n*** = K_2O + Na_2O, ***k*** = K_2O/n, ***c*** = $(2CO_2/\Sigma)\cdot100$ %, where: Σ is the sum of all components.

The main classification parameters are ***a*** (7 supergroups and 11 groups) and ***b*** (5 subgroups in each group). The author outlines the composition fields in coordinates ***a–b***, and shows the values of the parameters ***n, k, m*** using special geometric constructions (as in A. N. Zavaritsky's system). In this

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[6] Let us also note an amusing misunderstanding connected with the very construction of A. A. Predovsky's diagram: it illustrates the long-standing thesis of V. V. Belousov about the fundamental "incompatibility" of geology with mathematics. The fact is that, due to the large dispersion of the parameters, *a logarithmic scale* is used for them (0.001-0.01-0.l-1.0, etc.). However, within the logarithmic intervals, the scale is divided into *equal* intervals (1-2-3, etc.) ... No Predovsky followers noticed his gross error (as, obviously, affecting the position of the field contours), and it was reproduced in many publications!

case, the parameter ***n*** (total alkalinity) is used to isolate four classes, and the parameter ***k*** (potassium content) is used to isolate seven families.

A.N. Neyelov's classification and graphs are even more popular than those of A.A. Predovsky. St.Petersburg geologists especially often used them in their works (for example, A.V. Sochava and several others). It is important that the author himself (as well as A. A. Predovsky) successfully used his classification when processing a huge number of metamorphic rocks analyzes [184].

The advantages of the graph by A.N. Neyelov include a good choice of parameters. Thus, the alumino-silica module ***a***, although roughly, nevertheless reflects the clay content of clastic rocks, which allowed A. N. Neyelov to distinguish the fields of sandstones, siltstones and pelites, the boundaries of which mainly coincide with lithological ones. There is no doubt about the fundamental nature of the parameters with alkalis (***n*** and ***k***), traditionally used in petrology. They are clearly better than the ***K*** parameter of A. A. Predovsky. The undoubted merit of A. N. Neyelov is the use of such an informative parameter as the titanium module (***t***), unfortunately in the "unreadable" (non-traditional) form of molecular relations.[7]

Finally, A. N. Neelov, although he continues to use traditional lithotypes, tries to construct a real chemical classification – with the introduction of the appropriate terminclature ("siallites", etc.). However, this attempt is half-hearted; neither A. N. Neelov nor other lithologists or petrologists have ever raised the fundamental question of the relationship between *chemotypes* (taxa of chemical classification) and *lithotypes* (taxa of lithological classification). On the contrary, the possibility of constructing an independent chemical classification was resolutely rejected by the outstanding petrologist A. N. Zavaritsky [106], and nowadays — by the leading Russian lithologists V. T. Frolov [262] and V. N. Shvanov [276].

The considered classifications were complete – they claimed to be the systematics of the entire set of sedimentary and/or sedimentary-metamorphic rocks. Incomplete classifications use chemical composition only for some types of sedimentary rocks.

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[7] In general, the use of molecular relations instead of simple weight percentages is just a relic of the "atomic age romance" when it seemed that using the number of atoms instead of their mass would give us new knowledge. In fact, this is a mirage: atomic (or molecular) quantities are functionally related to weight percentages and, for this reason, are no better than the former. It is no accident that in petrochemistry A.N. Zavaritsky's complex taxonomy and others like it completely fell out of use, superseded by simple binary diagrams, where the coordinates are the components' weight percentages or their module ratios (for example, K_2O-TiO_2, etc.).

Among them, the most important is ***L.V. Pustovalov's classification***, which brought up a whole generation of Soviet lithologists. The L.V. Pustovalov's classification is based on migration ability of sedimentary rocks, "*since only based on this principle it is possible to arrange all sedimentary rocks in a successive classification series, reflecting their" relationship" (paragenesis)* [216, p. 100].

Hence, two different classification bases follow. *"The indicator of the mineral fragments' migration ability is, first of all, their size. Therefore, the size of their constituent fragments should be chosen as the main classification criterion for the class of clastogenic rocks; all other features are subordinate to this class. An indicator of the chemogenic components' migration ability is their chemical composition. Therefore, the main classification feature for a class of chemogenic rocks should be their chemical composition*" (ibid.).

As we can see, L.V. Pustovalov's [216] classification is preceded by genetic constructions: before classifying, we must attribute the rock as clastogenic or chemogenic. Among the "chemical differentiation products" L.V. Pustovalov distinguished *ferrolites, manganolites, barolites, cuprolites, silicolites, phosphorolites, ferrisilicalites, sulfidolites, calcitolites, dolomitolites, celestinolites, fluorolites, sulfatolites, halolites, aqualites, siallites and caustics.*[8]

As you can see, the L.V. Pustovalov's terms are constructed in different ways. Some of them are formed by adding the suffix "*lit*" to the chemical *element* name (phosphorolites, fluorolites, allites), others to the *mineral* name (calcitolites, celestinolites), and still others to the *oxide* name (silicolites). Here we can see some inconsistency. V.T. Frolov is also partly inconsistent, leaving the name "phosphorites" for the phosphate rocks, and for some reason calling the ferrous rocks "ferrito(?)lites", (more logically, of course, "ferrolites" or, even better, — "Fe-oxidolites", using a term from the latest classification of St. Petersburg and Moscow lithologists [238]).

In contrast to L.V. Pustovalov, foreign geochemists B. Moore and W. Dennen proposed a chemical classification not for biochemogenic, but for terrigenous rocks. On the triangle of Si, Al, and Fe atomic amounts, they distinguished families of orthoquartzites, sandstones, subgreywackes, greywackes, and shales [344]. It is difficult to judge the merits of this classification since we do not know the examples of its application.

The classification by M. P. Ketris, also proposed for terrigenous rocks, was an attempt to improve A.A. Predovsky's graph by a kind of "hybridiza-

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[8] Note that we made the first attempt to revive the completely forgotten L.V. Pustovalov's terms in 1986 [302] for several taxa name of our chemical classification, and then V.T. Frolov used many of these terms in his fundamental "Lithology" [261].

tion" it with A. N. Neyelov's graph – replacing the parameter ***F*** with the parameter ***a*** (Al_2O_3/SiO_2). However, a strong overlap of clay rock compositions was also found in the ***a–K*** coordinates on the graph [132].

There are also many lithological works in which the authors use different *normative recalculations* for lithological purposes. Thus, St. Petersburg lithologist V. N. Shvanov, who made a major contribution to the sandy rocks petrography [276] and in recent years headed a team of lithologists who created the latest lithological systematics [238), in 1974 proposed a *service* chemical classification of sandstones, intended to determine their mineral type [275]. For this, according to the data of chemical analysis, four normative components are calculated (feldspars, quartz, clay and "rock fragments", equated in composition to andesite-basalt), and then rather complex graph constructions are performed.

Yu.P. Kazansky's classification (1987) is proposed in the collective work of Siberian lithologists and petrologists "Sedimentary rocks (classification, characteristics, genesis)" [194]. Yu.P. Kazansky has never called this classification chemical, but, according to the author, it is "strictly mineralogical" [194, p. 21]: "*It is proposed to distinguish the largest subdivisions (classes) strictly on a mineralogical basis (the presence of a certain chemically close minerals association). They unite rocks, consisting of 50 % or more of rock-forming minerals of a similar type... The author subdivided the classes according to structural features into families, in which groups of rocks are distinguished*".

The author has distinguished a total of 15 classes (Table 1).

As can be seen from the table 1, ***all classes have chemical compound names, and not mineral names at all***. Only in class 5 the author used the names from the minerals taxonomy – the class (*silicates*) and the division within this class (*aluminosilicates*) — as equals (synonyms) [80]. ***Therefore, at the highest taxonomic level (and here we have classes), this classification is undoubtedly chemical.*** The only difference from the "full-fledged" chemical classification is that here the author set the boundaries for 50 % of the *chemical compound* (for example, $CaCO_3$), and in the chemical classification, the same boundary can be set for the *stoichiometric content of the chemical component* (for example, CO_2) corresponding to the given the content of the chemical compound: 50 % $CaCO_3$ content in the rock exactly corresponds to 22 % CO_2. Obviously, the difference in the method of specifying the class boundary (here the class of *carbonatolites*) is not fundamental — both methods are completely equal.

Table 1

Classes of sedimentary rocks according to Yu.P. Kazansky, 1987 [194, p. 22]

Class	Composition
Allite, or alumina	Gibbsite, boehmite, diasporas, corundum
Silicite, or siliceous	Opal, cristobalite, chalcedony, quartz, etc.
Iron oxide	Hydrogoethite, goethite, hematite, magnetite
Manganese oxide	Pyrolusite, manganite, psilomelan, brownite, hausmanite, etc.
Siallite or silicate-aluminosilicate	Feldspars, clay minerals, including minerals of the glauconite group, chlorites, zeolites, zircon, garnets, fragments of aluminosilicate rocks and volcanic glass
Phosphate	Apatite varieties, iron and aluminophosphates, monazite
Carbonate	Calcite, magnesian calcite, aragonite, dolomite, protodolomite, magnesite, siderite, rhodochrosite, strontianite, malachite, soda, throne, davsonite
Sulfate	Gypsum, hemi-hydrate, anhydrite, celestine, thenardite, mirabilite, astrakhanite, polyhalite, epsomite, kieserite, kainite, etc.
Chloride	Halite, sylvin, carnallite, bischofite, alunite*
Borate	Hydroboracite, colemanite, borax, etc.
Sulfide	Pyrite, marcasite, chalcocite, galena, sphalerite, chalcopyrite
Sulfuric	Native sulfur
Nitrate	Sodium and potassium nitrate
Fluoride	Fluorite (ratovkit)
Hydrocarbon (caustobiolite)	Shaped and structureless components of peat, coal, bitumen and bitumoids

* It is not clear how alunite $KAl_3(SO_4)_2(OH)_6$ got into the chloride class.

PART 1

GENERAL CLASSIFICATION AND DIAGNOSIS

CHAPTER 1

GENETIC TYPING OF SEDIMENTARY ROCKS

1.1. Classification problem

Geologists fully understand each other when using the term “sedimentary rocks”, although its meaning is quite far from the formal logical: not all sedimentary rocks are products of “sedimentation”. For example, eluvial and caustobiolithic rocks are not formally “sedimentary”. However, there has never been a major disagreement in understanding the scope of the term; almost everyone agreed that a "sedimentary" rock is, according to M.S. Shvetsov, ...“*a rock that exists under thermodynamic conditions characteristic of the earth's crust surface parts and is formed because of redepositing various rocks’ weathering and destruction products, chemical and mechanical precipitation from water (as well as from air and ice!* – Ya.Yu., M.K.), *the vital activity of organisms or all three processes simultaneously*" [70, vol. 1, p. 118].

A.F. Belousov gives a different, but nevertheless very close in meaning, definition of sedimentary rock [194, p. 7]: “*Sedimentary rocks of the Earth are non-artificial solid-phase aggregates, consisting of material of terrestrial origin, not directly related to the solidification of melts and the cosmic bodies fall; their formation is localized in the hydro- and atmosphere near the surface of the earth's crust and is associated with the deposition and weathering processes of a solid-phase aggregate*".

The author emphasizes that the central element in its definition is the concept of the **earth's crust surface**, “*which plays a key, controlling role in this system*” [ibid.].

Thus, both definitions emphasize the genetic nature of sedimentary rocks as exogenous formations — exoliths, according to V.T. Frolov [238].

It is known that sedimentary rocks classifications are either genetic (for example, M.S. Shvetsov distinguished 5 classes), or materially-genetic (N.M. Strakhov, N.V. Logvinenko – 10 classes). Only recently, St.

Petersburg and Moscow lithologists by the collective efforts have created a "structural-material classification of sedimentary rocks and their analogs" [238], from which, at least formally, the genetic element was completely excluded. The authors propose to consider this classification as a priority (basic natural science), and all others, built on other grounds, as private (“necessary, but targeted”).

The center of the *classification problem* formulated by the geographer and geochemist V.L. Kozhara [136] is the question of which classification should be considered “priority” or “basic”, and, accordingly, whether one should try to create a so-called natural classification at all.

The classification problem has undergone deep development by a large team of various scientists, united within the framework of the *classification movement*, created and led in our country in the 1980s by V.L. Kozhara [136]. Most of the participants in the classification movement agreed that there are no ideal (basic, natural, priority) classifications. A special scientific analysis showed that natural scientists rarely thought about the *question of the classification* purpose and the quality criteria of the created classifications - the classification process was and in many respects remained intuitive. As a result, writes V.L. Kozhara,

...“*the intuitive criteria of the one whose classification is better do not give hope for the end of the disputes in the foreseeable future. We need rational criteria*” [136, p. 8].

1.2. Four genotypes of sedimentary rocks in the sedimentary shell

Although at least two generations of Soviet lithologists were brought up on genetic and material-genetic classifications, which have recently enjoyed a bad reputation. The harshest criticism of material-genetic classifications we find in prof. V.T. Frolov [262, p. 27]: ...“*The more we study sedimentary rocks, the more obvious it is that it is impossible to combine genetic and petrograph classification in one scheme. Sedimentary rocks are polygenetic, and genesis is not directly correlated with material composition. It is not directly given in observations, but is only restored, most often by indirect signs, and incompletely, often erroneously, with a different, sometimes small degree of probability. Therefore, the orientation in classifications to identify genetic subdivisions most often leads to arbitrary hanging of genetic labels ...*”.

At the same time, the researcher by no means rejects genetic classifications: their huge cognitive role is recognized, and he suggests simply not to mix them with others [262, p. 27]: “*Genetic classifications, which should be built separately from petrograph ones, serve to systematize our knowledge of the rocks origin. They are increasingly participating in scientific knowledge itself as working hypotheses, models of the rocks and ores origin..., accelerating the* *collection and generalization of factual material and providing grounded paleogeological constructions ...*”.

Lithochemistry needs its own "purpose" classification, and it is quite natural that only chemical classification can act as such. However, there is no escape from genetic ideas - after all, even the very term “sedimentary rocks” is already genetic! Therefore, the construction of a "purpose" chemical classification is very useful to presuppose a general genetic typification of sedimentary rocks. *Its purpose* (in full agreement with V.T. Frolov) *is to systematize knowledge about the origin of sedimentary rocks at the highest hierarchical level – the level of the sedimentary shell.*

As V.T. Frolov clearly showed [261], it is necessary to distinguish two sides in the concept of “genesis of a rock”: the formation mechanism and the material source. For example, the definition of “volcanic-sedimentary rock” simultaneously contains information about the formation mechanism (sedimentary) and about the material source (volcanism). The definition “detrital rock” contains information only about the formation mechanism (fragmentation or clastogenesis), and the definition "terrigenous rock" contains information that the material source was the more ancient rocks of the continent.

It turns out that for the purposes of lithochemistry, it is possible to propose a convenient genetic typification of sedimentary rocks, using only one side of the concept of "genesis", namely the *material source* (Fig. 1).

As can be seen from the diagram, only four of the largest genetic types

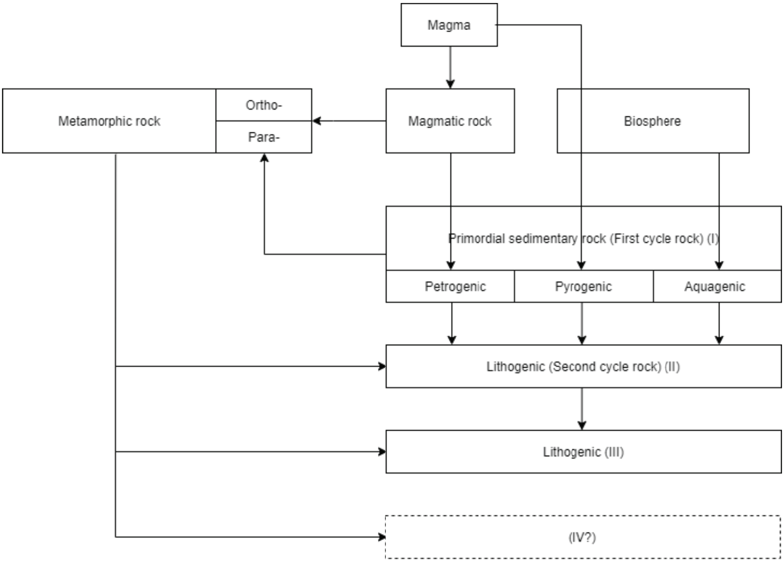

Fig. 1. Genetic typification of sedimentary rocks [301, p. 5]

of sedimentary rocks are distinguished (of course, as M.S. Shvetsov emphasized, there is always a mixed taxon).

Obviously, ***petrogenic*** rocks are petroclastic greywackes and arkoses, ***pyrogenic*** - ash tuffs, ***aquagenic*** – all biochemogenic rocks (carbonate, siliceous, phosphate, eluvial, combustible, saline). ***Lithogenic*** are, for example, lithoclastic greywackes or quartz sandstones, that is, rocks for which older sedimentary or parametamorphic rocks served as source material.[1]

Despite the obvious continuity of this typification with those already existing, it contains two fundamental features.

The first is the separation of primordial sedimentary rocks of the *first cycle rock* type (as they are commonly called in Western sedimentology) from lithogenic rocks of the *second cycle rock* type, formed during the recycling of old sedimentary and parametamorphic rocks. In each new biosphere-lithospheric cycle (II, III and, perhaps, IV?) with a duration of hundreds of millions of years (corresponding to the largest tectonic cycles), the composition of sedimentary rocks becomes more and more differentiated (polarized), moving away from petrogenic greywackes and arkoses, still very close in composition to parental basalts or granites.

The second feature is the giving of a high taxonomic status to pyrogenic rocks – volcanic tuffs. In the existing genetic and material-genetic classifications, they are usually “buried” in the taxon “detrital rocks”, that is, the formation mechanism is given priority over the parent substance. However, for lithochemistry, the second is much more important than the first.[2] In chap. 7–9 we will show that the proposed genetic typing serves as a natural basis for solving some problems of diagnosis in lithochemistry.

1.3. Differences between petrogenic and lithogenic rocks. Recycling processes

Petrogenic sedimentary rocks are closest in composition to the original magmatic rocks, although they undergo some changes in lithogenesis. The history of their formation is a directed process: weathering ⇒ transfer ⇒ sedimentation ⇒ diagenesis (catagenesis), to which the stage of modern hypergenesis (new weathering) can be added. In contrast to petrogenic rocks, lithogenic rocks at least once went through the full cycle

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[1] Note that in 1986 we distinguished only petrogenic and aquagenic rocks with a note about the possibility of separating lithogenic rocks, but the sharp boundary was not carried out between the first and third [302].

[2] It should be noted that L.B. Rukhin, a prominent Leningrad lithologist, suggested the exclusion of pyroclastic rocks from the clastic group back in 1953; he identified four taxa of the highest rank among sedimentary rocks: 1) pyroclastic, 2) clastic, 3) clay, 4) chemical and biochemical (cited from: [238, p. 11]).

"weathering ⇒ transfer ⇒ sedimentation ⇒ diagenesis ⇒ catagenesis ⇒ (metamorphism)[3] ⇒ weathering ⇒ transfer ⇒ sedimentation".

Petrogenic rocks usually preserve the initial correlations of chemical components and, therefore, correlations of petrochemical modules. Thus, they are characterized by a positive correlation between titanium content and iron content (TM – FerM) and a negative correlation between alkalinity and hydrolysability (NKM–HM).

The least altered petrogenic rocks of the *first cycle rock* type are represented mainly by *granitoid derivatives* – arkoses. Such arkoses are recognized by two important features: the presence of biotite and the preservation of plagioclases. They could have formed only under relatively mild weathering – in arid or cold climates – and most often are part of orogenic strata, the accumulation rate of which was high.

For example, the Paleogene (Eocene-Oligocene) arkoses in the Santa-Ilets ridge (Southern California) is richer in plagioclases (22.5 %) than most other arkoses and contains a noticeable amount of heavy minerals (2 %) and biotite (1.3 %). This is explained by the peculiarities of weathering in the drift source (granitoids of the Transverse ridge in the Mojave Desert) [356, p. 197]: "*The preservation of feldspars (particularly plagioclase), plus relatively unstable mafic minerals indicate mild chemical weathering of the source rocks*".

Comparison of the normative compositions of parent rocks, arkoses, and shales nevertheless allows us to conclude that even with such weathering, which is abnormally mild, about half of the original feldspars turned into clay minerals. True, the latter are contained not so much in the arkoses themselves (6.3 %), as in the interbedded shales (64 %). Due to the sedimentary differentiation of matter (the escape of a part of alumina and iron into clays), arkoses turn out to be noticeably more acidic and somewhat less ferrous in comparison with the original granitoids.

Sandstones of the Lower Cretaceous flysch in South Sikhote-Alin can serve as another example of *first cycle rock* type arkoses. As P. V. Markevich notes, they contain a noticeable amount of biotite (in total with muscovite from 1–3 to 5–6 %) [169, p. 30]: "*Only from crystalline rocks could the detrital, very fresh, almost unaltered biotite, which is part of the sandstones, be eroded. It can hardly be assumed that it could have been redeposited more than once, since, being unstable in hypergene conditions, this mineral quickly discolors, decomposes and is replaced by chlorite*".

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[3] In this cycle, the stage of metamorphism is not necessary. Tectonic inversion (uplift following subsidence) of platform sedimentary basins, often with many kilometers of sedimentary strata, can bring unmetamorphosed rocks into the sphere of hypergenesis (weathering) that have not even reached the last stages of catagenesis.

Among the petrogenic rocks are the remarkable sodium arkoses of the Achimov strata in Western Siberia, containing on average 4.6% Na_2O and 2.6 % K_2O. According to the St. Petersburg lithologist B.A. Lebedev,[4] the Achimov strata embraces the deposits of the Berriasian, Valanginian and Hauterivian and is distributed over the territory of almost all Western Siberia. The rock consists (in %) of quartz (27), chlorite + hydrobiotite, which are unusually abundant for arkoses (14), authigenic albite (4), potassium feldspar and relict plagioclase, strongly substituted by hydromuscovite and sericite, possibly paragonite (in sum 50–52). Small amounts of leucoxene, calcite (1 %) and three more calcium accessories – apatite, titanite, and epidote are present. Fragments of rocks amount up to 3 % of the rock. Among them, it is possible to identify medium and basic (?) effusive rocks, as well as problematic silicious rocks (most likely, silicified effusive rocks).

What kind of substrate could give rise to the Achimov arkoses? First of all, we should exclude the basic effusive substances, in which there cannot be so many alkalis (all the more – so much potassium); in addition, they have a much higher titanium content. For example, according to the average data of A.B. Ronov et al. [228], the main effusive rocks have the following titanium module (TM) values:

Geological age of effusives	**TM ($TiO_2/Al_2/O_3$)**
Phanerozoic	0.095
Riphean	0.115
Karelii	0.092
Late Archean	0.070
Catarchean	0.073

Granitoids seem to be more acceptable as a possible substrate of the Achimov arkoses. Thus, according to the clarkes[5] of K. Turekyan and K. Vedepol, the following TM values can be obtained:

Varieties of granitoids	**TM**
Calcium-poor (SiO_2 = 69.13, CaO = 2.21 %)	0.037
Calcium-rich (SiO_2 = 67.21, CaO = 3.54 %)	0.026

Achimov arkoses, however, have a TM significantly higher than granitoids, on average 0.040-0.045. There is nothing impossible in this, since with a distant transfer of sedimentary material (B. A. Lebedev suggests that the drift source was located in

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[4] We are grateful to our friend B. A. Lebedev for providing analytical data for lithochemical processing.

[5] Clarke in Russian geochemistry (introduced by academician Fersman in 1922) means average content of chemical element in the Earth's crust.

the Altai-Sayan folded area), one should expect TM growth characteristic of sandy rocks due to natural sizing (for more details, see Chapter 3).

Let us check, however, one more possibility: could the source region be essentially andesite? Referring to the A.N. Zavaritsky's status report [106, p. 265], we establish that, according to R. Daly (1933), andesites have the following values of the quantities of interest to us:

Andesites	**SiO_2**	**TM**	**NKM**
Andesites in general	59.59	0.044	0.32
Mica andesites	62.25	0.065	0.36

Note. NKM = $(Na_2O + K_2O)/Al_2O_3$.

As you can see, "andesites in general" would be suitable in terms of their titanium content, but it is difficult to understand how the content of alkali feldspars can increase so much during the transfer process (in the Achimov arkoses, NKM = = 0.47–0.48).

As a result, it seems to us the most plausible that during the formation of the Achimov strata, rocks of the plagiogranite type, rich in feldspars and biotite, predominated in the drift source. To clarify this interesting question, it would be useful to study the indicator ratios of trace elements: REE, as well as elements of the Fe group, the distribution of which in acidic (granitoids) and intermediate (andesite) rocks has noticeable differences.[6]

With the aging of sedimentary or sedimentary-metamorphic strata, the petrogenic rocks proportion increases and the lithogenic rocks proportion decreases. According to V. M. Sinitsyn, "*the significant distribution in the Proterozoic sediments of greywackes, arkoses and hydromica clay shales may be not so much a consequence of the special climate of their formation time (dry or cool), but rather a consequence of insufficient processing of this sedimentary rock material by weathering due to its ancient age*" [236, p. 62–63].

The well-known "arkose phenomenon" can serve as a particularly striking confirmation of this idea. As V.N. Shvanov noted [276, p. 179], in the history of the Earth there were two peaks of accumulation of arkose sandstones: one in Karelian and the other even more powerful in the Riphean. Both are genetically related to the global granitization of the earth's crust at the end of the Archean. The resulting granitoids were destroyed during long continental breaks, which apparently corresponded to the Kenoranian (2800–2600 Ma) and Karelian (2000–1900 Ma) first-order diastrophisms [234]. On the contrary, arkoses are not at all typical for Phanerozoy and, according to V.N. Shvanov, "*apparently, they are not found among typical platform deposits*" [276, p. 179].

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[6] The book was in print when prof. B. A. Lebedev told the authors that this diagnosis was fully confirmed by new data.

Recyclization, that is, repeated exposure to the weathering and transfer processes (dynamic sorting of sediment), has several consequences: 1) crushing of debris particles and a decrease in the content of polymineral rock fragments in psammites due to the release of monomineral grains; 2) change in the values of petrochemical modules and break-down of their primary correlation. For example, according to M.A. Beridze [17], on the southern slope of the Greater Caucasus, among the Lower Jurassic sandstones, there are two genetic types: 1) petrogenic quartz, formed due to erosion of subsynchronous quartz keratophyres; 2) lithogenic greywackes, the petrofund of which was a metamorphic basement of intermediate composition. Module diagrams[7] can show that these sandstones are markedly different; The most noticeable differences are in the normalized alkalinity of the NAM, which reflects the feldspar/mica ratio: during the formation of petrogenic sandstones, it decreased, while during the formation of lithogenic sandstones, on the contrary, it increased in comparison with the initial value in the substrate.

Another example is the Cretaceous and Paleogene sandstones of Japan [336]. Some of them have the characteristic features of the *first cycle* rock: a positive correlation between titanium and iron content (TM—FerM modules), a negative correlation between hydrolysate and alkalinity (HM—NKM), and a low (close to the initial) titanium module. The other part (Paleogene sandstones of the upper Shimanto subgroup) with a minimum HM has a higher TM value, which may be a sign of recycling.

Arkose and related feldspar-quartz sandy rocks can form during the erosion of not only granites, but also various acidic parametamorphites – gneisses and crystalline schists. In the first case, arkoses are petrogenic, their recycling in the modern biosphere occurs for the first time (and generates the *second cycle* rock); in the second case, arkoses are lithogenic, their recycling occurs at least a second time (and generates sediments of the *third cycle* type).

An example is the alluvial deposits of the river Neus in North Carolina, which drains Triassic petrogenic and lithogenic arkoses [338]. Recycling of this material in the alluvium of the river Neus and its tributaries in a warm humid climate led to some change in the primary composition of arkoses, however, relatively small. In alluvial sands, quartz is accumulated in the coarsest fractions and the destruction of micaceous rocks, which began in the first cycle, continued – until their complete disappearance. However, it is essential that this process takes place mainly in the young weathering crust, and not during transportation. The strong correlation between the content of micaceous matter and the particle size proves that the formation of fine frac-

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[7] The construction and application of module diagrams will be the subject of our detailed exposition in Ch. 4.

tions occurs due to the destruction of larger ones. W. Mann and V. Cavaroc [338] concluded that the most distinct petrograph effect of recyclization is an increase in the ratio of polycrystalline quartz/felsic rocks. If we formulate this conclusion in terms of lithochemistry, then during arkoses recycling, a decrease in a) the HM hydrolysate module and b) the NKM normalized alkalinity module should be observed due to a change in the feldspar/mica ratio in favor of mica.

The most striking effect of sedimentary differentiation is, of course, the formation of oligomictic quartz sandstones strata. After N.M. Strakhov's fundamental work [249] no doubts stayed that such rocks could form only because of deep chemical weathering of an acidic substrate. However, is a *single* weathering sufficient, or is it necessary to re-weather the sedimentary material? In other words, can quartz sandstones be petrogenic formations of the first cycle type, or are they certainly lithogenic rocks – the product of recycling of older sedimentary strata with a lower quartz content? In this regard, S. Nathan's results are very interesting. He studied the Greenland Lower Ordovician turbidite series in the NW of New Zealand [346]. Very similar rocks are observed on the southeastern coast of Australia, proving the former belonging of the strata to a single basin.

A stratum with a thickness of at least 5200 m and a length of over 400 km fills a trough-type structure. It is an alternation (in a ratio of approximately 1: 2) of argillites and quartz graywacke beds, which, judging by the small fraction of rock fragments, should be more correctly called oligomictic sandstones with chlorite-sericite cement. The presence of ancient detrital zircon, which is treated as plutonic, and the domination of quartz leave no doubt that only granites or gneisses could serve as a petrofund, and the "maturity" of the material indicates the processes of deep weathering.

Was this weathering a single one – directly at the drift source? S. Nathan considers this incredible, given the huge volumes of sediments and its very monotonous nature [346, p. 700]: "*Furthermore, deep weathering would usually result in the formation of kaolinite, but this was apparently absent in the Greenland Group; also, the absence of potash feldspar (which is generally more resistant to weathering than plagioclase) is not easily explained. Apart from these specific objections, however, the Greenland Group cannot be considered in isolation, as the Ordovician sediments of New Zealand and Australia are characteristically quartzose (Cooper 1975), and thus a source of continental dimensions is necessary*".

As a result, S. Nathan concludes that the Greenland series could have formed only because of the recyclization of former sedimentary strata, already significantly enriched in quartz, and the number of cycles was more than one.

One of the recycling reliable lithochemical signs is the sharply increased value of the TM (titanium module). As A. A. Migdisov showed long ago, the TM of clastic rocks increases due to the processes of dynamic material sorting — natural sizing.

For example, processing of twelve analyzes of quartz sandstones and quartzites of the Armenian carbonate-terrigenous sub-platform D_3–C_1 formation [230] shows that these highly siliceous rocks are characterized by hyper-high TM value: the average TM value is from 0.139 to such unusual values as 2.213. Obviously, we are dealing with well-sorted (and, most likely, recycled, lithogenic) clastic material, from which the clay admixture was removed during numerous washings. Probably, this process manifested itself to the maximum in quartzites - the rocks of the least clay and most titanium.

Another example of recycling is the Devonian titanium-bearing sandstones of the Timan [116]. Here, the Middle Devonian deposits (Pizhemskaya formation) are industrially titanium-bearing: they contain, on average, from 2.20 to 8.9 % TiO_2. Our processing of 231 analyses (from I. N. Burtsev) showed that pure quartz sandstones of the Upper Devonian (Yaran Formation) are much poorer in titanium than the Middle Devonian (TiO_2 0.31–1.30 %), but invariably show high TM values from 0.100 to 0.600. When plotting points on the module diagram in the coordinates "HM (hydrolysate module) – TM (titanium module)", a clear negative correlation is found, which reflects the process of sandy sediment natural sizing – washing out of clay and relative accumulation of heavy fractions. All this suggests that pure quartz sandstones D_3 were formed mainly due to the washing and redeposition of sandy sediments D_2 on the shelf and in this sense can be classified as formations of the *second cycle* type.

An even more spectacular example of recycling is the Devonian clay sediments in the Middle Timan, where in 1977 the Ukhta geologists uncovered the ancient weathering crust (WCr) by wells on the clay-carbonate rocks of the Upper Riphean Bystrinskaya formation [213].

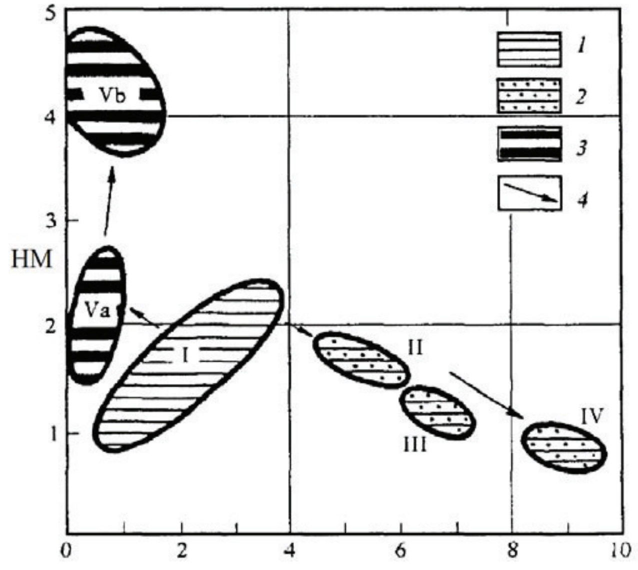
The crust was metamorphosed and almost did not differ in appearance from the calcareous quartz-chlorite-sericite shales of the substrate. For this reason, it became obvious that it could well have been previously unnoticed by geologists, aiming at searching for "obvious" unmetamorphosed bauxite-bearing Devonian-age crusts. Meanwhile, as shown by analyzes (Table 2), the usual type of greenish-gray shales turned out to be true *alkaline hydrolysates* (clusters I-III, V), up to *alkalites* (cluster IV). Even elements of the zonal crustal profile have been preserved: the chlorite-sericite zone at the bottom and the chlorite-diaspora-sericite zone at the top. However, the recycling phenomenon – the involvement of the ancient weathering crust material in a new sedimentary cycle – turned out to be even more remarkable. This process is represented here by two lines (see arrows in Fig. 2).

Table 2

Average chemical rock composition from ancient and Devonian weathering crusts by the substrate of Riphean carbonate-argillaceous rocks in the Middle Timan. *Compiled according to V. P. Abramov et al., 1977* [213, p. 138–139]

Oxides	I	II	III	IV	Va	Vb
	Ancient crust (normo-hydrolisate)	Different types of crusts (alkaline normohydrolysate)	Overlaid crust		Ancient crust	
			Ti alkaline normohydrolysate	Alkalite	Ti superhydrolisate	
n	6	7	4	2	3	3
SiO_2	32.70	39.33	31.20	43.95	27.87	16.67
TiO_2	1.72	1.23	1.97	1.95	2.16	2.89
Al_2O_3	39.31	32.00	36.15	30.15	39.50	47.30
Fe_2O_3	2.33	2.14	10.02	2.12	7.03	10.33
FeO	8.35	9.20	4.27	3.46	9.26	8.28
MnO	0.02	0.01	0.03	0.01	0.02	0.03
MgO	1.45	1.66	1.57	2.32	0.71	0.92
CaO	0.13	0.11	0.27	0.61	0.31	0.43
Na_2O	0.15	0.48	0.19	0.30	0.08	0.10
K_2O	2.06	6.30	5.17	8.66	0.47	0.64
P_2O_5	0.03	0.03	0.24	0.08	0.18	0.18
LOI	11.30	7.06	8.69	6.42	12.60	12.62
Total	99.54	99.54	99.77	100.01	99.66	100.38
HM	1.65	1.14	1.68	0.86	2.14	4.15
FM	0.40	0.33	0.51	0.18	0.61	1.18
AM	1.24	0.81	1.16	0.69	1.47	2.85
TM	0.044	0.038	0.055	0.065	0.055	0.061
FerM	0.26	0.34	0.41	0.17	0.41	0.37
NKM	0.06	0.21	0.15	0.30	0.01	0.02
AlcM	0.10	0.10	<0.10	<0.10	0.20	0.20

Note. 1. In all tables of the same type, the lithological names of rocks (top line) and / or lithochemical definitions (see Ch. 2.5) are given. 2. Roman numerals – clusters, Arabic – compositions outside clusters. 3. n is the number of analyzes.



(Na_2O+K_2O), %

Fig. 2. Module diagram for rocks from ancient and Devonian weathering crusts on the substrate of carbonate clay Riphean rocks in the Middle Timan. *Compiled according to the data of V.P. Abramov et. al., 1977* [213, p. 138–139]. WCr: 1 – ancient; 2 – recycled (Middle Devonian?); 3 – overlaid (Frasnian); 4 – the expected direction of the processes

Line 1 (cluster I ⇒ Va ⇒ Vb) is the formation of a new, Lower Frasnian WCr with boehmite, kaolinite, and late chamosite; the second episode of crust formation led to the formation of rocks more hydrolysate than the ancient WCr.

Line 2 (cluster I ⇒ IV) is the redeposition (in the Middle Devonian?) of the ancient WCr with the accumulation of alkalis in it with a slight decrease in hydrolysability (as it were, a reverse resilicification process with realkalisation) - this is how the Middle Devonian (?) deposits were formed in the upper reaches of the river Tsilma. In this case, the positive correlation between the HM–NKM disappears, which was in the original crust.

It can be assumed that the ancient WCrs involved in recycling were not the same. In some cases, they were significantly micaceous (an increase in the amount of alumina mica is accompanied by an increase in HM, hence there is positive correlation of HM with alkalis). In other cases, the ancient WCr was probably more feldspar (in clusters II–IV, the NKM value is noticeably higher than in cluster I) and was formed on two substrates – less and more titanium (clusters III and II, IV, respectively), which was partly inherited in the newly formed Lower Frasnian crust (clusters Va and Vb, respectively).

As L.V. Anfimov showed by comparing the microdensity of quartz grains, even the Lower Riphean terrigenic strata of the Southern Urals are not petrogenic derivatives of the Archean crystalline basement of the Russian Platform. The clastic material that entered the Riphean sedimentary basin was, in general, recycling product of the Upper Karelian (Lopian-Vepsian) terrigenous strata. This explains the good roundness and poor sorting of quartz grains characteristic of the Riphean clastic rocks.[8]

As we know, in the Riphean stratotype section of the Southern Urals, arkoses and subarkoses sharply dominate. However, extraquartz sandstones appear in the Lemezin Subformation of the Zilmerdak Formation of the Upper Riphean. All researchers who have studied these deposits agree that they are products of acidic substrate's deep chemical weathering. In this regard, we note that the Ural geologists L.V. Anfimov, M.T. Krupenin, and V.G. Petrishcheva have established appreciable distinctions in REE distribution between the Upper Riphean sediments, on the one hand, and Middle and Lower Riphean sediments, on the other hand, and have suggested that the latter were recycled during the Upper Riphean. [7]. Thus, it turns out that the material of the Lemezin sandstones was recycled twice.

It is known that in the section of the western slope of the Urals and the Cisurals, essentially quartz sandstones or sands appear more than once: in sediments O_1 (Telposs, it is also Manitanyrd, or Obeiz formation in the North of the Urals), D_2 (diamondiferous Takatin stratum), D^1_3 (Pashiysk sandstones), C^2_1 ("coal-bearing horizon" at the base of the Visean), J_2 (Sysol formation in the territory of the Mezen syneclise). As N.M. Strakhov has shown long ago, all of them are derivatives of humid weathering crusts – members of *lepigenic sedimentary formations* [294]. At the same time, the participation of quartz grains recycled from more ancient (for example, Riphean) strata in these rocks is quite admissible. However, to verify the correctness of this idea, fine mineralogical and geochemical methods are needed.

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[8] Anfimov L. У. The terrigenous sediments sources in the Riphean basin of the South Urals // Precambrian Eur.: Stratigr., Struct., Evol. Miner.: MAEGS-9: 9th Meet. Assoc. Eur. Geol. Soc. (St. Petersburg, 4—15 Sept., 1995). — St. Petersburg, 1995. P. 1–2.

Brief conclusions

1. The so-called classification problem consists in finding the best basis for classification. Sedimentary rocks can be classified on various grounds. Chemical composition can serve as one of such grounds, especially since many of the existing lithological classifications, upon closer examination, have a chemical (and not mineralogical) basis.

2. Genetic typification of sedimentary rocks permeates all existing classifications, even if it is not specified explicitly. However, it is better to use genetic characters only when identifying taxa of the highest rank. There are four such taxa in total: petrogenic, aquagenic, lithogenic and pyrogenic rocks. When identifying these taxa, only one side of the concept "genesis" is – the material source. In this case, the chemical composition of petrogenic and pyrogenic rocks is still quite close to the composition of magmatic rocks, while the composition of aquagenic and lithogenic rocks can be sharply polarized because of the "sedimentary differentiation" processes [217].

3. Such differentiation during the formation of aquagenic rocks is associated with biochemogenic processes of minerals resynthesis from aqueous solutions, while during the formation of lithogenic sedimentary rocks, the recyclization of previously formed sedimentary or sedimentary-metamorphic rocks occurs in the hypergene process. As a result of such recyclization (which could be repeated in the geological history of the Earth, probably, up to four times?), the chemical composition of some lithogenic rocks (for example, essentially quartz sandstones) can also differ very sharply from the composition of magmatic rocks.

4. An important feature of lithogenic (recycled) rocks is not only the polarization of their chemical composition, but also the violation of correlations between the components that originally existed in magmatic rocks.[9]

5. An excellent criterion for the recognition of lithogenic terrigenous-clastic rocks, the material of which has undergone intensive dynamic sorting, can be the value of the titanium module TM (TiO_2/Al_2O_3).

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[9] As the reviewer of this book Prof. V. N. Shvanov pointed out to us, Yu. K. Burkov's work contain valuable developments on the question of subtle geochemical differences between the endogenous and exogenous material of sedimentary rocks. One of such works is a little-known booklet *Mathematical processing of geochemical data for modeling the structure and genesis of sedimentary strata during regional geological studies. Methodical recommendations* / Yu.K. Burkov. V. S. Pevzner, I. D. Macedon, et. al. – Saint-Petersburg, 1992. – 70 p.

CHAPTER 2

CHEMICAL CLASSIFICATION: GENERAL ISSUES

> *“The disadvantage of any, even the most perfect, system is precisely that it is a system. That is, by definition, for the sake of its existence it must exclude something, to consider something as alien and for as much as it is possible, to equate this alien to non–existent".*
>
> Joseph Brodsky. Journey to Istanbul //
> Joseph Brodsky in the Original Size.
> Leningrad, 1990. P. 28.

It was noted above that lithochemistry needs its own classification of sedimentary rocks, namely, a classification on a chemical basis. After the program article by A.F. Belousov “On the foundations of the effusive rock petrochemical classification” [16], few researchers have any doubts that the chemical composition (and not only mineral) may well be used as the basis for the classification of *magmatic* rocks. The practice of petrology in recent decades also confirmed this conviction – the chemical composition appears in petrology as the first basis for classifications and then appears more than once when taxa of a lower order are identified [23]. Indeed, for magmatic rocks, chemical composition is a fundamental characteristic, on which the mineral-structural characteristics also largely depend.

However, regarding sedimentary rocks, the case seems at first glance completely different. It is far from obvious that for them, the chemical composition is to the same degree a fundamental characteristic as the mineral-structural one[1]. After all, the latter is closely related to the genesis of rocks and seems to be much more significant than the chemical composition.

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[1] G. Rosenbusch’s capital textbook, translated here in 1934, "Descriptive petrography", on which a whole generation of Soviet geologists was educated, says in relation to "layered" (sedimentary) rocks quite unambiguously: *"... the composition of matter [in them] is not in an internal causal connection with the entire material of the rock", as a result of which" their taxonomy cannot rest on such a solid foundation as we have for igneous rocks*"(Rosenbusch, 1934, p. 471; cited from: (238, p. 10]).

Sedimentary rock examples of almost the same chemical composition, but of completely different nature, immediately come to mind: quartz sandstone (clastic terrigenous rock) and phtanite (biochemogenic silicious rock); detrital limestone (detrital carbonate rock) and pelitomorphic limestone (chemogenic or biogenic carbonate rock); quartz sandstone with abundant carbonate cement (clastic rock) and silica limestone (biochemogenic rock) etc. In these examples, the structural (not even mineral) characteristic is so important and the chemical one is so secondary that any idea of the chemical basis of the classification seems absurd.

Leningrad lithologist V. N. Shvanov clearly formulated the question of the chemical classification role in relation to the sandy rocks classification [276, p. 129–130]: "*Since the chemical sandstone composition consists of several material components, and the mineral-petrographic type of sandy rock is established based on the composition and ratios of only clastic components, it will never be possible to create such classification schemes of the chemical composition, which would be identical to the classification schemes built according to the composition of fragments <…> Classification by chemical composition, no matter what parameters based on, cannot be an independent taxonomic and nomenclature system, but only an auxiliary one that translates into the language of chemical elements those categories that are established based on the relationship between actually observed and accounted for debris components*".

V. N. Shvanov justifies such a decisive preference for the mineral-structural classification to the chemical one (and in this matter all lithologists are in solidarity) by the fact that the former reflects genetic ideas, and the latter does not.

Another prominent Russian lithologist prof. V. T. Frolov brings under his criticism the philosophical basis of the "systems approach" [262, p. 27–28]: "*Sometimes, to universalize the separation of sedimentary rocks, researchers classify them according to their chemical composition and passed off as the main ones. However, this violates the main requirement – to subdivide the system (or combine into a system) according to the directly "underlying" level of substance organization. The chemical composition for rocks is not such and can be a systemic feature only for the minerals classification*"[2].

In fact, the examples given by the author and considerations given by lithologists do not discredit the idea of chemical classification. They only tell us the following provisions.

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[2] It remains to sympathize with the philosophically unenlightened petrologists: after all, in modern petrology, classifications have long become chemical, and no one is embarrassed that the chemical composition is not "the underlying level of organization of matter".

First, one should not build a chemical classification as a *substitute* for lithological – a mistake we made in 1986 [302]. ***Chemical classifications are created for the needs of geochemistry, not lithology.***

Secondly, the opposition of even the newest structural-material classifications of V.T. Frolov [261, p. 260] and the team of lithologists [238] to chemical classification is a bluff. The "material composition" refers to the mineral composition, while ***the very systematics of minerals is based on a chemical basis*** (silicates, oxides, phosphates, etc.). We have already seen that all classes of sedimentary rocks in the Yu. P. Kazansky's classification [194, p. 22] are essentially chemical classes. Likewise, could the taxa of V. T. Frolov [261] be not essentially chemical: "I. Oxide. II. Saline. III. Organic. IV. Silicate"?

Finally, thirdly, the chemical classification toolkit should be rich enough to reflect the differences in the rock composition even similar in gross chemical composition[3].

2.1. Some basic principles

As V. L. Kozhara notes, the classification problem "*is complicated by a multitude of a priori truths – ideas fed rather by inner convictions, by faith, than by considerations of a rational nature. There is too much a priori, often not written (hidden between the lines) among classifiers and classification theorists. This axiomatics represents a virgin growth that has not yet been touched by Occam's razor. It is almost obvious that there are fruitless ideas*" [136, p. 13].

There is no doubt that we also have fruitless ideas. We will analyze one of them (the morphostructural basis of the classification) below, in section 2.3. However, we will try to explicate our initial principles so that they do not have to be found "between the lines".

1. Purpose of chemical classification. Why do we need a chemical classification if there are lithological ones, more so if the collective efforts of Petersburg and Moscow lithologists have finally created a modern *structural-material systematics of sedimentary rocks and their analogs* [238], free from the flaws of the previous (genetic and material-genetic) classifications?

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[3] For example, one can easily distinguish quartz sandstone from phtanite by the value of the TM titanium module (with the rare exception of spongolites, the TM of quartz sandstones of the second cycle type is much higher than the TM of phtanites), not to mention the fact that these rocks almost always differ markedly in alkalinity. (NKM of phthanites is higher), in terms of sodium content (NKM of phthanites is higher), in ferrum content (FerM in phthanites is higher), and in the content of TOC (much more in phtaiites). We do not take into consideration trace elements, the content of which (for example, Y, Mo, Se, Cr) phtanite has nothing to do with quartz sandstone.

We must repeat once again: chemical classification is necessary not for lithology, but for geochemistry, namely, for that section of it, which we call *lithochemistry*. It is no coincidence that geochemists created most chemical classifications, not lithologists. The purpose of chemical classification is ***to transform "data" (results of sedimentary rock chemical analysis) into "information".*** This information is genetic – it represents knowledge about the source of the material and the mechanism of sedimentary rock formation [261].

Chemical classification is used in two essentially different situations: a) when there is sufficient lithological information; b) when such information is insufficient or absent.

In the first situation, it provides the lithologist and geochemist with certain *additional information* about the rock – such that cannot be extracted only from lithological data. It cannot claim for anything more in this situation. For example, the increased Mg content of a certain pelitomorphic rock may indicate the presence of a pyrogenic admixture in it and provide a basis for genetic attestation of the rock as a *tuffoid*.

In the second situation, the role of chemical classification is much more significant – it can *partially or completely replace* the lithological one. This is obvious for deeply metamorphosed sedimentary rocks that have completely lost their primary structural and mineral characteristics. That is why chemical classification was in demand primarily in the geology of metamorphism.

However, the literature often lacks elementary lithological information about normal unmetamorphosed rocks; in this case, the chemical certification of rocks *is forced to replace* such information. For example, having an analysis of "sandstone" without additional lithological information, we certify it in accordance with the chemical classification, which makes it possible to largely compensate for the lack of lithological information. Thus, sandstone with HM = 0.23, NKM = 0.42, $Na_2O + K_2O = 4.3\%$, TM = 0.020 is undoubtedly arkose[4].

Very often, geologist gives the definitions of lithotypes in the field (only macroscopically); and in this form they are included in the scientific literature, accompanied by chemical analysis. In this case, the chemical classifi-

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[4] In this regard, let us allow ourselves a lyrical digression on the theme "Oh, times, oh, manners!" We live in a time when the art of identifying and describing rocks under a microscope (both in petrology and in lithology) is dying off before our eyes, but the literature is flooded with a huge number of cheap (and therefore generally available) chemical analyzes. The numbers of optical constants of minerals have almost disappeared from scientific publications (most lithologists of new generations do not know how to determine them), but a rare article is published without a chondrite-normalized distribution curve of rare-earth elements, which was very rare back in the 1960–1970s. Therefore, a modern specialist may not distinguish quartz from acidic plagioclase in thin sections but must be able to correctly process the chemical analysis of the rock.

cation with its precise boundaries makes it possible to significantly clarify (or even completely change) the initial definition of the lithotype. For example, "argillite" turns out to be essentially a silicious rock, an unremarkable "siltstone" turns out to be tuff, etc.[5]

In all these situations, the problem of the relationship between the boundaries of lithological and chemical taxa, that is, *lithotypes and chemotypes*, comes to the surface. We will investigate this problem in detail in Ch. 5.

2. Simplicity and ease of classification. The classification is intended for ordering (inventory) and systematization of many thousands of chemical analyzes of a wide variety of sedimentary rocks and their analogues. One chemical analysis should ideally be sufficient to classify a rock to a particular taxon based on scanty, often insufficient literary data. Therefore, signs of taxa identification should be analytical data or their simple combinations (sums and ratios). From these positions, the classifications operating with molecular amounts of chemical components, or with preliminary calculation of special normative components, seem inconvenient. Normative recalculation is a powerful tool for lithochemistry. However, it should be applied only when necessary – *after lithochemical rock certification*, and not precede it. For example, having an analysis of a highly aluminous metamorphic rock (sericite-chloritoid pyrophyllite shale) with $Al_2O_3 = 30.13\%$ [304, p. 89], we first certify it as a *normohydrolysate* (according to the value of HM = 0.60) and only if necessary, with the help of a normative recalculation, we will determine the content of alumina carriers in it – mica, chloritoid and pyrophyllite.

3. Completeness of the classification. The classification should cover all genotypes of sedimentary rocks – petrogenic, lithogenic, pyrogenic and aquagenic. Some of the previous chemical classifications do not satisfy this requirement, including L.V. Pustovalov's classification.

4. Continuity of the base with one division [274]. This principle is violated in the well–known sedimentary rock classification, which is still taught at universities [159]: 1) clastic, 2) clay, 3) aluminous, 4) ferrous, 5) manganesian, 6) phosphatic, 7) silicious, 8) carbonate, 9) salts, 10) caustobiolites. Researchers distinguish the first group by the sediment formation mechanism, the second – by the particle size, groups 3–9 – partly by chemical, partly by mineralogical composition, and group 10 – by origin and ability to burn. It is noteworthy that this illogicality of the classification, which would

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[5] Our practice counts dozens of examples of this kind, and some episodes of lithochemical diagnostics were of fundamental importance for the geology of entire regions of the North Urals and Pai-Khoi: redefining colored "silica" as tuffoids, "silicious lenses" as highly specific siliceous-chamosite nodules, nothing notable "phtanites" as phosphorites, "quartz sandstones with pyrite" as oligonite nodules, etc. [74, 297].

seem to indicate its imperfection, receives an ideological justification [159, p. 92]: "*When classifying various groups of sedimentary rocks, one should not give preference to any sign over others for the sake of monotony or false harmony*".

5. Consistency (adherence to principles) or conscious application of the iterative "M ⇒ T procedure" (see Ch. 5, Section 5.1). If a new classification basis is given, then it should be adhered to, even if it contradicts tradition. This is the question of the priority of *chemotypes* over *lithotypes*, which we specifically investigate in Ch. 5.

6. Succession. New knowledge is not created from scratch but grows out of the old one. Therefore, no matter how logical the new classification is, the geologist should be able to find traditional types of rocks in it. This first of all requires avoiding excessive purism in terminology.

For example, following the pattern of the names of chemotypes: silites (from Si + LIThos), siallites (from Si + Al + LIThos) – carbonaceous rocks should be called *carbolites* (C + LIThos). However, we preferred to use for them a very apt term by N.B. Vassoevich – *cahytolites* (CArbon + HYdrogen + LIThos), which perfectly expresses the hydrocarbon specificity of biogenic organic matter (OM) fossilized in the sedimentary shell. It has already entered the literature and turned out to be very convenient for a unified description of black shale [300, p. 27][6]. For the same reasons of continuity, deliberately violating the order of naming chemotypes, we have kept in the classification the excellent V. Goldschmidt's chemical and genetic terms – "hydrolysates" and "evaporites".

Similarly, authors of the modern structural-material lithological systematics V.G. Kuznetsov and D.K. Patrunov at first, following the logic, placed in the center of the traditional triangle "calcite–dolomite–clay" a triangle of mixed rocks – "marls", limited by the sides of the 50 % content of three components. However, they had to abandon this beautiful scheme, yielding to the lithological tradition [238, pp. 166–167]: "*This formally correct construction contradicts the traditional definition of marl as a rock in which at least 25 % of clay material, since in the central – "marl"– field will be located and rocks in which the clay content is a few percent. It is this circumstance – 25 %, not the 50 % border – that first of all predetermines the need for an asymmetric division of the classification triangle*".

7. Flexibility is not dogmatic. If the classification claims to be used, then sometimes we need to neglect some of the principles declared in it. Thus,

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[6] Please note that in the newest structural-material "Systematics" of St. Petersburg and Moscow lithologists (238] there is a "carbolites" taxon but these are not all carbonaceous, but only **coal** rocks; carbonaceous rocks of the oil series received their own name - "bitumolites" The fact is that the parent term carbon can mean not only "carbon", but also "coal." No wonder the coal system is called carbon!

when assigning the boundaries of several taxa, we chose those that do not quite accurately provide the condition for a 50 % content of the component.

For example, the 20 % CO_2 border for carbonatolites in most cases means not 50% carbonate, but less – only 44% calcite or 47.7 % dolomite. This "unprincipled" decision ($CO_2 = 20\%$) was made to avoid the loss of a huge number of real limestones and dolomites (which no geologist would name otherwise), which we need to place in other taxa, strictly following the principle of 50 % carbonate. We acted even more "unscrupulously" with the choice of the border for *aqualites* and *cahytolites* – unlike other rocks, here 50% (water and organic matter) was set not by mass, but by volume; we had to consider that the specific gravity of water and organic matter is very different from the specific gravity of ordinary rock-forming minerals.

It is obvious that principle 5, on the one hand, and principles 6 and 7, on the other, contradict each other, but this contradiction is dialectical – one cannot avoid it. Any classifier inevitably finds himself between the Scylla of dogmatism (and this is nothing but unshakable adherence to principles) and the Charybdis of unprincipled eclecticism (and this is continuity and flexibility taken to the extreme)[7].

2.2. Typification of hypergenesis processes as a prerequisite for typification of sedimentary rocks

In a historical review of chemical classifications, we can see different researchers evaluated the significance of chemical composition traits in different ways, giving them unequal weight. Therefore, some characters (for example, the molecular ratio Al_2O_5/SiO_2 in A.N. Neelov) served to distinguish the largest taxa, while others – to identify taxa of the lowest order. Obviously, the prioritization was not arbitrary: the researchers were guided, firstly, by the purposes of classification (albeit not always explicitly), and, secondly, by one or another *a priori information* regarding the set of sedimentary rocks that must be divided into subsets, i.e., classified. L.V. Pustovalov performed such a priori (genetic) information in the clearest form.

Although the extremes of "genetism" are completely alien to us, L.V. Pustovalov's fundamental idea – to classify sedimentary rocks in some correspondence with the processes that gave rise to them – seems to us deeply true and not at all outdated. The task is to set the basis for the classification, which, if possible, would reflect the main processes of the hypergenesis zone – would be *informative* in this sense.

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[7] Recall, however, that of these two monsters, Charybdis is much more dangerous: after all, Scylla ate only six sailors, while Charybdis swallowed the whole ship ... Therefore, the cunning classifier Odysseus ordered his rowers to steer closer to Scylla and away from Charybdis!

Obviously, this idea is by no means original – the creators of all classifications without exception proceeded from similar attitudes [238, p. 8–22] are local researchers, L. V. Pustovalov, V. T. Frolov, A. A. Predovsky and A. N. Neelov. For example, by suggesting parameter ***F***, A. A. Predovsky proceeded from the [212, p. 17] ...“*tendency for the transformation of matter during weathering and sedimentation established in lithology. The first of them is the silica separation from femic components*”.

Thus, the typification of hypergenesis processes is a natural prerequisite for their end product classification – sedimentary rocks.

According to A.B. Ronov [224], the main processes in the hypergenesis zone are hydrolysis, clastogenesis, oxidation–reduction, dissolution, chemo- and biogenic sediments from solutions, complexation and sorption. Clastogenesis is a mechanical process, while others are chemical and physicochemical. Let's try to briefly consider the essence of each process (with the necessary additions) and indicate its result – sediment (sedimentary rock) or its essential components.

Chemical (biochemical) and physicochemical processes

Dissolution (= leaching) – the result is eluvium and karst. The process is of rock-forming importance for weathering crusts; however, as is obvious, it "stands outside the brackets" of the formation of all totally – not only aquagenic, but also lithogenic rocks.

Hydrolysis is the main process for the clay mineral formation. It occurs mainly in weathering crusts, but also during underwater exhalations. Consequently, it is of rock-forming importance in the formation of weathering crusts, as well as all clay and hydroxide rocks, including the formation of ferrum and manganese volcanogenic-sedimentary hydroxide ores. Hydrolysis can proceed with a constant valence of mineral forming elements (for example, Al) or be accompanied by their oxidation (for example, $Ti^{3+} \Rightarrow Ti^{4+}$, $Fe^{2+} \Rightarrow Fe^{3+}$).

Sedimentation with polymerization is the main process for the authigenic silicate formation (for example, glauconite and leptochlorites), which are synthesized from solutions by polymerization of monomeric subunits. The process has rock-forming importance for silicate aquagenic rocks, but, of course, it also proceeds during the formation of essentially terrigenous clay minerals. For example, we can consider the formation of montmorillonite from chlorite as a combination of “dissolution + hydrolysis”: a brucite layer must be removed from the chlorite structure, and water molecules and absorbed cations must be “inserted” in its place. However, these processes are already insufficient for the formation of montmorillonite from pyroxenes and amphiboles, due to the sharp difference in the crystal structures of the substrate and the product. Therefore, it is more probable that montmorillonite is synthesized from solutions in weathering crusts on the basic rocks or basic tuffs. We know that the most widespread clay mineral, dioctahedral hydromica, is chemically closer to the structurally alien trioctahedral biotite, and not to the structurally related dioctahedral muscovite [143]. Therefore, "terrigenous" hydromica should to a large extent be a polymeric product of resynthesis from solutions, that is, partly an authigenic mineral. Finally, authigenic quartz, a rock-forming mineral of silica rocks is also a polymer product (its predecessor was the opal of silica plankton shells and skeletons of sponges).

Simple sedimentation is the main formation process of carbonates, phosphates and other sparingly soluble compounds and, accordingly, a rock-forming process for carbonate and some other rocks[8].

Sedimentation of readily soluble salts due to solvent removal is a halogenesis process that is of rock-forming importance for salt rocks (evaporites).

Oxidation–reduction was of the most important rock-forming value in the Late Archean (Ontarian) and Early Proterozoic (Karelian) [234]. Only in these epochs on Earth were thick strata of ferrous quartzites formed because of oxidation in the hydrosphere (followed by hydrolysis): $Fe^{2+} \Rightarrow Fe^{3+}$. In subsequent epochs, due to changes in the composition of the Earth's atmosphere, the bulk of Fe^{2+} was oxidized on the continents, not reaching the ocean. In the Phanerozoic, the weathering crusts and the diagenetic zone of subaqual sediments became the main arena for redox processes [249]. Accordingly, redox processes played rock-forming role for some hydrolysate rocks (eluvial brown iron ore), nodules and, totally, for sedimentary ores (sulfide, leptochlorite, siderite, sulfuric, etc.).

Sorption (adsorption on the surface + absorption in the volume + chemisorption) does not have an independent rock-forming role, but sometimes it gives the rocks specific features. So, sedimentary iron ores necessarily carry a harmful phosphorus admixture because of the phosphate–ion sorption; natural clay sorbents (montmorillonites and glauconites) are "doped" with admixtures of sorbed metals (Ni, Cr, etc.), the content of which can reach a few percent. A bright illustration of the chemisorption process efficiency is the most powerful concentrations of Ge, Ga, U, V, Cr, Ni in isolated fragments of coalified wood. For example, the Ge content in the ash of such inclusions reaches 8 %, V – 7, Cr – 2.5, Ni – 8.14 %, etc. [291, 292].

Fossilization (conservation) is a process not specified by A.B. Ronov. It is always accompanied by polymerization and is responsible for the accumulation of organic matter (OM) in the sedimentary shell, both terrigenous and

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[8] In this case, it does not matter that this process most often occurs in the tissues of living organisms — this does not change its chemical essence.

aquagenic. As we know, OM accumulates solar energy [51]; it is thermodynamically unstable and can only be preserved in a fossilized state. Therefore, the processes of accumulation of carbonaceous rocks (cahytolites) – coals and black shales – strongly depend on the rate of "mineral" sedimentation and on the oxygen content in the sediment. Cahytolites can be formed either during very rapid burial of OM (coals), or during slow burial, but under anoxic conditions (many black shale-domanicoids) [300].

Mechanical Processes

Clastogenesis, or fragmentation of rocks. By itself, it can only give rise to eluvium; however, since clastogenesis accompanies or precedes all other hypergenesis processes, it has a rock-forming role.

The next four processes, A.B. Ronov did not indicate, although their importance in lithogenesis is enormous.

Granulometric differentiation is the natural classification of particles by size in a water or air environment, for example, the separation of pelitic and aleurite fractions during the flysch formation.

Gravitational differentiation is the natural classification of particles by weight in the same media, for example, the formation of placers.

Natural flotation – the floating of particles heavier than liquid, with the help of air bubbles and other natural "flotation reagents". Even small gold particles can be transported by flotation.

Combination of these processes has the most important rock-forming role – it creates the granulometric spectrum of sedimentary rocks, both petro-lithogenic and aquagenic. Simultaneously with the differentiation of particles by size and specific gravity, they are separated by chemical composition. Therefore, mechanical processes contribute to the further differentiation of the sedimentary rocks' chemical composition in comparison with the average composition of magmatic rocks. As a result of the combination of chemical and mechanical processes in hypergenesis, rocks with contrasting chemical compositions arise: quartz sandstones, bauxite, iron ores, etc.

Mixing of different sized particles, specific gravity and composition is a process that occurs in the alluvium of large rivers with numerous tributaries, in alluvium of intermontane depressions and in the ocean at the continental foothill, where gravitational currents dump their load. If the watersheds, for example, are with granitoids, basic rocks and metamorphic rocks, then in the alluvial sediments a mixture of minerals and rock fragments from all these sources should be expected. Such, for example, is the composition of the psephites of the basal Alkesvozhskaya sequence in the Paleozoic Uralid complex in the Subpolar Urals, which contains fragments of diabases, rhyolites, and metamorphic slates [111].

In addition, mixing occurs in the epicontinental seas during storms, floods, and seaquakes. As a result, already differentiated sediments can become poorly sorted again.

Finally, ice sheets are a particularly potent mixing agent. That is why V.M. Goldschmidt considered the glacial deposits of Scandinavia to be a natural "average sample" of the crystalline rocks of the Baltic shield, that is, he admitted the complete absence of hypergene processes of material differentiation by composition.

A.F. Belousov emphasized the most important lithogenic significance of mixing. He considers it necessary to reflect this in the genetic classification of sedimentary rocks [194, p. 8]: "*An important enlarged genetic subdivision of rocks is the division into classes of fractionates (products of fractionation, decomposition of matter) and mictites* (products of mixing)) <...>? *It eliminates the orientation of petrologists only towards the recognition of fractionation (differentiation), which until recently was almost self-contained. It is clear enough that the mixing factor is much more pronounced at the rock level than at the mineral level, where it is limited by solid–phase mutual solubility (isomorphism). At the level of mineral aggregates (rocks) there is a possibility of unlimited phases mixing*".

So, if mechanical differentiation (and most chemical processes) contributes to the polarization of the sedimentary rocks' chemical composition (their increasing distance from the magmatic rocks' average composition), then mechanical mixing led to the opposite result [183]. And although both tendencies are manifested during the formation of both petrogenic and lithogenic rocks, *lithogenic rocks are as a rule more differentiated than petrogenic ones. Re-entry of material into the sedimentary cycle still more often leads to its differentiation than to mixing.*

2.3. Morphostructural basis of classification: dream and reality

The first version of our chemical classification, proposed in 1986, contained two bases – the *main* chemical and the *additional* morphostructural ones [302, p. 8]: "*Chemical processes (and, accordingly, the chemical composition of sedimentary rocks) are the main prerequisite for classification, and mechanical processes (and, accordingly, structural characteristics) are subordinate, additional prerequisite. This allows us to set a single (chemical) basis for the classification, using a structural characteristic to distinguish taxa of a lower rank*".

We considered it necessary to somehow reflect the clastogenesis in the classification [302, p. 13]: "*The fundamental fact is the presence of debris in sedimentary rocks (the result of clastogenesis processes). True, debris is also present in effusive rocks* (and, we will add now, in eruptive ones)*, but the role* *of this feature in magmatic rocks is immeasurably less than in characterizing sedimentary rocks. The content of fragments in petrogenic rocks* (of course, we will add now, also in lithogenic rocks) *is strongly correlated with the composition of the latter (for example, the series: gravelstone–sand–aleurites–pelites, in which the contents of* A_2O_3*,* TiO_2*, etc. is increasing). For aquagenic rocks, the presence and content of debris carry important genetic information (for example, pelitomorphic and detrital limestones) and, therefore, also have significant classification value*".

Based on this ideology, 11 chemotypes were initially subdivided into two orders in terms of debris content: *stratiform (stratoliths) and non-stratiform (astratolites)*. The latter included all nodules, secretions, clastic dikes, and mineral pseudomorphs based on the remains of fauna and flora. Separately, it was proposed to distinguish the taxon of concrezoids – stratiform rocks indistinguishable from nodules in composition. In turn, stratoliths were subdivided into *families of clastolites* (more than 50 % of fragments) and *pelitolites* (less than 50 % of fragments). The combination of the chemical type with morphostructural orders and families gave a classification grid – 44 *genera*.

It was proposed to indicate both characteristics when determining the kind of sedimentary rock: chemical and structural. For example, detrital limestone should be called *carbonate clastolite*, silica stratal phosphorite – *phosphate–carbonate concrezoid*, etc. (Table 3).

However, the subsequent ten–year practice of lithochemical stud-

Table 3

Classification of sedimentary rocks on two grounds – chemical composition (types) and morphostructural characteristics [302, p. 30]

Types	Morphostructural characteristics			
	Stratolites			Astratolites
	Clastolites	Pelitolites	Concrezoids	
Silites	44 kinds			
Siallites and siferlites				
Hydrolysates				
Alkalites				
Carbonatolites				
Evaporites				
Phosphatolites				
Sulfidolites				
Cahytolites				
Aqualites				
Mixtoliths				

ies showed that the morphostructural branch of the classification immediately dried up – it did not take root on the living trunk of chemical taxa. Therefore, neither the authors themselves, nor any of our followers (for example, E.Z. Gareev, L.I. Oparenkova, M.V. Isherskaya, M.V. Rykus, M.M. Filippov, G.V. Ivensen, Z.I. Petrova, V.A. Makrygina, V.I. Silaev, E.M. Pinsky, etc.) have used morphostructural definitions when using the chemical classification.

The classification-86 was too "romantic": it claimed to replace imperfect lithological classifications. There was no such need and there is no such need; lithological classifications had to be improved (which was done by V.T. Frolov, V.N. Shvanov and others), and the chemical classification should be built as one of the alternatives ("target" according to V.N. Shvanov).

Indeed, if the chemical classification is applied in the presence of sufficiently detailed lithological information, then, due to the additional, subordinate nature of chemical features, it would not occur to anyone to call quartz sandstone "silica clastolite". If it is used when there is a lack of lithological information (when it is most needed), then, although the structural characteristics of the rock can often be "guessed" (for example, to determine that it is quartz sandstone, and not phtanite or jasper), again, there is no need to abandon traditional lithological terms. Therefore, the diagnosis "this hypertitanic supersilite is most likely a lithogenic quartz sandstone of the *second cycle* type" does not make any sense to replace the diagnosis "is a silica clastolite". For the former contains genetic information, while the latter does not, at least not explicitly.

So (according to Shakespeare) "*enterprises of great pith and moment with this regard their currents turn awry and lose the name of action*"[9]. Of course, the idea of a structural coordinate is quite life–giving, but for a lithological proper, not for a chemical classification. It has been implemented with great success in the newest Systematics of Sedimentary Rocks and Their Analogs [238], which specifies 29 material classes, and identifies 4 families (clastolites, pelites, crystalline organolites and intraclasts) are in 11 genera (and subgenera) and 28 species.

2.4. Normative recalculations: strong drug

As already mentioned, elements of normative recalculation are present in many classifications. They cannot be completely ruled out; for example, to set the boundaries of *carbonatolites* or *phosphatolites* chemotypes, one should assign such a content of CO_2 and P_2O_5, which would correspond to 50 % of the normative components (minals) – calcium carbonate and phosphate.

Normative recalculation is an important heuristic tool for the geochemist. For example, in petrology, the establishment of the fact that a rock is over-

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[9] W. Shakespeare. Hamlet. Act 3, Scene 1.

saturated or undersaturated with silica allows one to predict whether it should contain quartz or not. Moreover, a purely technical procedure for the normative recalculation of silica-chamosite nodules forced the construction of two new septechlorite endpoints, which emphasized the specificity of these minerals [289]. The normative recalculation is indispensable for an accurate assessment of the mineral composition of sedimentary rock – when it has already been established at a qualitative level. For example, when examining a thin section of a sandstone, we note the presence of quartz, plagioclase, potassium feldspar and carbonate in the rock and estimate their amount very roughly; recalculating the chemical analysis, we get not only the exact content of these minerals, but we can also write down the mica and carbonate formulas and even determine the number of plagioclases. All this provides important additional information about the rock. For an accurate calculation of the rock mineral composition, we used normative recalculations extremely widely, especially when working on metamorphic strata [75, 98, 111, 178, 297, 308, etc.]

However, the very procedure of normative recalculation has a certain "narcotic" effect. ***The combination of components in stoichiometric ratios (it does not matter whether molecular amounts or weight percentages are used for this) can create the illusion of obtaining new information even when it is not there.***

Examples of this kind are numerous; we will show only one.

A.I. Burago developed a complex method of normative recalculation for terrigenous rocks, based on "*using the ratios of petrogenic elements that make up the minerals of the clay-mica and terrigenous rock fraction*" [36, p. 169]. Previously, by means of statistical calculations, the author established in advance the obvious, namely, that "*almost all petrogenic elements that make up clay minerals are in mutual functional dependence*" [ibid.]. Then he simply postulates that at least 90 % of the gross amounts of MgO and H_2O are contained in the clay fraction. All terrain rocks are divided into two groups using the ratio H_2O^+/H_2O^-: group 1, $H_2O^+/H_2O^- < 6$ – little chlorite and kaolinite; group 2, $H_2O^+/H_2O^- > 6$ – chlorite and kaolinite prevail. Further, for these two groups, the author gives a recalculation algorithm using five auxiliary tables, including the logarithm of some values. As a result, the author calculates the chemical composition and content of the clay fraction in the rock and the normative composition of the clastic part. The latter, in turn, consists of "free" components (SiO_2, Fe_2O_3, K_2O, $TiO_2+P_2O_5$, MnO, TOC) and standard minerals – albite, anorthite, potassium feldspar, calcite and ilmenite.

This whole complicated procedure seems to us very vulnerable to criticism.

Firstly, the initial setting is extremely doubtful – the use of minus water as one of the parameters, i.e., hygroscopic moisture. In the presence of montmorillonite, this value may turn out to be too variable, and then the division of rocks into two groups becomes meaningless.

Secondly, why is a normative recalculation necessary if it does not contain minerals of the clay-mica fraction (kaolinite, hydromica, montmorillonite, chlorite, and sometimes other more exotic ones, for example, palygorskite or glauconite)?

Thirdly, if SiO_2, Fe_2O_3, CORG values can be interpreted as quartz (or chalcedony, opal), hematite and organic matter, then what do “free” K_2O, $TiO_2 + P_2O_5$ and MnO mean? According to A.I. Burago, K_2O means potassium in the absorbed complex. However, it should be K^+, not K_2O, and in addition, the amount of such potassium in the rocks is so small that it should be commensurate with the conversion errors. In the same way, if it is possible to admit the presence of a part of phosphate in the rock in a sorbed (on ferrum hydroxides) form, then apatite is still the obviously dominant form of phosphate in sedimentary rocks, but by no means free phosphate ion. As for MnO, it is, of course, present in most cases in the composition of carbonate and therefore should be presented not in the form of MnO, but in the form of $MnCO_3$.

Fourth, finally, in this strange recalculation, such important components of sedimentary rocks as sulfur and sulfate are missing. Probably, the author, who worked on the Mesozoic or Cenozoic terrigenous strata of the Far East, simply did not come across rocks rich in pyrite or sulfates; but it is obvious that this situation is not a common case.

As a result, we conclude that the A.I. Burago’s technique not only does not have any advantages over routine normative recalculation, but also in principle and procedurally it raises great doubts. The disadvantages of the technique are too obvious to be recommended for use.

2.5. General scheme of chemical classification

So, in order to systematize the chemical composition of sedimentary rocks (sedimentites), in 1986 we proposed a chemical classification [302], an important part of which was the previously developed system of petrochemical modules [295].

We will call a *petrochemical parameter* a certain value of the "absolute" content of chemical analysis components used as a classification border. The ratio of two components or some function of them (for example, two sums), following Academician N.M. Strakhov and many other researchers, will be called the *petrochemical module.*

As a basis for the classification, on the one hand, the authors used the parameters (in mass. %), i.e., certain threshold contents of CO_2, P_2O_5, SO_3, $(Na_2O + K_2O)$, S, C_{org} and some others, and on the other – modules. Thus, the classification algorithm is two-stage. First, taxa are distinguished by parameters, and then the rest of the sedimentary population (where the threshold grades are not reached) are classified by modules.

The chemical classification includes 11–12 main chemical types of sedimentary rocks, and among them there are 2–3 times more classes (Table 4).

Although the authors developed the classification for normal sedimentary rocks, it turned out to be suitable for recognizing rocks of a different genesis. In particular, the classification makes it possible to recognize tuffs and tuffites, as well as effusive rocks. For the diagnosis of volcanic–sedi-

Table 4

The chemical classification scheme of sedimentary rocks and their analogues. According to [302, p. 31] with changes in the part of "classes"

Types	Subtypes	Classes
Silites HM < 0.30	Silites Pseudosilites - $MgO > 3$ %	Hyper-, super-, normo-, myosilites
Siallites and siferlites HM = 0.31—0.55	Siallites and siferlites Pseudosiallites and pseudosiferlites - $MgO > 3$ %	Hypo-, normo-, super sialites and siferlites
Hydrolysates HM > 0.55	Hydrolysates Pseudohydrolysates - $MgO > 3$ %	Hypo-, normo-, super-, Hyperhydrolysates
Alkalites - $Na_2O + K_2O > 8$ %	Ca + Mg + Fe + Mn	Na, K
Carbonatolites - $CO_2 > 20$ %	Na	Ca, Mg, Ca-Mg, Mg (Fe), Ca-Fe-Mg-Mn, etc.
Evaporites - $SO_3 > 20$ %,	Sulfatolites	Ca, Mg, K, Na, Ba, Sr
Cl, Br, J, F> 20 %,	Halolites	Na, K, Mg, Ca
$NO_3 > 37$ %,	Nitratolites	Na, K
$B_2O_3 > 20$ %	Boratolites	Na, K, Mg, Ca
Phosphatolites - $P_2O_5 > 20$ %		Ca, Al, Fe
Sulfidolites - S> 20 %		Fe, Cu, Zn, etc.
Cachitolites - $C_{org} > 15$ %		O, H, N
Aqualites - $H_2O > 20$ %		

mentary and volcanic rocks, the classification provides the identification of "pseudo-sedimentary" rocks subtypes, namely – *pseudosilites, pseudosiallites* and *pseudohydrolysates* – respectively, within the types of silites, siallites and hydrolysates. One can distinguish these subtypes by abnormally high MgO contents. The subtype of ferrous rocks – siferlites – is also largely represented not so much by normal-sedimentary, as by volcanic-sedimentary and volcanic rocks of basic composition. Finally, the taxon of anomalously alkaline rocks (alkalites) is only partially represented by sedimentary rocks (but they are specific and may, for example, be alkaline tuffs); an important part of the alkalite type is made up of alkaline effusive and metasomatic rocks.

So, chemical classification, in addition to being a tool for describing normal sedimentites, also contains criteria for distinguishing them from volcanogenic-sedimentary or volcanic ones. In addition, as the practice of geochemical studies of ancient strata of the North of the Urals (1986–1997) has shown, the classification turned out to be quite suitable for diagnosing the substrate of metamorphic rocks, revealing certain advantages over the well-known classifications of A.A. Predovsky [211] and A.N. Neelov [183].

Any rock of the sedimentary shell contains no more than 18–20 rock-forming components:

SiO_2	FeO	Na_2O	C_{org}	B_2O_3
TiO_2	MnO	K_2O	S	NO_3
Al_2O_3	MgO	P_2O_5	H_2O	SrO, BaO
Fe_2O_3	CaO	CO_2	SO_3	Cl, F

The first five components are quite sufficient to characterize the oxide-silicate petro-, litho-, pyrogenic, and some aquagenic rocks, which are most widespread in the lithosphere. With their help, it is possible to describe the rocks of silicious, clay, sand, as well as aluminum, iron and manganese ores. In the modern material-genetic classification, these groups of rocks are called *silicalites* and *oxidolites* [238]. To describe the indicated sedimentites, one petrochemical parameter is sufficient – the hydrolysate module HM [299, p. 28].

The hydrolysate module (HM) is designed to quantify the two most important hypergene processes – leaching and hydrolysis. During the infiltration of meteoric waters, mobile components are removed from the rocks, including not only alkalis and alkaline earths, but partly also silica. In this case, because of hydrolysis, hydrolysate elements accumulate, which form hardly insoluble hydroxides (Al_2O_3, Fe_2O_3, TiO_2). A measure of this substance's hypergene differentiation process is the ratio between hydrolysates and silica:

$$HM = (Al_2O_3 + TiO_2 + Fe_2O_3 + FeO + MnO)/SiO_2.$$

The non-hydrolysate components FeO and MnO are also included in the module numerator. It is because we cannot reliably judge that the Fe (II) and Mn (II) determined by the analysis of the rock are the primary forms of finding these elements in the sediment. A significant part of them could initially have the form of Fe_2O_3 and MnO_2 and be reducted during diagenesis (and for metamorphic rocks and much later – during metamorphism). Thus, iron should be included in the hydrolysate module, neglecting the fact that FeO is not a hydrolysate component. The same applies to MnO with the addition that MnO can only be a conditional analytical form of expressing the Mn present in the rock.

Only in those cases when the rock contains a lot of carbonates or sulfides with Fe and Mn, the inclusion of FeO and MnO in the hydrolysate module becomes doubtful. For such situations, M.P. Ketris developed special corrections for calculating the HM (only that part of FeO and MnO that is not bound in carbonate or sulfide form, is included in the HM). However, firstly, the very methodological basis of such corrections is not quite clear (because diagenetic $FeCO_3$ can be obtained from Fe_2O_3 that was present in the sediment and, without taking this into account, we will artificially underestimate the hydrolysate module). And secondly, such situations are quite rare. Therefore, it is possible to recommend calculating the hydrolysate module HM without corrections.

Long-term practice has shown that HM is a parameter of rocks, which is more versatile and efficient than the well-known aluminosilica module AM, the scope of which is very limited.

According to the HM module values, one can distinguish three main types of silicon and terrigenous sedimentary rocks, which make up most of the sedimentary shell:

HM	**Rock type**
> 0.30	Silites
0.30–0.55	Siallites and Siferlites
< 0.55	Hydrolysates

The silite type embraces silicious (aquagenic) and substantially quartz (lithogenic) rocks, but, oddly enough, rocks completely quartz-free, but poor in alumina and iron, can also get here. These are specific formations, very rich in magnesium, either pyrogenic (picrite tuffs) or aquagenic (palygorskite clays). The presence of such rocks makes it necessary to provide for the establishment of two subtypes, which differ in magnesian content: silites and *pseudosilites* (MgO > 3 %).

Silite proper are divided into three classes:

HM	**Silite Classes**
< 0.05	Hypersilites
0.06–0.10	Supersilites
0.11–0.20	Normosilites
0.21–0.30	Miosilites

The ***siallite and siferlite type*** is distinguished by HM values of 0.31–0.55. As in the silite type, we can find here volcanic–sedimentary and even volcanic rocks. For their recognition, firstly, the absolute MgO contents are used (*pseudosiallites* and *pseudosiferlites* are distinguished, with MgO > 3 %) and, secondly, the value of the auxiliary ferrous module FerM, which separates siallites from siferlites by the value = 0.75.

Most of the silty-clay rocks, a significant part of the greywackes, and even some arkoses belong to the siallites proper. According to the HM values, it is advisable to distinguish three classes of siallites proper:

HM	Siallite classes
0.30–0.35	Hyposiallites (reduced hydrolysate)
0.36–0.48	Normosiallites (normal hydrolysate)
0.49–0.55	Supersiallites (increased hydrolysate)

Practice shows that hyposiallites are most often not so much clay as clastic rocks (for example, clay siltstones); they are related to myosilites. On the contrary, supersiallites are a natural transition from siallites to hydrolysates. The need to select the supersiallite gradation, i.e., siallites enriched more than the norm in hydrolysate material, is evident at least since earlier the border of hydrolysates was drawn according to HM values = 0.50 [295] and only later it was raised to HM = 0.55 [302]. Practice shows that HM values higher than 0.48 in clay rocks always reflect the content of either aluminous (kaolinite) or ferrous minerals (chamosite, Fe hydroxides). In other words, such clays are genetically related to hydrolysates – weathering crust products.

The isolation of magnesian rocks – *pseudosiallites* – is of exceptional diagnostic importance. As a rule, such compositions are not found among normal sedimentary rocks. In most cases, pseudosiallites are pyrogenic rocks – basic tuffoids or their direct derivatives (for example, bentonite clays). The magnesium carrier in pseudosiallites is chlorite or montmorillonite (less commonly, palygorskite). A rarer, but also very important case is the combination of magnesiality with potassium content, caused by biotite content in the rocks. Such rocks can be either medium petrogenic arkoses or alkaline tuffoids.

The hydrolysate type is distinguished by HM values of more than 0.55. Pyrogenic sedimentary or volcanic rocks can also be present here, which are recognized by their magnesiality, which requires the separation of two subtypes: proper hydrolysates and *pseudohydrolysates* (MgO > 3 %). Note that sometimes even the most genuine hydrolysates on the basite substrate (and even more so, hyperbasite) still retain high MgO contents, for example, hydrochlorite, vermiculite, and montmorillonite clays from weathering crusts. This does not seem strange if we remember that chlorite is essentially a two-phase mineral, and one of its "phases" is hydroxide, $Mg(OH)_2$. An attempt to avoid this by raising the limit of the MgO content, for example, up to 5 %, turns out to be ineffective – the inconvenience of this is greater than the benefit. **In this case, we have an ineradicable defect of any strict classification – the immobility of predetermined boundaries, which otherwise will cut nature "according to the living."** The proper hydrolysates are divided into four gradations:

HM	Gradation of hydrolysates
0.56–0.85	Hypohydrolisates
0.86–2.0	Normohydrolisates
2.1–10	Superhydrolisates
> 10	Hyperhydrolisates

The HM value of 0.85 is typical for such an indicator mineral as kaolinite (note that, theoretically, in pure kaolinite, HM is equal to the aluminosilica module AM), and the lower limit of superhydrolysates is set by the HM value equal to 2; this is the lower limit of the aluminosilica module for industrial bauxite.

The main difference between *hypo*– and other hydrolysates is that the latter must necessarily contain free oxides (or hydroxides) of Al or Fe, while the former may or may not contain them. The scope of “hyperhydrolysate” gradation application is not yet very clear, although it is obvious that such units are high quality Fe or Al ores. Note that if at low MnO contents, which are 0.1–0.3% in most sedimentary rocks, the inclusion or non–inclusion of MnO in the hydrolysate module does not significantly change anything, then in Fe–Mn oxide ores the calculation of HM without MnO would be a gross error.

So, the hydrolysate module HM is the main classification parameter for aluminosilicate and oxide sedimentary rocks, which makes it possible to distinguish three large types of them. One must distinguish all other chemical types simply by the threshold content of one of the components. Such a content (parameter) is assigned in such a way that the standard mineral formed by this component (carbonate, sulfate, phosphate, etc.) is at least 50% by weight of the rock. This threshold value is not reached in silites, siallites and siferlites. There are eight such types in total: alkalites (Na_2O + K_2O> 8%), aqualites (H_2O> 20%), carbonatolites (CO_2> 20%), phosphatolites (P_2O_5> 20%), evaporites (SO_3, Cl, Br, I, B_2O_3> 20%, NO_3> 37%), sulfidolites (S> 20%), sulfurolites (S> 50%), cahytolites (C_{org}> 15%). The ninth type is mixed rocks – mixtoliths, in which more than 50% is accounted for not one, but the sum of two (or more) components.

Alkalite type: the amount (Na_2O + K_2O) is more than 8 %. This type includes not common, but very specific sedimentites with a completely definite genetic load, for example, alkaline tuffs and products of their transformation in epigenesis – zeolite, mica, feldspar, dawsonite rocks.

Indeed, the condition of 8% of the total alkalis requires the presence of at least: albite – 74.0, orthoclase or microcline – 47.6, muscovite – 67.8, analcime – 76.9, phillipsite – 72.7, dawsonite – 74.8, thrones – 17.4 (in %) etc. in the rock. According to the leading element, one can distinguish either two classes of alkalites (K and Na), or three, with the addition of the sodium–potassium (Na–K) class.

Aqualite type: H_2O more than 20%. The term was proposed by L.V. Pustovalov [216], revived by us [302, p. 21] and then V.T. Frolov [261, p. 260]. The border of 20% instead of 50% is explained by the large difference in the density of water and other minerals. It is known that the density of H_2O can be less than one (ice) and more than one (brines); on average, the volume of H_2O can be taken as 2.5 times greater than the volume of rock-forming minerals; therefore, 50% H_2O by volume will correspond to approximately 20% H_2O by mass. The aqualite type includes frozen (icy) rocks and all modern subaqueous sediments saturated with water.

Carbonatolite type: CO_2 over 20%. The term was proposed by L.V. Pustovalov [216]. We [302, p. 21] and then V.T. Frolov [261, p. 260] revived it. The modern structural material "Systematics" [238] also contains such a taxon.

This type includes all carbonate rocks and many "marls", i.e., rocks with a content (according to the classification of G. I. Teodorovich) 30–70 % of the insoluble residue. The designation of the border for the CO_2 content assumes a 50% content of carbonate matter in the rock. However, the CO_2 content in different carbonates differs markedly; accordingly, the threshold CO_2 content is different – from 15.3 % for davsonite to 26.1 % for magnesite (Table 5).

Table 5

The content of CO_2 in the rock with different amounts of carbonate minerals in it [302 p. 22]

Mineral	Carbonate mineral content, %	
	100	50
Calcite or aragonite Ca [CO_3]	44.0	22.1
Magnesite Mg [CO_3]	52.2	26.1
Dolomite CaMg [CO_3] 2	47.7	23.8
Rhodochrosite Mn [CO_3]	38.3	19.1
Siderite Fe [CO_3]	38.0	19.0
DawsoniteNaAl[CO_3] $(OH)_2$	30.5	15.3

Thus, the 20 % CO_2 limit we have chosen is formally too low; for pure limestone, it will only account for about 46% of calcite, and for pure dolomitite, about 48% of dolomite mineral.[10] And yet, setting a low thresh-

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[10] The volume fraction of carbonates in mixed silicate-carbonate rocks is even lower than the mass fraction due to a noticeable difference in the specific weights of rock forming carbonates (on average 2.80 g/cm^3) and silicates (on average 2.65 g/cm^3); therefore even 50% by weight will only be 47% by volume.

old of 20% makes a lot of sense; actually even highly silica or highly sandy limestones and dolomites ***are always macroscopically defined by a geologist as "carbonate rocks".*** Therefore, to call a rock with 45–46% calcite somehow differently (for example, carbonate silite) means in advance to sharply increase the discrepancy between chemotypes and lithotypes, which we would like to avoid.

Using the results of phase "carbonate" analysis [295, p. 26] and considering the mineralogical composition of carbonate rocks, we distinguish eight classes of carbonatolites.

Class 1: calcium (limestone); CaO/(MgO + FeO + MnO) > 3.8.

Class 2: magnesium–(iron)–calcium (dolomite and/or ankerite limestones); CaO / (MgO + FeO + MnO) from 3.8 to 2.

Class 3: calcium–(iron)–magnesium (dolomite and/or ankerite rocks); CaO / (MgO + FeO + MnO) from 2 to 0.8.

Class 4: magnesian (magnesite rocks); MgO> (CaO + FeO + MnO).

Class 5: calcium–iron–magnesium (sideroplesite rocks); (MgO + FeO + + MnO)> CaO.

Class 6: iron–manganese (siderite and oligonite rocks); (FeO + MnO) > > CaO + MgO.

Class 7: calcium–manganese (manganocalcite and phodochrosite rocks); MnO > FeO + MgO.

Class 8: sodium (davsonite rocks); Na_2O >> (CaO + MgO + FeO + + MnO).

Lithology has long practiced the processing of carbonate analysis data by recalculating them into standard minals: $CaCO_3$, $MgCO_3$, $FeCO_3$, $MnCO_3$. In 1986 we proposed a simplified version of processing carbonate analyzes without such recalculation [302, p. 23].

The simplification consists in the refusal of balancing the sum of oxides (CaO, MgO, FeO, MnO) with CO_2 by means of standard recalculation: it is conventionally assumed that these oxides passed into the HCl extract only from the carbonate phase. For highly carbonate rocks, this assumption is correct; However, in rocks with a high yield of insoluble residue (i.r.), for example, carbonate clays (i.r. 75–95 %), some of the MgO or FeO in the HCl-extract is obviously non-carbonate. However, definitions of CO_2 are not always accurate enough for such rocks [295, p. 16], and therefore the normative recount does little to help the cause; there is always uncertainty in choosing the correct conversion sequence, for example, CaO –> MgO –> FeO, or, conversely, FeO –> MgO –> CaO?

The sum (CaO + MgO + FeO + MnO) is taken as 100 %, and carbonate analysis is represented by a point in the equilateral triangle FCM proposed by M. P. Ketris with vertices F (FeO + MnO)–C(CaO)–M(MgO). In the future, instead of an equilateral one, we used a more convenient right–angled triangle for manual work, in which it is enough to postpone only the F and M parameters along the axes. However, in the computer age these and similar handicraft techniques are no longer needed: the computer “does not care” which graph to draw.

The FCM triangle shows the first six classes of carbonatolites out of eight (Fig. 3).

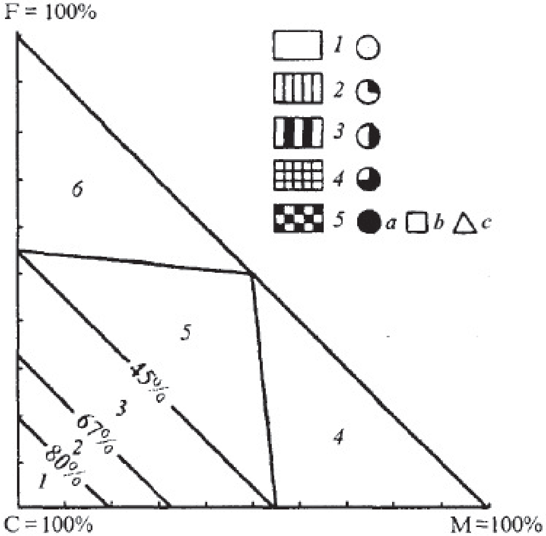

Fig. 3. FCM triangle [74, p. 16].

Classes (fields of composition of carbonatolites): *1* – Ca, *2* – Mg (± Fe)-Ca, *3* – Ca-Mg (± Fe), *4* – Mg, *5* – Ca-Fe-Mg, *6* – Fe-Mn. The legend for rock types within clusters (*left*) and outside them (*right*): *1* – pure carbonate rocks, i.r. ≤10%; *2* – clay (silica, sandy) carbonate rocks, i.r. 10–30 %; *3* – carbonate marbls, i.r. 30–50%; *4* – clay marl (silica, sandy), i.r. 50–90%; *5* – carbonate-free rocks, i.r.> 90% (*a* – clay, *b* – sandy, *c* – silica)

Phosphatolite type: P_2O_5 over 20%. V.I. Luchitsky used the term in 1948 [162] and we revived it [302, p. 23]. L.V. Pustovalov called such rocks phosphorolites, V.T. Frolov first used the traditional term "phosphorites" [261, p. 261], and then, in the newest “Systematics” (238, p. 148], – phosphatolites.[11]

The most common mineral of sedimentary phosphorites is fluorapatite with the formula $9CaO\cdot 3P_2O_5\cdot CaF_2$. Theoretically, it contains 42.2 % of

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[11] We draw the reader's attention to the terminological discrepancy between the tabular inset in the specified monograph (Table II, 5), and the text. On the inset, the authors call the phosphate rocks phosphorolites, and in the text (V.T. Frolov) – phosphatolites.

P_2O_5; therefore, at a 50 % content of this mineral in the rock, the lower border of phosphatolites would be equal to 21.5 % of P_2O_5. However most sedimentary phosphorites are composed of francolite, which also contains an admixture of CO_2 (fluorine-carbonate-apatite); therefore, the P_2O_5 content in francolite is lower than in pure fluorapatite. This allows a “round” figure of 20 % to be assigned as the phosphatolite border.

In the type of phosphatolites, the following classes can be distinguished: calcium (most phosphorites), iron (vivianites), aluminum (aluminophosphates of the vavellite type). The rarer phosphates of vanadyl, uranyl, lead and other elements are hardly rock-forming, so there is no need to isolate the corresponding classes of phosphatolites.

Evaporite type: SO_3, Cl, Br, I, B_2O_3 > 20 %, NO_3 > 37 %. The term was introduced by V. Goldschmidt and was widely used in geochemistry as a genetic one. We revived it for chemical classification [302, p. 23], and then V. T. Frolov used it [261, p. 260]. In the newest “Systematics” this term is replaced by the term "haloliths". According to G.A. Belenitskaya and V.V. Kurylenko, the term evaporites is unsuccessful, since “*it does not cover the entire volume of the considered set of rocks*” [238, p. 199][12]. Evaporites embrace rock and potassium-magnesium salts, gypsum, anhydrite, borate and saltpeter deposits – all these are products of evaporation of solutions in arid lithogenesis. We can distinguish subtypes of sulfatolites, halolites (or galogenolites), nitratolites, and boratolites by anions. Only the first two subtypes are briefly described below.

Sulfatolites subtype: SO_3 more than 20 %. The term was used by L.V. Pustovalov [216], revived by us [302, p. 23] and is used in the newest “Systematics” [238]. This subtype includes gypsum, anhydrite, barite, more rare sulfate deposits, as well as some secondary products of epigenesis, for example, sandstones with anhydrite cement.

It is almost impossible to set the border of sulfatolites in terms of the 50 % content of the sulfate mineral due to the huge difference in the composition of these minerals. Thus, the anhydrite, the richest in sulfate, contains SO_3 almost 2.4 times more than mirabilite (58.8 and 24.9 %); the difference between gypsum and barite is about 13 % SO_3 (46.6 and 34.3 %, respectively), etc. In this situation, the choice of the border should be oriented towards some average value. Thus, at 20 % SO_3, the rock may contain about 43 % gypsum, or about 58 % barite, or about 52 % alunite. It may be more expedient to lower this limit even to 15 % SO_3; this ques-

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[12] In our opinion, the fact that such minerals as halite, barite, or fluorite can be formed not only in the evaporite process is still insufficient basis for to abandon the convenient traditional term. For example, many "black shales" are not black at all, but gray, greenish and even yellow ... [297a; 300, p. 8—11].

tion can be answered only by experience in the application of chemical classification.

As for the classes, in the subtype of sulfatolites researchers easily distinguish them by cations: calcium (gypsum-anhydrite), magnesium (epsomite), sodium (thenardite-mirabilite), barium (barite), etc.

Haloliths (or halogenolites) subtype: Cl (Br, I, F) more than 20 %. L. V. Pustovalov introduced this term. He included only rock and potassium salts (halitolites and sylvinolites). In the newest "Systematics", haloliths also include sulfatolites [238]. We chose the Cl content = 20 %, it is intermediate between bischofite (17 %) and sylvinite (23.9 %), but much less halite (30.3 %). The subtype is easily divided into classes according to Na, Mg, K, Ca cations. It also contains stratiform fluorite deposits of sedimentary or volcanogenic-sedimentary type.

Sulfidolite type: **S more than 20 %**. The term belongs to L. V. Pustovalov [216], was revived by us [302, p. 24], and Yu. L. Verba and V. T. Frolov used it in the newest "Systematics". They point out that "*two ferrous sulfides – pyrite and marcasite – play an essential rock-forming role, that is, they form rocks that consist of more than 50 % of the named minerals. The rest of the sulfides – copper, polymetals, tin, etc. – are found as impurities and rarely form accumulations that, according to the generally accepted nomenclature, could be attributed to the corresponding rock*" [238, p. 237].

This type includes various sulfide phyto- and zoomorphoses, and from stratiform formations – mainly intensely sulfidized "black shales". The choice of the type border is no less controversial than for sulfatolites, since the sulfur content in sulfides differs sharply: from a maximum of 53.5 % in pyrite to a minimum of 13.4 % in galena. In this situation, it is advisable to focus only on the three most common sulfides: pyrite, pyrrhotite and chalcopyrite. The value of 20 % S corresponds to an intermediate value between 27 and 17.5 % (at 50 % content of pyrite and chalcopyrite in the rock, respectively) and almost exactly corresponds to 50% pyrrhotite – sulfide, which is quite typical for many black shales. If necessary, the type of sulfidolites can be divided into classes according to the sulfide-forming metal: iron (pyrite-marcasite-pyrrhotite), copper-iron (chalcopyrite), etc.

In 1986 we assumed that this type should also include deposits of native sulfur [302, p. 24], but that was a mistake.

Sulfurolite type: S more than 50%. The merit of the "sulfuric rocks" separation as an independent taxon belongs to V. T. Frolov, who in the newest "Systematics" called them sulfulites (earlier he called them sulfurites). He's writing: "*Sulfulites are unique: one mineral is rock-forming, and this is native sulfur*" [238, p. 241].

Cahytolite type: C_{org} over 15%. The term "cahyt" was proposed by N.B. Vassoevich [45] instead of the term "organic matter" as abbreviation "ca" (CArbon) + "hy" (HYdrogen). Accordingly, he suggested calling fossilized organic matter (OM) buried in sedimentary rocks (sedimentites) sedicahytes.

It is not easy to determine the border of the cahytolite type, because the OM content or its analytical index C_{org} strongly depends on the degree of sedimentite catagenesis. It varies from 45 % in living phytoplankton to 100 % in graphite. According to the C_{org} content in dry sedimentite, N.B. Vassoevich [46, p. 4] distinguished the following classes of sedimentites:

Classes of sedimentites	C_{org}, mass %
With a highly scattered OM	Less than 0.61
With moderately scattered OM	0.62–2.5
With moderately concentrated OM	2.6–10.0
With highly concentrated OM	10.1–40.0
With highly concentrated OM	More than 40.0

Since the rock containing 50 mass % of the sapropel type OM should contain about 22 % C_{org}, then the border of the cahytolite type will be in "highly concentrated" OM, that is, somewhere between 10 and 40 % C_{org}. However, when identifying the type of cahytolites, we must deviate from the principle of assigning a border of 50% by mass of the component and choose the traditional lithological assignment of the border – 50 % by volume. Actually, the density of fossilized organic matter (cahytes) is much lower than the density of rock-forming minerals. Therefore, the condition of 50 % OM by mass, which is equivalent to the requirement for an ash content of no more than 50 %, is too "tough", and only coals and even far from all oil shale could satisfy it!

If at the beginning of catagenesis we take the average density equal to 1.45 g/cm^3 for OM, and 2.72 g/cm^3 for the mineral matrix (the intermediate value between the average densities of silicates – 2.65 and carbonates – 2.80 g/cm^3), then OM will occupy a volume of 1.876 times larger than mineral matrix. Therefore, 50 % OM by volume is only 26.6 % by weight. With a carbon content 60 % in OM (peat stage), we obtain a 16 % C_{org} content in the rock.

As a result of all these considerations, we have chosen the border of the cahytolite type in terms of the C_{org} content = 15 %, which approximately corresponds to the upper limit of the C_{ORG} content for the black shale–house of Nikites. Note that ***in most black shales, the C_{org} content is much lower.*** For example, the famous oil shale of the Green River Eocene Formation in the United States contains only about 14 % OM or about 11 % C_{org} [300, p. 137].

It would be tempting to expand the scope of the cahytolite type by including the *former cahytolites*, which lost a significant part of their OM during catagenesis. For example, as calculations show [300, p. 15], if the rock with C_{org} = 10 % contains OM of the aquagenic (sapropel) type and is now at the stage of catagenesis G, then at the peat stage it should have contained C_{org} = 19 %, that is, such a rock *was cahytolite*. Unfortunately, this expansion is hardly possible. First, the lithological information accompanying chemical analysis is often so scarce that it is impossible to judge the degree of rock catagenesis. Second, if the loss of C_{org} in catagenesis can still be estimated, then the loss of C_{org} in metamorphism cannot be calculated at all; because of C_{org} "burnout" in redox reactions, any initial C_{org} content can drop to zero, for example, in ferrous quartzites [300, p. 16].

We can perform the division of cahytolites into classes following the traditional separation of “humic” and “sapropel” OM, thus forming the classes of O- (oxygen) and H- (hydrogen) cahytolites. However, N.B. Vassoevich [45] emphasized the insufficiency of such a division. In his opinion it is necessary to distinguish not two, but *three* structural and molecular groups of cahytes: lipid–lipoid (sapropel proper) *aline* (ALiphatic and ALicyclic); protein–carbohydrate *amicahyn* (AMIno acids and CArboHYdrates); *aromatic* (actually humus) *arconic* (ARenas CONdensed). In accordance with this, three classes of cahytolites can be distinguished: H-, N- and O-classes. From this it follows that for a strict classification of cahytolites, it is not enough to determine only C_{org} alone, an elemental analysis of OM with the determination of H_{org} and N_{org} is also required.

Mixtolite type. In rocks of a mixed composition, or mixtolites, the contents of the components listed above do not reach the threshold, but at the same time they are big enough to reflect this in the name of the type by appropriate definition. What does “big enough” mean? If we follow the lithological tradition, then this is either 1/2 or 1/4 of the threshold content. However, there are no strict rules on this score, and the classification of mixed rocks remains largely an informal procedure. As V.N. Shvanov considers [276, pp. 124–125], in lithology *“rocks with three or more components, in which none of the components reaches 50 %, are called mixed. There is no single nomenclature of such rocks <...> The simplest way to name such rocks is enumeration of components in ascending order, indicating percentages, for example, clay (10 %)-aleurite (20 %)- carbonate (30 %) sandy (40 %) rock”.*

In lithochemistry, when assigning the boundaries of the *determinant components*, we proceed more from experience and “common sense” than from formal considerations. For example, $Na_2O + K_2O$ = 5 %, not 4 % (1/2 of 8 % is the threshold value for alkalites) was chosen as the border of the “alkaline” mixtolites. The point is that the clarke values of $Na_2O + K_2O$

for clay shales before the Cambrian and Phanerozoic fall within the interval 3.45–5.16 % [228, pp. 142–144]. Therefore, it makes sense to orient the alkaline mixtolites' border to the upper limit of the clarke interval.

In addition, it is useful to reflect the content of two minor components – titanium and manganese – in the name of any rocks (not necessarily mixed) (Table 6). The boundaries of the sedimentites varieties – titanium and manganese – are also assigned considering their clarkes in shales (0.68–0.90 and 0.10–0.13 %, respectively). The arbitrariness of this choice is obvious, but our practice has shown that the boundaries > 2 % TiO_2 and > 1 % MnO were very successful.

Table 6

The limits of the determinant components' contents, 1988 [300, p. 23]

Determinant component	Content, %	Definition
$Na_2O + K_2O$	5–8	Alkaline
CO_2	10–20	Carbonate
P_2O_5	3–20	Phosphate
$S_{sulphide}$	3–20	Sulphide
C_{org}	3–15	Carbonaceous
Halogens, sulfate, borate	3–20	Chloride, etc.
TiO_2	>2	Titanic
MnO	> 1	Manganese

CHAPTER 3

CHARACTERISTICS OF PETROCHEMICAL MODULES. SIALLITE STANDARD

3.1. Petrochemical modules

The formation of sedimentary rocks in the biosphere leads to the fact that an aquagenic component is necessarily present in them – even in petrogenic and pyrogenic rocks, not to mention lithogenic ones. As for the actual aquagenic rocks, by definition, the aquagenic component in them even prevails over the others. ***The presence of material from both petro-lithogenic and aquagenic roots makes sedimentary rocks initially heterogeneous; this is their fundamental difference from magmatic rocks***[1].

Therefore, the classification of sedimentary rocks simply by the percentage of components, as in the systematics of magmatic rocks (for example, in the coordinates SiO_2 – ($Na_2O + K_2O$)), is suitable only for substantially aquagenic rocks. We saw that taxa – carbonatolites, phosphatolites, etc. – are formed according to the parameters values (threshold concentrations) of CO_2, P_2O_5, SO_3, S, C, which provide 50 % of the normative carbonate, phosphate, sulfate, sulfide, and organic matter. Other components are used only to distinguish taxa of a lower rank.

However, for rocks where the fractions of the petro-litho-pyrogenic and aquagenic components sum are comparable, these two groups of components serve as *diluents for each other.* In such cases, the “absolute” contents of the components are little informative, and we must operate with normalized contents – modules. Researchers traditionally use various modules in petrochemistry (for example, many “numbers” by P. Niggli are modules); among them, for example, is the “agpaite coefficient” $(Na_2O + K_2O)/Al_2O_3$ – in weight percent or in molecular amounts. In lithology, the most popular modules are alumosilica (Al_2O_3/SiO_2), which is often called “silicon”, “Pettijon's maturity coefficient” Al_2O/Na_2O, titanium module TiO_2/Al_2O_3. The inventors of chemical classifications, as we have seen, either use traditional modules

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[1] Exceptions are highly specific rocks such as kimberlites, which contain fragments (and matrix) of magmatic rocks along with fragments of sedimentary and/or metamorphic rocks.

(module ***a*** by A.N. Neyelov), or construct new ones, for example, module ***F*** by A. A. Predovsky.

The need to use modules instead of "natural" numbers of chemical analysis was very clearly argued by the Canadian lithologist G. Middleton in relation to sandstones [343, p. 1013–1014]:

"The original porosity of sandstones is about 20–30 per cent, and consequently the percentage weight of any oxide other than one contained in the cement will be reduced by about 25 per cent if a cement is introduced before compaction. Hence little importance can be ascribed to the weight per cent of any oxides, as quoted in the chemical analysis, without correcting for the introduction of cement. Such a correction is very difficult to make. Even in the case of a carbonate cement, it is not known whether some of the carbonate may not have been present as rock or fossil fragments rather than as introduced cement. The exact composition of the carbonate is also not known. In the case of silica a correction is not possible without a detailed petrographic investigation of the rock. Hence it is clear that ratios between oxides must be studied in preference to actual weight per cent".

Petrochemical modules are artificial structures that are built based on a priori considerations. For example, in the process of weathering SiO_2 and Na_2O are removed and Al_2O_3 accumulates; therefore, the values of the modules Al_2O_3/SiO_2 and Al_2O_3/Na_2O should increase with weathering, and, therefore, their numerical values can serve as a measure of the sediment "chemical maturity".

The information content of a module is determined by its variance: the stronger the latter, the more sensitive indicator of hypergenesis processes this module can serve. However, the ratio variance depends on the numerator and denominator variances, which can be very different. For example, TiO_2 value (in %) in the titanium module (TM) numerator can change by an integer order of magnitude, while Al_2O_3 value (in %) in the denominator, at best, can change by a factor of 2–3, and usually much less. Therefore, the TM value dispersion is determined, as a rule, by TiO_2 dispersion. But in this case why do we need TM at all? Isn't it better to use just an unnormalized TiO_2 content?

Similar reasoning prompted Irkutsk geologists to perform interesting statistical research of the A.N. Zavaritsky's petrochemical coefficients [3]. They found out to what extent the dispersion of the coefficient is determined by the dispersion of the individual oxides included in it. For example, if the coefficient formula includes eight oxides, and its dispersion by 80 % is set by only three determining oxides (as in the formula for the coefficient ***s***), then the other five are simply not needed – they are excessive. Their influence on the coefficients value must not exceed the contribution made by analytical errors.

The research showed that for the group of igneous rocks supersaturated with alumina, the "excess" (i.e., the percentage of excess oxides in the coefficient formula) was for the coefficients ***s, a, b, c, Q*** and ***t*** from 37.5 to

87.5 %. The last figure refers to the coefficient ***c***, built from eight oxides; one can replace the coefficient ***c*** by the CaO content.

The high contribution of the *determining oxide* (at the level of 50–90 % of the coefficient total variance), considering the mutually correlated nature of the change in the rock-forming components, "*explains the confidence of researchers who have been working for a long time with a relatively narrow chemical composition group of rocks <...> who believe that and without recalculations for numerical characteristics, directly from the content of individual oxides, one can see that the rock belongs to the very fractional ranks of A.N. Zavaritsky's system"* [3, p. 31].

As a result, the authors conclude: *"Neither meaningful concepts, no matter how deep they may be, nor the more declarative approach in themselves guarantee the validity of petrochemical expression. Its validity must be proved by a special analysis"* (ibid.).

It might seem that these very strong statements discredit the application of our modules system, since it has not been subjected to mathematical analysis. However, the richest practice of lithochemistry serves as a substitute for "special analysis" for us: it determines the validity of one or another module. Here, we note only two circumstances.

First, the composition of sedimentary rocks itself is immeasurably more varied than the composition of any magmatic rock. A lithologist, getting acquainted with the analyzes of some magmatic series, often thinks that "*this is all the same!*" – so sometimes the differences seem to him so small that petrologists treat them very respectfully. Therefore, in lithology, it is often impossible to determine the rock simply by the leading oxide, for example, by the SiO_2 content. Indeed, if the analysis shows 75 % SiO_2, then it is most likely sandstone (but it can also be a clay-silica shale). But if a neighboring sample showed 60 % SiO_2, this does not mean that we have argillite here: it may just be carbonate sandstone, the non-carbonate part of which contains the same 75 % SiO_2. Of course, the experienced lithologist will immediately perceive several oxides in the analysis; it will not hide from him that in this analysis the CO_2 content or the value of losses at ignition are abnormally high. But the point of a formal taxonomy lies precisely in the fact that it could be used by any specialist – both experienced and beginner. In this simple example, a HM value of 0.18 will immediately indicate that the rock cannot be a clay rock in any way[2].

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[2] At the Pushchino symposium on classiology (1982), a well-known Moscow specialist in the field of mathematical statistics S.A. Aivasian talked about one of the diagnostic systems in medicine: according to a set of a large number of signs (symptoms of the disease), the computer makes a diagnosis. He was asked: "Why is all this necessary if an experienced doctor makes a diagnosis without any computer?" He replied (we do not vouch for the accuracy of the citation, but we guarantee the meaning of the answer): "Yes, this system will not replace a first-class specialist; but it may well replace the average specialist – for this it was created."

Secondly, the excessiveness of some indicator is not an absolute sin – *it can be expiated by its universality*. Indeed, if TM dispersion is determined by TiO_2 dispersion, then for some narrow problem (for example, to isolate clusters by titanicity), TM can be replaced by TiO_2. However, without the TM value, we will not be able to "enter" the extensive classification grid, which gives a nontrivial information. For example, a rock with a TiO_2 content of only 0.5 % may turn out to be hypertitanic (TM> 0.085), while an alumina rock even with 2 % TiO_2 may well be normotitanic (TM 0.021–0.065). Meanwhile, such a difference in the TM values, as we will see below (see Section 4.4), may have an important genetic meaning.

Thus, we conclude that the replacement of petrochemical modules with components' content in most cases is not justified. This does not bring tangible benefits, but the loss of information is obvious.

Above, two modules have already been briefly described that were used to distinguish taxa of the highest rank – types (hydrolysate module HM) and subtypes (ferrous module FerM). For additional characterization of sedimentites, we use several more modules: alumosilica (AM), femic (FM), titanium (TM), potassium (KM), sodium (NM), the sum of sodium and potassium, or normalized alkalinity module (NKM)[3], alkaline module (AlkM), redox module (RM). The values of each module change in a certain interval; it is obvious that this interval should be graded – divided into at least three parts corresponding to the values "normal", "lowered" and "increased". You can add more gradations "very low" and "very high", and then there will be not three parts, but five [295]. The choice (*assignment*) of gradations is an informal procedure. We propose to focus on the average composition of siallites – use the "siallite standard".

Let us touch on the question of the *modules' form*. Actually the geological literature is flooded with modules in an "inverted" form. For example, Al_2O_3/TiO_2 (instead of $TM = TiO_2/Al_2O_3$), Al_2O_3/ Na_2O (instead of $NM = Na_2O/Al_2O_3$), SiO_2/Al_2O_3 (instead of $AM = Al_2O_3/SiO_2$), etc. As a curiosity, you can indicate the works where the authors give in tables (apparently, just in case) both forms of modules one after the other [64]. Unfortunately, the scientific community has not worked out any rules about which form of modules (M or 1/M) should be used.

We prefer to calculate modules in such a way that their values are less than one: we consider that in this form they are easier to interpret. It is pertinent to recall

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[3] We draw the attention of readers that this abbreviation of the normalized alkalinity module (NKM) was not established immediately. At first, the sum of modules (HM + KM) was simply written without a special designation [295, p. 32). Then there were attempts to use the designation NAM, or, as in G.V. Ivensen [114], TNA, or "total normative alkalinity" (more correctly, of course, "normalized").

that in *isotope geochemistry*, ratios are traditionally used in precisely this form (the ratio of a rare isotope to a predominant one, for example, $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{34}S/^{32}S$). However, we are aware that our preference (as well as the preferences of other researchers) is more due to habit than rational considerations.

3.2. Siallite standard

Siallites and siferlites, which together embrace practically all terrigenous rocks, constitute a significant part of the sedimentary shell. For example, in the Phanerozoic part of the continental sedimentary shell, terrigenous rocks account for about 69 % by volume [229, p. 25]. If we restrict ourselves only *to clay rocks of continental platforms*, then their share will account for about 43 % of the total volume of these global structural units' sedimentary shell [229, p. 50]. Due to the special position of siallites as the most widespread rocks, their gradations in iron content, alumina content, titanicity, alkalinity and femicity form a kind of "standard" that can be used as a guide when characterizing other types of rocks.

The researchers developed this standard gradually; proposed in 1981 [295], it has undergone intensive practical testing. Table 7 shows it as of 01.01.1999 with those changes and additions that appeared in the process of working with thousands of our data bank analyzes. Instead of the previous five-membered [295] or three-membered [302] gradations, it turned out to be more convenient to use four-membered ones – with the prefixes *hypo-, normo-, super- and hyper-* (Table 7).

At the same time, the gradation of the "norm" accounts for at least half of the module values' entire range; we proceed from the plausible assumption that the set of module values is continuous and follows a normal distribution. However, a more correct procedure would not be "volitional" (intui-

Table 7

"Siallite standard" – gradations of siallites and siferlites

Class	HM	TM	FerM	FM	NKM	AM	AlkM
Hypo-	0.30–0.33	< 0.030	< 0.30	< 0.10	< 0.20	< 0.20	< 0.30
Normo-	0.34–0.48	0.03–0.07	0.30–0.55	0.10–0.20	0.20–0.40	0.20–0.35	0.30–1.50
Super-	0.49–0.55	0.071–0.1	0.56–0.70	0.21–0.25	0.41–0.45	0.36–0.40	1.51–3.00
Hyper-		> 0.100	0.71–0.75	> 0.25	> 0.45	> 0.40	> 3.00

Note: HM – hydrolysate module – $(TiO_2 + Al_2O_3 + Fe_2O_3 + FeO + MnO)/SiO_2$; TM – titanium module – TiO_2 / Al_2O_3; FerM – ferrous module – $(Fe_2O_3 + FeO + MnO)/(TiO_2 + Al_2O_3)$; FM – femic module – $(Fe_2O_3 + FeO + MnO + MgO)/SiO_2$; NKM – module of normalized alkalinity – $(Na_2O + K_2O)/Al_2O_3$; AM – alumino-silica module – Al_2O_3/SiO_2; AlkM – alkaline module – Na_2O / K_2O; redox module (RM) – FeO / Fe_2O_3. FerM values are given for siallites only.

tive) *assignment* of gradations but *finding* them on the frequency distribution curves (see Section 4.4).

It is interesting to compare the average compositions of the earth's crustal rocks with the siallite standard. To judge the composition of *igneous rocks*, we will use the A.A. Beus's average data [18] (Table 8). As we can see, the most common types of igneous rocks are certified as:

granites and felsic effusives – hypotitanic hyperalkaline myosilites,
granodiorites – normotitanium superalkaline hyposiallites,
andesites – normotitanium normoalkaline pseudosiallites,
basalts are hyperfemic pseudohydrolysates.

Note that in addition to a slightly increased manganisity, andesites are similar in HM and a few other modules to clays and, as was noted long ago, most closely correspond to the average composition of the earth's crust.

Let us now turn to the average composition of the geospheres and the earth's crust using the latest model by A. B. Ronov et al. published in 1990 (Table 9).

Table 8

Average composition of igneous rocks according to A. A. Beus, 1981 [18] and petrochemical modules

Components and modules	Granite $N = 65$, $n = 1967$	Liparites etc. $N = 50$, $n = 969$	Grano-diorites $N = 30$, $n = 523$	Andesites $N = 54$, $n = 866$	Basalts platform $N = 23$, $n = 445$	Basalts geosynclinals $N = 25$, $n = 369$
SiO_2	72.60	73.30	65.30	59.00	49.20	49.20
TiO_2	0.29	0.22	0.64	0.64	1.50	1.68
Al_2O_3	13.90	13.50	16.34	17.00	15.40	16.40
Fe_2O_3	1.02	1.40	1.58	2.40	3.20	3.30
FeO	1.45	0.82	2.82	4.20	9.30	7.85
MnO	0.05	0.05	0.09	0.15	0.17	0.18
MgO	0.55	0.40	1.83	3.16	6.48	6.50
CaO	1.55	1.00	3.35	6.10	9.25	9.82
Na_2O	3.60	3.50	3.74	3.60	2.50	2.64
K_2O	4.20	4.40	3.05	2.10	0.85	0.98
H_2O	0.50	1.10	0.80	1.00	1.00	1.00
P_2O_5	0.14	0.11	0.26	0.30	0.15	0.30
Other	0.15	0.20	0.20	0.15	0.30	0.15
Total	100.0	100.0	100.0	100.00	100.00	100.00
Na_2O+K_2O	7.80	7.90	6.79	5.70	3.35	3.62
NKM	0.56	0.59	0.42	0.33	0.22	0.22
HM	0.23	0.22	0.33	0.42	0.60	0.60
TM	0.021	0.016	0.039	0.049	0.097	0.102
FM	0.042	0.036	0.10	0.17	0.39	0.36
FerM	0.18	0.17	0.26	0.38	0.75	0.63

Note. *N* is the number of regions; *n* is the number of analyzes.

Table 9

The average chemical composition (in mass %) of rocks, geospheres and the earth's crust according to the model of Ronov–Yaroshevsky–Migdisov, 1990 [229]

Components, mass %	1	2	3	4	4a	4b	5
SiO_2	54.55	54.71	51.82	63.81	61.79	66.02	48.69
TiO_2	0.87	0.85	0.66	0.54	0.58	0.48	1.12
Al_2O_3	16.72	16.17	12.89	14.92	14.45	15.44	17.74
Fe_2O_3	3.37	0.92	2.50	1.75	1.75	1.75	
FeO	5.21	7.29	2.91	3.68	4.53	2.75	10.81
MnO	0.16	0.16	0.11	0.09	1.10	0.06	0.22
MgO	4.86	4.89	3.32	2.83	3.53	2.07	6.70
CaO	8.30	8.64	9.93	4.08	4.93	3.14	11.69
Na_2O	3.01	2.75	1.96	3.02	2.56	3.53	2.71
K_2O	1.98	1.64	2.23	2.84	2.28	3.46	0.07
P_2O_5	0.20	0.20	0.16	0.14	0.14	0.14	0.25
C_{org}	–	0.07	0.48	0.05	0.10	–	
CO_2	0.16	1.10	7.21	0.90	1.64	0.08	
SO_3	0.02	0.06	0.22	0.10	0.11	0.09	
S^{2+}	0.04	0.05	0.22	0.066	0.05	0.08	
Cl	0.02	0.06	0.54	0.02	0.02	0.02	
F	0.04	0.02	0.046	0.05	0.06	0.04	
H_2O^+	1.13	0.76	3.04	1.17	1.42	0.90	
$-O = S, Cl_2, F_2$	–	0.049	0.251	0.060	0.057	0.063	
Total		100.0	100.0	100.0	100.0	100.0	

Note *1* – initial material of the sedimentary shell: volcanic rocks of folded zones (basic: medium: acidic = 56:34:10); *2* – the calculated average composition of the continental crust (thickness 43.6 km, mass $18.05 \cdot 10^{24}$ g); *3* – sedimentary shell (5.1 km, mass $1.90 \cdot 10^{24}$ g); *4* – granite-metamorphic shell, or "granite metasphere" (thickness 16.9 km, weight $6.80 \cdot 10^{24}$ g); *4a* – metamorphic part of the granite metasphere (51.5 % of its volume); *4b* – magmatic part of the granite metasphere (48.5 % of its volume); *5* – granulite-basic shell, or "basalt metasphere". The composition is determined by the difference between 1 – the original material of the earth's crust – and 4b – magmatic melting from it (thickness 21.6 km, mass $9.35 \cdot 10^{24}$ g).

Given in table 9 data allow to certify:

– The original matter of the earth's crust, as well as the continental earth's crust, as a superfemic pseudosiallite.

– Granulite-basic geosphere – as a hyperfemic pseudo-hydrolysate.

– Granite-metamorphic geosphere – as normosiallite.

– The sedimentary shell – as a pseudosiallite.

Thus, normosiallite is nothing more than a composition corresponding to the granite-metamorphic shell of the Earth – the product of its "past biospheres", according to Vernadsky [51]. This composition meets the norm in all other parameters – titanicity, alkalinity, iron content and femicity.

The sedimentary shell, in comparison with the granite-metamorphic layer, is not only more basic, but also more magnesian. Both are determined by the contribution of carbonate rocks: the CO_2 calculation gives 16–17 % of carbonates, and direct estimates of the carbonates volume in the sedimentary shell of the continental block give 15.9 % of carbonates containing 5.73 % MgO [229, p. 54].

Thus, at the end of the twentieth century the scientists have reliably proven what seemed obvious to F. Clarke back in 1889, namely, that ***the presence of the sedimentary shell has almost no effect on the average composition of the continental crust***. The latter turns out to be close (but still more femic) to the composition of the original volcanic rocks of the folded zones, roughly corresponding to andesites.

Along the way from the initial igneous rocks to the formations of the sedimentary shell, the following changes occur:

a) the HM decreases noticeably – from 0.48 (super siallites) to 0.37 (normosiallites),

b) the alkalinity (NKM) increases markedly – from 0.26 to 0.33,

c) iron content (FerM 0.50 $\Rightarrow$ 0.41), femicity (FM 0.25 $\Rightarrow$ 0.17) and magnesium content (MgO 4.86 $\Rightarrow$ 3.32%) decrease,

d) the CaO content increases (8.30 $\Rightarrow$ 9.93%).

The first three tendencies are, overall, quite explainable in terms of the initial andesite substrate *granitization* with subsequent inheritance of its composition in sedimentary rocks.

Let us now consider the petrochemical modules in more detail.

3.3. Modules normalized to SiO_2

3.3.1. Hydrolysate module (HM)

Recall that the siallite standard for HM corresponds to the values: 0.30–0.33 (hyposiallites), 0.34–0.48 (normosiallites), 0.49–0.55 (supersiallites).

Table 10 summarizes the HM values calculated for the average compositions of continents' sedimentary rocks, estimated by A.B. Ronov et al. [229].

Table 10

Average HM values in the sedimentary shell

Rocks	Riphean + Vendian			Paleozoic			Mesozoic + Cenozoic		
	1	2	3	1	2	3	1	2	3
Sandy	0.44	0.23	0.19	0.20	0.28	0.26	0.24	0.25	0.25
Clay	0.42	0.42	–	0.41	0.42	0.38	0.44	0.40	0.44

Note. Hereinafter, in similar tables: 1 – platforms, 2 – geosynclines, 3 – orogens.

Below are the HM values for I seismic layer sediments of the oceans and sedimentary shell:

Sediments	**HM**
Sandy-silty	0.36
Clay	0.43
Carbonate-clay	0.33
Carbonate	0.39
Silica	0.17
Volcanomictic	0.38
Sedimentary shell (no effusive)	
Continental block	0.34
Ocean block	0.37
Sedimentary shell total	0.35

According to the standard for siallites, all clay and volcanomictic rocks are certified as normohydrolysate, while others are hypohydrolysate. The highest HM value (at the upper limit of the normal siallites) is in the Meso-Cenozoic clay strata, and the lowest is in the silica deposits of the oceans.

All sandy rocks are certified on average as silites. It is very curious that since the Paleozoic, normosilites disappear and sandy rocks become myosilites, i.e., formations are either more clay or more feldspar.

3.3.2. Aluminosilica module (AM)

The HM use has greatly narrowed the scope of the previously very popular aluminosilica module. In any case, it is doubtful to use AM as a basis for classification, as A.N. Neelov did [183]. We can offer gradations of chemotypes shown in table 10a.

Compared to the siallite standard, silites and siferlites are less, and hydrolysates are more aluminous rocks. The lower alumina content of phos-

Table 10a

Chemotype gradation by AM module

Chemotype	Hypo-	Normo-	Super-	Hyper-
Silites	< 0.05	0.05–0.20	> 0.20	–
Pseudosilites	< 0.10	0.10–0.25	> 0.25	–
Siallites and pseudosiallites	< 0.20	0.20–0.35	0.36–0.40	> 0.40
Siferlites and pseudosiferlites	< 0.15	0.15–0.25	0.26–0.30	> 0.30
Hydrolysates	< 0.15	0.16–1.00	1.01–3.00	> 3.00
Alkalites	< 0.10	0.10–0.40	0.41–0.60	> 0.60
Carbonatolites	< 0.10	0.10–0.40	0.41–0.80	> 0.80
Phosphatolites	< 0.03	0.03–0.20	0.21–0.30	> 0.30

phatolites and the higher content of alkalites and carbonatolites are not so trivial. Note also that pseudosilites are generally more alumina than silites. Since (all other things being equal), the presence of micas increases and the presence of feldspars decreases AM, a decreased AM value can sometimes give some information about the presence of feldspars in the rock.

Table 11 summarizes the AM values calculated for the average compositions of sedimentary rocks of the continents, estimated by A.B. Ronov et al. [229].

Table 11

Average AM values in the sedimentary shell

Rocks	Riphean + Vendian			Paleozoic			Mesozoic + Cenozoic		
	1	2	3	1	2	3	1	2	3
Sandy	0.12	0.16	0.14	0.14	0.19	0.18	0.17	0.18	0.17
Clay	0.31	0.28	–	0.29	0.30	0.24	0.34	0.28	0.30

Below you can find the AM values for the sediments of the oceans' first seismic layer and in the sedimentary shell:

Sediments	**AM**
Sandy-silty	0.24
Clay	0.28
Carbonate-clay	0.21
Carbonate	0.22
Silica	0.10
Volcanomictic	0.23
Sedimentary shell (no effusive)	
Continental block	0.24
Ocean block	0.24
Sedimentary shell total	0.24

Thus, according to the standard for siallites, clay rocks are certified as normoalumina, and all sandy rocks and silica sediments are hypoalumina.

The AM values for the sedimentary shell (0.24) and for the granite–metamorphic layer (0.23) are practically the same. This picture is interpreted by A. B. Ronov as follows [229, p. 67]: *"The negligible increase in the size of the aluminosilica module in the sedimentary shell in comparison with the granite-metamorphic layer indicates that the ratio constancy of alumina to silica, established for the sedimentary shell of the oceans and continents, <...> is inherited from the granite-metamorphic layer".*

However, a completely opposite interpretation seems no less plausible. It is in the spirit of V. I. Vernadsky's ideas: ***is it not because the AM values in the sedimentary shell and the "granite" metasphere are so close that the second represents "former biospheres", that is, it was formed according to the substrate ancient sedimentary shells?***

Researchers have always used aluminosilica module as an intensity indicator of substance sedimentary differentiation. However, this factor is not the only one; the composition of the *petrofund* plays an important role. Thus, without considering the difference in the composition of the petrofund among the largest structural elements of the earth's crust: *oceans ⇒ orogens ⇒ geosynclines ⇒ platforms* in the sedimentary shell, an increase in AlkM should be expected due to increased chemical weathering. However, the data of A.B. Ronov et al. [229], presented by us in the form of a table 12 show that this is not the case.

Table 12

Irregular fluctuations in the AM value in clay
and sandy sedimentary rocks of continents and oceans.
Compiled according to the data of A.B. Ronov et al. 1990 [229, p. 50–53]

Sedimentary rocks	Oceans*	Continents		
		1	2	3
Clay	0.28	0.30	0.28	0.29
Sandy	0.23**	0.15	0.18	0.17

* Rocks and sediments of the I seismic layer.
** Sandy-clay rocks.

As noted by A.B. Ronov et al., the average AM value of the sedimentary shell [229, p. 61–63] "*remains practically unchanged in this series of structures. The magnitude of the aluminosilica module in the clays and sands composing these complexes varies in a series of the same structures within wide limits. These facts give us grounds to assume that the processes of SiO_2 and Al_2O_3 separation manifested with different intensities in individual types of rocks <...> seem to be mutually compensated <...>. Such a planetary leveling of the sedimentary matter differentiation results is, apparently, deep meaning that is yet to be solved*" [229, p. 50–53].

In our opinion, one should not look for a "deep meaning" here, because the influence of the petrofund composition on the AM value is obvious. The sands of the platforms (at least the largest – the oldest ones) were formed mainly due to the acidic petrofund (granitoids and acidic gneisses), and the sands of geosynclines, orogens, and the ocean – mainly due to basalts and andesites with their high AM. For example, in the "sands" of the oceans, the SiO_2 content is even lower (!) than in platform clays: 56.8 and

57.3 %, respectively. Clay matter in the oceans is essentially authigenic (ferrous smectites, etc.) and is formed mainly on the substrate of basic volcaniclastics. And although smectites are relatively silica minerals (their AM is lower than in other clay minerals), the increased alumina content of the substrate (AM of tholeiitic and subalkaline basalts is 0.30 and 0.32) results in AM not lower than in clays of continental geosynclines, which theoretically should be more "differentiated".

In fact, the profound difference in the terrigenous rocks' composition of the platforms, on the one hand, and geosynclines, orogens, and oceans, on the other, is not at all in alumina, but in magnesium and iron content. While the former are silites, siallites, and hydrolysates, as a rule, the latter often turn out to be pseudosiallites, pseudo-hydrolysates, and syferlites.

In some works, one can find examples of using AM together with HM, when the distribution of the former is completely symbatic with the distribution of the latter. Such is, for example, the stratotype section of the Riphean of the Southern Urals, studied in detail by E. Z. Gareev [66, 67, 170]. In such situations, it is unnecessary to use AM, which does not provide additional information in comparison with the universal parameter HM.

So, the presented average data significantly compromise the AM module, narrowing the scope of its application in comparison with the HM hydrolysate module. However, it should be emphasized that this applies mainly to terrigenous sedimentites. On the contrary, for many *aquagenic rocks* the "good old AM module" is a very useful tool for description and diagnosis.

Such are, for example, the Cretaceous Mn-bearing phosphorites of NW Germany [362] and many carbonatolites. For the latter, such modules as HM, FerM, or FM do not have such a clear meaning as for silicate or oxide rocks, because a significant proportion of Fe, Mg, and almost all of Mn are in them in the carbonate form. In this case, it is preferable to use AM instead of HM, since alumina and silica can be considered completely non-carbonate components without much risk. In combination with NKM or the number of alkalis, AM can be used here for diagnostic purposes. For example, as can be judged from the data of the summary by H. James [337, p. W25–W26], the AM of the Precambrian siderites is much lower than that of the Phanerozoic. Actually in the former there is much more quartz because they are closely related to ferrous quartzites.

When processing the data on the Lower Riphean carbonates of the South Urals associated with magnesites [258], we can use AM to reveal a nontrivial difference between the rocks "terrigenous-carbonate" and "clay". It turns out that the series of rocks "dolomitic ⇒ carbonate-terrigenous ⇒ terrigenous-carbonate ⇒ clay" is by no means a single series because carbonates contain silty or sandy impurities (low ASM), and not clay. Note that this circumstance is very typical for *ancient carbonate rocks*, for example, for the Middle Riphean (?) Shchekurya and Upper Riphean Moroin formations in the Subpolar Urals [75, 178].

3.3.3. Femic module (FM)

A.A. Predovsky, apparently, has taken the idea of the parameter ***F*** from petrochemistry: it resembles the "number" ***fm*** in the P. Niggli's system and the parameter ***b*** in the A.N. Zavaritsky system. In form, our FM module completely coincides with the ***F*** parameter in A. A. Predovsky's classification [211], with the difference that we calculate it (like all other modules) simply by weight percent, and not by molecular amounts:

$$FM = (Fe_2O_3 + FeO + MnO + MgO)/SiO_2.$$

While the geochemical association of trivalent hydrolysates $Fe_2O_3+Al_2O_3$ is typically hypergenic, the association FeO + MgO, on the contrary, is typically hypogenic. Therefore, the FM module is very useful for recognizing petro- and pyrogenic sedimentites, in particular volcanoclastic greywackes, as well as basic metavolcanics; such rocks almost always have FM > 0.10. We can offer chemotype gradations shown in table 12a.

Table 12a

Chemotype gradations by FM module

Chemotype	Hypo-	Normo-	Super-	Hyper-
Silites	< 0.03	0.03–0.10	0.11–0.15	> 0.15
Pseudosilites	< 0.10	0.10–0.15	0.16–0.20	> 0.20
Siallites	< 0.10	0.10–0.20	0.21–0.25	?
Pseudosiallites	< 0.15	0.15–0.25	> 0.25	?
Siferlites and pseudosiferlites	< 0.25	0.25–0.35	0.36–0.45	>0.45
Hydrolysates and pseudohydralisates	< 0.15	0.16–1.00	1.01–2.00	>2.00
Alkalites	< 0.05	0.05–0.20	0.21–0.30	> 0.30
Carbonatolites	< 0.20	0.20–3.00	3.01–5.00	>5.00
Phosphatolites	< 0.05	0.05–0.40	0.21–0.60	> 0.60

According to our data, siallites with FM > 0.25 apparently do not exist in nature; these are either magnesian rocks (pseudohydrolysates), or ferrous ones – siferlites.

The frequency distribution of the FM value is similar to the normal one; for example, fig. 4 shows the FM distribution in the aggregate of siallites.

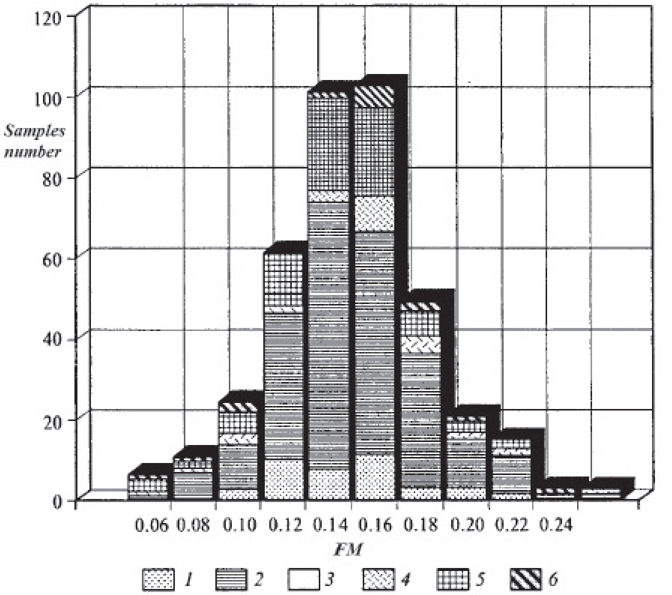

Fig. 4. Frequency FM distribution in siallites (401 samples, 3962 analyzes).
Rocks: 1 – sandy, 2 – silty–clay, 3 – silica, 4 – tuffoids, 5 – metamorphic rocks, 6 – others

Below are the FM values for the sediments of the oceans' first seismic layer:

Sediments	**FM**
Sandy-silty	0.15
Clay	0.18
Carbonate-clay	0.15
Carbonate	0.21
Silica	0.09
Volcanomictic	0.21
Sedimentary shell (no effusive)	
Continental block	0.15
Ocean block	0.16
Sedimentary shell total	0.15

Table 13 summarizes the FM values calculated for the average compositions of continents' sedimentary rocks, estimated by A.B. Ronov et al. [229]. As you can see, according to the standard for siallites among the continents' sandy rocks, only Phanerozoic orogenic can be classified as normofemic, and all others are hypophemic. All continents' clay rocks are normofemic. Silica oceanic deposits are distinguished by low femicity. The increased FM of carbonates is determined, of course, by dolomite, and volcanomictic ones – by an admixture of magnesian-ferrous clastic.

Table 13

Average FM values in the sedimentary shell

Rocks	Riphean + Vendian			Paleozoic			Mesozoic + Cenozoic		
	1	2	3	1	2	3	1	2	3
Sandy	0.07	0.09	0.06	0.07	0.10	0.11	0.09	0.09	0.11
Clay	0.14	0.17	–	0.11	0.15	0.20	0.12	0.12	0.17

Since in most magmatic rocks (excluding alkaline-ultrabasic and alkaline-basic) femicity is negatively correlated with alkalinity, the most effective FM use is paired with some indicator of alkalinity. In addition, the "endogenous" nature of the positive correlation (Fe, Mg) –Ti makes the use of the FM–TM or FM–FerM graph informative. For example, the use of such plots makes it possible to distinguish clay rocks with allogenic chlorite (above FM and TM) from rocks with authigenic ferrous chlorite (above FerM, below FM and TM).

Apparently, using FM in the indicated combinations, it is possible to distinguish two types of bentonite rocks [197]: 1) with halmyrolytic apo-ash montmorillonite formed on the mica substrate (FM and TM below, NKM above), and 2) with montmorillonite from weathering crust, formed over the substrate of amphiboles, pyroxenes, and chlorite (FM and TM above, NKM below).

3.4. Alkalinity indicators

3.4.1. Total alkalinity ($Na_2O + K_2O$)

The total alkalinity index ($Na_2O + K_2O$) is used instead of the normalized alkalinity NKM in cases when the NKM dispersion is low, and this module stops working. This situation is typical for silicious rocks, and among terrigenous rocks – for some greywackes. The characteristics of this indicator should be given above – when distinguishing the alkalites type.

3.4.2. Normalized alkalinity (NKM)

This module is the sum of sodium (NM) and potassium (KM) modules:

$$NKM = NM + KM = Na_2O/Al_2O_3 + K_2O/Al_2O_3 = (Na_2O+K_2O)/Al_2O_3.$$

To avoid confusion when describing the alkalinity of rocks, let us agree to call the NKM value simply *alkalinity* (hypoalkaline, normal alkaline, etc.), and the "absolute" alkalinity (Na_2O+K_2O) – *total alkalinity*. Obviously, NKM is nothing more than the “agpaite coefficient” known in petrology in weight percent. V. Goldschmidt introduced this coefficient $(Na_2O+K_2O)/Al_2O_3$ into petrology, and Danish geologist N. Ussing in 1911 proposed the term “agpaite” for nepheline syenite from South Greenland. Today, petrologists distinguish magmatic rocks according to the value of the agpaite coefficient: alkaline-earth (< 0.55), plumasite, or miaskite (0.55–0.85), agpaitic proper (0.85–1.50), and ultra-agpaitic (> 1.50).

In 1960, the Canadian lithologist G. Middleton, who apparently did not know anything about the "agpaite coefficient", applied it to construct a genetic classification of sandstones on a tectonic basis, and later I.V. Khvorova named the value $(Na_2O + K_2O)/Al_2O_3$ "Middleton coefficient". G. Middleton himself motivated the coefficient use as follows [343, p. 1014]: “*Alumina and alkalies occur in sandstones in: clay minerals; micas; feldspars; glauconite; argillaceous or micaceous rock fragments; and volcanic rock fragments. ...both alkalies and alumina occur essentially in two main groups of minerals: (1) clay minerals, micas, and chlorites, and (2) feldspars. None of these minerals are commonly quantitatively important as authigenic minerals, although traces of authigenic feldspar and mica are not rare. Hence, if a chemical investigation of sandstones is to be independent of diagenetic factors, it may be based upon ratios between* Al_2O_3 *and alkalies or between individual pairs of oxides*”.

At the same time, G. Middleton pointed out the continuity of his approach with the ideas of P. Krynine (an American lithologist of Russian origin), since a low value of the coefficient is typical for clay minerals, and a high value for feldspars [343, p. 1014]: “*If ... there are two series of sandstones, one characterized by high feldspar content and relatively low content of clays and micas (the arkoses) and the other characterized by a relatively low content of feldspars and high content of clays, micas, chlorites, and argillaceous rock fragments (the graywackes) as maintained by Krynine (1948) ... then a histogram* [of the frequency distribution of the ratio] *distribution for the ratio alkalies/*Al_2O_3 *might show a bimodal distribution* [if there is a relatively low occurrence of intermediate types] ”.

Based on the material of 168 sandstones analyzes, he managed to obtain a semblance of a bimodal graph. But it was necessary to exclude “quartzites” (Al_2O_3 <5%) and all glauconite sandstones from the statistical sample. In our opinion, there is no need for such restrictions, unless one restricts oneself in advance with an artificial bimodal model. ***The NKM module has much more universal applicability, far from being limited to sandstones alone.*** As we noted on the example of the Upper Devonian Pai-Khoi silicites, NKM “*will be increased even if alkalis are included in the composition of low-alumina silicates – alkaline amphiboles, ferrous smectites, ferrous hydromicas, where* Fe^{3+}

plays the role of Al^{3+} *<…> Both <…> tendencies – an increase in the content of feldspars and an increase in the iron content of authigenic silicates – are just characteristic of the basic volcanic material and the products of its change*” [295, p. 32].

So, the NKM contains information on the ratio of the two main types of alkaline aluminosilicates: feldspars and micas. Since micas are much more alumina minerals than feldspars, ***low NKM values indicate the predominance of micas, and high values indicate the predominance of feldspars.*** For example, the NKM value for muscovite is 0.31. If NKM of the rock is greater than 0.31, then it necessarily contains potassium feldspar (or some other high-potassium mineral), and if NKM is less than 0.31, then the presence of potassium feldspar, although possible, is no longer necessary.

Since acidic plagioclases are much more widespread in sedimentary rocks than potassium feldspars, Na_2O is most often included in albite–oligoclase (rather than paragonite), and K_2O is in hydromica (rather than potassium feldspars). The first increases the NKM value, and the second, on the contrary, decreases it. Hence, it is clear why, as a rule, NKM in sandstones is higher than in clay rocks. However, in clay rocks containing appreciable amounts of alkali-free aluminosilicates (chlorite, kaolinite, montmorillonite), the NKM value will also be lowered.

Our experience shows that the presence of feldspars is necessary to be considered with the NKM values not lower than 0.40. Of course, the presence of feldspars is not at all forbidden even at lower NKM values, but in this case they are not rock-forming. These considerations allowed to use the NKM gradations shown in table 13a.

Table 13a

Chemotype gradations according to the NKM module

Chemotype	Hypo-	Normo-	Super-	Hyper-
Silitsand pseudosilites	< 0.20	0.20–0.50	0.51–0.70	> 0.70
Siallitesand pseudosiallites	< 0.20	0.20–0.40	0.41–0.45	> 0.45
Siferlites and pseudosiferlites	< 0.15	0.15–0.40	0.41–0.45	> 0.45
Hydrolysates and pseudohydralisates	< 0.05	0.05–0.30	0.31–0.40	>0.40
Alkalites	< 0.30	0.30–0.70	0.71–1.00	>1.00
Carbonatolites	< 0.10	0.10–0.50	0.51–0.100	> 1.00
Phosphatolites	< 0.20	0.20–0.60	0.61–0.80	> 0.80

It turns out that only hydrolysates have lower alkalinity than siallites and siferlites. All other chemotypes are noticeably more alkaline, and this conclusion is not trivial for silica, carbonate, and phosphate rocks.

Frequency distributions of the NKM value are close to normal. For example, Fig. 5 and 6 show the NKM distribution in silites and siallites. In

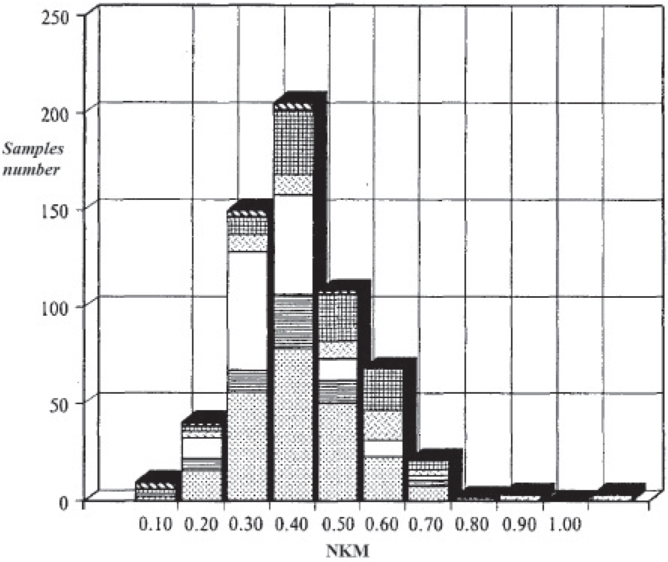

Fig. 5. Frequency distribution of the NKM value in silites (630 samples, 11735 analyzes). See the legend in Fig. 4

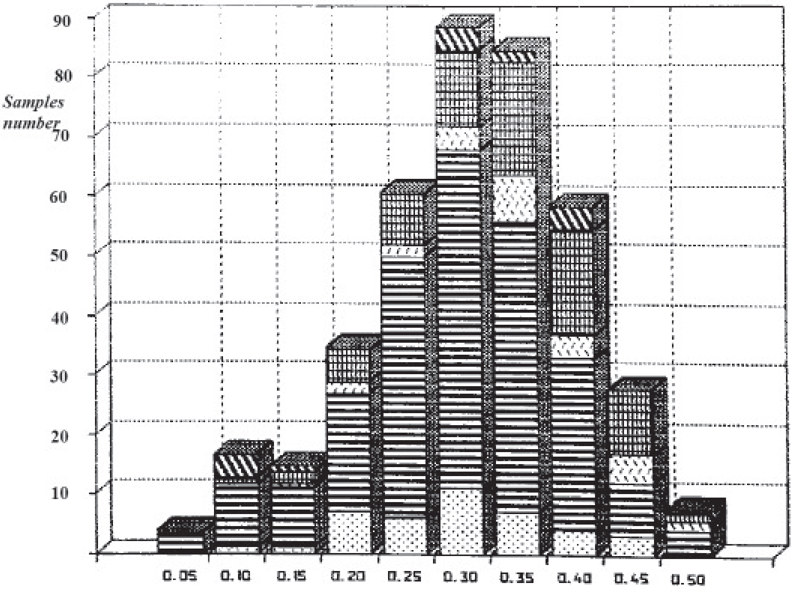

Fig. 6. Frequency distribution of the NKM value in siallites (401 samples, 3962 analyzes). See the legend in Fig. 4

silites, the distribution is slightly right asymmetric, while in siallites, on the contrary, it is distorted by left-handed asymmetry (apparently, due to low alkaline and aluminous rocks, transitional to hydrolysates). Incidentally, a comparison of these distributions clearly shows that silites are generally noticeably more alkaline than siallites; the modal NKM value for silites is 0.40–0.50, and for siallites 0.30–0.35.

Obviously, the NKM module can serve as a tool for recognizing the admixture of feldspar pyroclastics in sedimentary rocks [295, p. 32] and, accordingly, to distinguish stratiform meta-effusives from parametamorphites. However, from the above it is clear that the "sensitivity" of this parameter is higher in relation to felsic volcanics than basic ones. In the first, there are few or no alkali-free aluminosilicates, and in the second, there are a lot of them (dark colored minerals), which lowers the NKM value to the level characteristic of pelitoids. For this reason, for the basic rocks' diagnostics, it is necessary to use NKM in tandem with another informative module, for example, NKM–FERM.

Table 14 summarizes the NKM values calculated for the average compositions of continents' sedimentary rocks, estimated by A.B. Ronov et al. [229].

Table 14

Average NKM values in the sedimentary shell

Rocks	Riphean + Vendian			Paleozoic			Mesozoic + Cenozoic		
	1	2	3	1	2	3	1	2	3
Sandy	0.37	0.39	0.46	0.31	0.37	0.40	0.31	0.37	0.30
Clay	0.33	0.30	–	0.24	0.30	0.26	0.19	0.26	0.23

Below are the NKM values in the I seismic layer sediments of the oceans and in the sedimentary shell:

Sediments	**NKM**
Sandy-silty	0.30
Clay	0.28
Carbonate-clay	0.31
Carbonate	0.41
Silica	0.43
Volcanomictic	0.35
Sedimentary shell (no effusive)	
Continental block	0.34
Ocean block	0.32
Sedimentary shell total	0.34

Thus, all terrigenous sedimentary rocks, on average, are normal alkaline according to the siallite standard, while carbonate and silica rocks are super alkaline. If we can explain the increased alkalinity of the silica rocks by the admixture of feldspar pyroclastics in them, the interpretation of the increased NKM in carbonate rocks is not so clear. Perhaps this is due to the contribution of arid carbonate strata, in which an admixture of authigenic feldspars is possible.

Sometimes the NKM value in terrigenous rocks also turn out to be much higher than in feldspars. We encountered such a situation when processing the A.I. Koptev's analyzes [140], who studied the Cenomanian quartz sands of the Kaluga and Smolensk regions. In some samples, the NKM value even exceeded unity (for comparison, the NKM of orthoclase is 0.92). Actually, these sands contain glauconite, in which the NKM value is increased since part of the alumina is replaced by iron. ***Thus, the hyperalkalinity of psammites (in obligatory combination with hyperferruginosity) may indicate the presence of glauconite in them***.

Finally, evaporite deposits should differ by sharply increased NKM value – where alkalis are included in the composition of salts, and not of alumina silicates. For example, analyzes of the Devonian "sandstones and siltstones" in the Chayanda area in the western part of the Vilyui syneclise (materials by G.V. Ivensen) showed the NKM values often exceeding one. In combination with the increased contents of chlorine and sulfate, it indicates the salinity of this terrigenous strata.

Alkaline module (AlkM). The Na_2O/K_2O ratio is an important characteristic that distinguishes clay rocks ($Na_2O << K_2O$) from clastic rocks ($Na_2O > K_2O$), except for some potassium arkoses and clay rocks with a predominance of montmorillonite. The quantitative ratio of alkalis in one form or another necessarily appears in all petrochemical systematics. Let us recall that A.A. Predovsky [211] used the difference $\boldsymbol{K} = K_2O - Na_2O$, while A. N. Neelov [183] borrowed from P. Niggli the parameter $\boldsymbol{k} = K_2O/(K_2O+Na_2O)$.

In contrast to other modules, due to its large variance, we use logarithmic gradations for the AlkM (Table 14a).

It turns out that the AlkM gradations for different chemotypes differ markedly from the siallite standard. The AlkM rate in most chemotypes is much wider than that of siallites; totally, silites, syferlites, phosphatolites are rocks, on average, more sodium-rich than siallites, and hydrolysates and alkalites are less sodium-rich.

Experience has shown that super- and hypersodium rocks are almost always either arkoses or metabasites, or, finally, albite metasomatites (at high contents of Na_2O), while hyposodium rocks are, as a rule, pelitoids.

Table 14a

Chemotype gradations of AlkM module

Chemotype	Hypo-	Normo-	Super-	Hyper-
Silites and pseudosilites	< 0.20	0.20–1.80	0.81–2.50	> 2.50
Siallitesand pseudosiallites	< 0.30	0.30–1.0	1.1–3.0	> 3.0
Siferlites and pseudosiferlites	< 0.30	0.30–2.0	2.01–3.0	> 3.0
Hydrolysates	< 0.20	0.20–1.5	0.51–2.0	> 2.0
Pseudohydrolisates	< 0.20	0.20–2.0	2.01–3.0	> 3.0
Alkalites	< 0.10	0.10–1.0	1.01–3.0	> 3.0
Carbonatolites	< 0.10	0.10–1.5	1.51–3.0	> 3.0
Phosphatolites	< 0.20	0.20–2.0	2.01–3.0	> 3.0

Table 15 summarizes the AlkM values calculated for the average compositions of continents' sedimentary rocks, estimated by A.B. Ronov et al. [229].

Table 15

Average AlkM values in the sedimentary shell

Rocks	Riphean + Vendian			Paleozoic			Mesozoic + Cenozoic		
	1	2	3	1	2	3	1	2	3
Sandy	0.42	0.73	0.97	0.34	1.33	1.43	0.68	1.06	0.74
Clay	0.22	0.69	–	0.16	0.41	0.62	0.48	0.34	0.44

Below are the AlkM values for the sediments of the oceans' first seismic layer and in the sedimentary shell:

Sediments	**AlkM**
Sandy-silty	0.73
Clay	0.74
Carbonate-clay	0.80
Carbonate	1.14
Silica	1.23
Volcanomictic	1.59
Sedimentary shell (no effusive)	
Continental block	0.74
Ocean block	0.89
Sedimentary shell total	0.74

Note. The same figures for the continents and the sedimentary shell total are a consequence of rounding off in the calculation; the corresponding exact numbers are 0.736 and 0.742.

Thus, according to the standard for siallites, platform shales of the Riphean-Vendian and Paleozoic are hyposodium (respectively, superpotassium); carbonate, silica, and volcanomictic sediments of the ocean are super sodium, and all others are normal sodium. The reason for the increased sodium content of carbonate and silica rocks is obviously the same as for the increased alkalinity: an admixture of pyro- and volcanoclastics. The same (and obvious) explanation has the supersodium content of oceanic volcanomictic deposits.

The increased sodium content of clay rocks against the norm in combination with increased magnesian content serves as an excellent indicator of the montmorillonite presence in them. Such, for example, are the "schlieren formation" clays of the Oligocene of Armenia, studied by I.Kh. Petrosov [205, p. 220]. Their essentially montmorillonite composition is distinguished, firstly, by high sodium content (AlkM 0.65–1.07 versus Phanerozoic norm for “shales” 0.36 [228, pp. 142–144]), and secondly, by the presence of magnesian varieties (three out of eight analyzes are pseudosiallites), which can partly be explained by the presence of dolomite. However, as in most similar cases, such dolomite should be considered authigenic, inheriting its magnesium from volcanogenic silicates.

In addition, we know that the Precambrian clay rocks are characterized by an increased content of Na_2O, because of which the alkaline module AlkM in them is higher than in Phanerozoic rocks [228]:

Age of clay strata	**AlkM**
Aldanian (Katarchean)	0.54
Ontarian (Upper Archaean)	0.78
Karelian (Lower Proterozoic)	0.67
Riphean (Upper Proterozoic)	0.43
Phanerozoic	0.36

The generally accepted explanation for this phenomenon is that the Pre-Cambrian continental crust is substantially more basic (and therefore relatively more sodium-rich) than the Phanerozoic. However, in the Karelian deposits (Cobalt Series, Canada), clay rocks with excessively high AlkM values are known – more than one, which is typical not for pelitoids, but for greywackes. As E. Pettijohn and H. Bastron noted long ago [348], these are *varbaceous argillites*, i.e., products of ice lithogenesis, in which the chemical weathering of the substrate is minimal. Thus, ***all other conditions being equal, the abnormally high alkaline module AlkM value in pelitoids could serve as a means of diagnosing glacial deposits.***

Occasionally, an *increased AlkM* of minerals can be found in *carbonate rocks*. We are probably facing two different cases here. In the first case, the alkalinity (NKM) is also increased: this means that the rock contains albite and little clay matter. For example, for the Middle Devonian limestones of the Middle Urals (59], the values of AlkM 1.0 and NKM 1.18 are obtained, for the Oligocene marls of the Turgai trough [31] – 1.36 and 0.40, respectively, for the Famennian-Tournaisian limestone of the Pechora Urals (our data) – 10.0 and 0.65, respectively. In all these cases, the increased AlkM value is created by an admixture of feldspar (albite) pyroclastics. In the second case, the NKM is small; the reason for the high AlkM is unclear and may lie in analytical errors (?). For example, in the Neogene dolomite limestone of the Western Baikal region [124] and in the siderite ores of the Lebedinskoe Kursk Magnetic Anomaly deposit [34], the AlkM and NKM values are obtained, respectively, 1.0 and 0.03, 1.50 and 0.07. Considering the negligible total alkalinity of these rocks (0.02 and 0.15 %, respectively), we cannot exclude that the analysis errors simply affected the AlkM and NKM modules values.

Finally, the *phenomenon of increased sodium content of many phosphatolites* deserves attention. For example, in the Paleozoic black shale strata of the Lemva zone of the North of the Urals and Pai-Khoi, Na_2O is always present in carboniferous nodular phosphorites. Petrochemical calculations invariably showed the normative albite, which sometimes could be confirmed by X-ray analysis of insoluble nodule residues. We assumed that albite is "*either a crystalloclastic material <...> or, which is more likely, authigenic formations, which, according to V.A.Melezhik, arose during the decay of migratory sodium phosphates. According to him, this is how phosphate containing nodules with albite were formed in the Proterozoic volcanogenic-sedimentary sequence of the Imandra–Varzuga belt on the Kola Peninsula* <...>" [296, p. 122].

A.V. Sochava, who studied the metamorphic strata of the Karelians in the west of the Vitim-Aldan Shield, also drew attention to the geochemical association Na_2O – P_2O_5. He believed that "*the constant presence of* P_2O_5 *in association with* Na_2O *suggests that the processes of rocks albitization established by petrographic methods were accompanied by their enrichment with phosphates. It is very likely that the products of this process are associated with the metasomatic effect on terrigenous sediments of hydrothermal solutions, genetically related to the centers of volcanism of sodium specialization and related to the ore genesis of stratiform copper deposits <...> In some cases, the process of rocks enrichment with phosphates occurred without a noticeable change in sodium content .. The phosphorus accumulation was accompanied by an increase in the iron oxide content...*"[4] [246, p. 57–58].

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[4] However, such an association is often sedimentary and is due to the sorption of phosphates on ferrous hydroxides (authors' note).

3.5. Titanium module (TM)

The significance of the titanium module (TM = TiO_2/Al_2O_3) as an important geochemical constant of hypergene processes was demonstrated in the works of A.A. Migdisov in the 1960s, devoted to the study of the sedimentary cover of the Russian Plate [179]. He found that clay rocks have a distinctly lower TM than sandy ones: 0.030–0.060 versus 0.055–0.075. The reason for this is the dynamic sorting of the material, leading to the partial separation of heavy titanium-bearing accessories and lighter clay matter (alumina carrier). We call this empirical regularity the *Migdisov law*. According to A.A. Migdisov's data, TM depended on the climatic and facies characteristics of the rocks: it was higher in humid sediments than in arid ones, and higher in shallow-water than in deep-water (calm-water).

Subsequently, our works in the Pechora Urals [295] confirmed all A.A. Midisov's conclusions and showed the important role of one more factor – the titanicity of the petrofund. Genetically associated with more titanium mafic rocks, terrigenous rocks had TM significantly higher than those associated with acid rocks (for example, arkoses).

Thus, over time it became clear that TM in terrigenous rocks should be correlated with at least two parameters: with HM (inverse correlation in clastic lithogenic rocks) and with FM (less often with FerM) – a direct correlation in petrogenic and pyrogenic rocks. The first reflects the relationship between TM and dynamic sedimentation facies, and is generated by hypergenesis, while the second reflects the relationship of Ti with Fe and Mg in the magmatic process.

Obviously, provided other equal conditions, the recycling of sedimentary material should lead to an increase in TM; therefore, in lithogenic rocks, TM should be higher than in petrogenic rocks (see Section 1.3). This is the basis for the TM using method for the primary substrate diagnostics of metamorphic rocks. For felsic rocks (with small or moderate HMs corresponding to silites and siallites), large TM values will correspond to sandstones, and small ones – to felsic tuffs. For more basic rocks (with HM corresponding to siallites and hydrolysates), higher TM values will be characteristic of metabasites, and lower values of metapelites. For example, if for metapelites even TM = 0.060 can be regarded as somewhat increased (if these are not Fe–hydrolysates, in particular, Precambrian iron ores, in which TM is usually increased), then for most metabasites TM values > 0.070 are quite normal.

We use the chemotype gradation according to the TM value, shown in table 15a.

Compared with siallites, only alkalites are, on average, less titanium rocks. The titanicity of all other chemotypes is higher than that of siallites, and the TM of ferrous and magnesian rocks – siferlites and pseudohydro-

Table 15a

Chemotype gradations according to the TM module

Chemotype	Hypo-	Normo-	Super-	Hyper-
Silites and pseudosilites	< 0.020	0.020–0.80	0.081–0.120	>0.120
Siallitesand pseudosiallites	< 0.030	0.030–0.070	0.071–0.100	>0.100
Siferlites and pseudosiferlites	< 0.040	0.040–0.100	0.101–0.150	>0.150
Hydrolysates	< 0.030	0.030–0.100	0.101–0.150	>0.200
Pseudohydrolisates	< 0.040	0.040–0.150	0.151–0.250	>0.250
Alkalites	< 0.010	0.010–0.050	0.051–0.100	>0.100
Carbonatolites	< 0.020	0.20–0.080	0.081–0.200	>0.200
Phosphatolites	< 0.010	0.10–0.080	> 0.080	

lysates – is especially high. It is quite understandable since there are many basites and their derivatives among them. At the same time, if the increased titanicity of carbonate rocks was already known earlier from the works of A.A. Migdisov and ours, then the fact of the increased titanicity of silites, hydrolysates and phosphatolites is nontrivial.

The frequency TM value distribution in siallites is close to normal (Fig. 7), while in silites it has a strong right-handed asymmetry and is close to lognormal (Fig. 8).

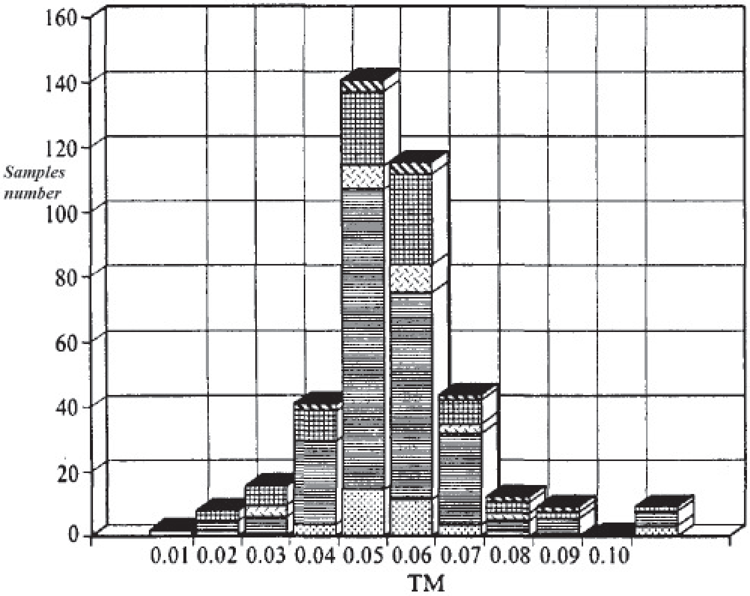

Fig. 7. Frequency distribution of TM value in siallites (401 samples, 3962 analyzes). See the legend on fig. 4

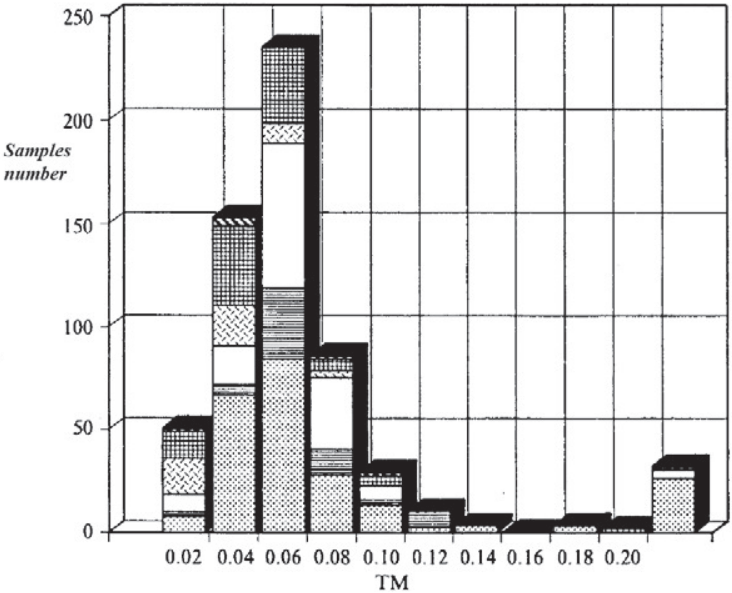

Fig. 8. Frequency distribution of the TM value in silites (630 samples, 11 735 analyzes). See the legend in Fig. 4

Let us consider the materials on the TM use in more detail, first examining the average values.

Table 16 summarizes the TM values calculated by us for the average compositions of continents' sedimentary rocks, estimated by A.B. Ronov et al. [229].

Below are the TM values for sediments of the oceans' first seismic layer and in the sedimentary shell:

Sediments	**TM**
Sandy-silty	0.057
Clay	0.058
Carbonate-clay	0.048
Carbonate	0.059
Silica	0.049
Volcanomictic	0.073
Sedimentary shell (no effusive)	
Continental block	0.051
Ocean block	0.057
Sedimentary shell total	0.051

Table 16

Average TM values in the sedimentary shell

Rocks	Riphean + Vendian			Paleozoic			Mesozoic + Cenozoic		
	1	2	3	1	2	3	1	2	3
Sandy	0.056	0.053	0.053	0.048	0.048	0.051	0.060	0.048	0.051
Clay	0.041	0.054	–	0.059	0.042	0.058	0.047	0.049	0.050

Table 16 data means that ***all average compositions of sedimentary rocks are normal-titanium according to the siallite standard.*** A typical exception is volcanomictic sediments and ocean rocks, which are super-titanium. This is natural, since the volcano- and pyroclastic admixture in them is basic, with a high titanicity. As D. Spears and R. Canaris-Sotiriou correctly note, "*The addition of volcanic material to the normal sediment may either increase or decrease the whole rock* TiO_2/Al_2O_3 *ratio depending on the ash composition. Volcanic contributions may thus be recognized* <…>" [353, p. 345].

Obviously, acidic ash should decrease the titanicity of the sediment, while the basic ash should increase it. For example, according to E.M. Emelyanov's data [103], in the upper layer of bottom sediments of the Atlantic Ocean, the maximum Ti content is observed in volcaniclastic sediments (on average 1.13 % Ti or 1.88 % TiO_2), and the minimum – in biogenic carbonate sediments (0.12 % Ti or 0.2 % TiO_2).

If we plot the average compositions of the silty sandy rocks of the Russian Plate, calculated by A.B. Ronov and colleagues, aged from Riphean to Neorene, inclusive [227], on the HM–TM module diagram, we can observe a wide band of negative correlation: the higher the HM, the lower titanicity of silty-sandy rocks (Fig. 9). It is obvious that here both tendencies of TM changes are summed up, caused by the "substrate" and "dynamic" factors of sediment genesis. On the one hand, we should correlate the drop in titanicity with an increase in the "arkose" content of sandy-siltstone rocks since the parent felsic rocks are characterized by low TM values (especially rhyolites). On the other hand, we can see the Migdisov law manifestation – an increase in TM value with an increase in the dynamic sorting of clastic material, which is characteristic of oligo- or even monomictic quartz sands with low HM values, corresponding to super- and hypersilites. For example, pure quartz sands and sandstones in the Paleogene of the East European platform [214, p. 157] show TM values from 0.108 to 4.333.

High TM values as a reflection of the petrofund titanicity. As follows from the Leningrad geologists' data (Table 17), the main reason for the abnormally high TM values in the metasedimentary rocks of the Karelians of the Kola Peninsula is the increased Ti content in the petrofund due to tuffaceous material [12, p. 1697]: "*In the composition of the silty-pelitic fraction of the*

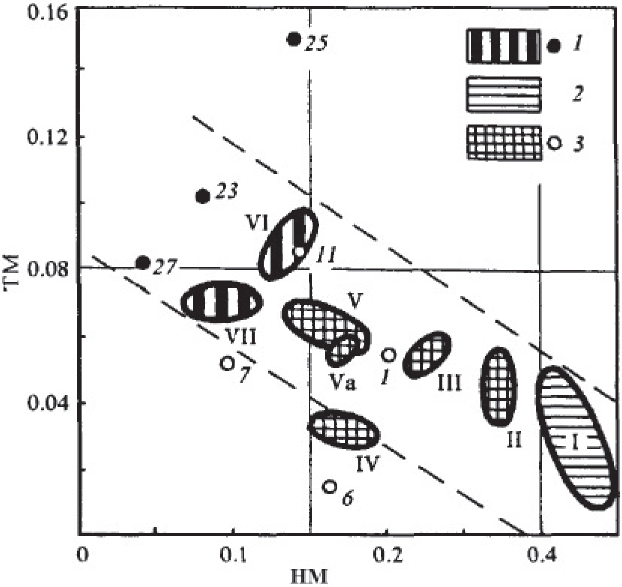

Fig. 9. Module diagram for average compositions of Russian plate silty-sandy rocks. Each point corresponds to 5–90 analyzes of average samples made up of 5–1362 samples. *Compiled according to the data of A. B. Ronov, A. A. Migdisov and K. Hane, 1995* [227, pp. 326–327].

Geological age: 1 – Cretaceous-Neogene, 2 – Carboniferous-Permian, 3 – different (but with a predominance of the Paleozoic)

carbonaceous rhythmites of the Pechenga and Kuolajϑrva metasediments, we observe the presence of a fine-grained leucoxene aggregate, which develops in separate interlayers composed of tuffaceous material. A significant presence of leucoxene ... is noted in tuffaceous rhythmically layered aleuropelites of distant deep-water facies. Tuffaceous carbonaceous psammites and pelites of the fourth sedimentary horizon of the Kuolajϑrva synclinorium are especially enriched in titanium (up to 6.2 % TiO_2)".

Most of these rocks are also enriched in iron, which is also volcanic, and iron minerals can make some contribution to the total titanium content, since the composition of detrital and authigenic hematite contains up to 4.16 % TiO_2. And the Migdisov law could be only of secondary importance for these rocks, that is, the dynamic separation of titanium and aluminum. We can see this in the metapelites composition of the second sedimentary sequence of the Pechenga: these are formations of highly dynamic facies – flows and deltas. However, it is significant that in these facies the clastic material was initially enriched in titanium due to the erosion of rich in titanium magnetite-bearing

Table 17

Anomalous average TM values in the Mesoprotosoic metasedimentary rocks of the Pechenga and Kuolajärva structures of the Kola Peninsula.

Compiled according to the data of A.M. Akhmedov, A.S. Voinov [12]

Metamorphic rocks	n	TiO_2, %	Al_2O_3, %	TM
Pechenga synclinorium				
2nd sedimentary stratum (Kuetsjärva)				
Metapelites	7	1.40	16.10	0.087
3rd sedimentary stratum (Kolosjoki)				
Arkose metapsammites	11	1.64	9.70	0.169
Metaaleurolites	8	1.98	14.30	0.138
4th sedimentary stratum (Pilgujarvi)				
Greywacke metapsummites	20	1.04	11.75	0.188
Greywacke metapelites	20	1.49	17.69	0.084
Magnesian metaaleurolites	11	1.78	11.90	0.149
Basal metapelites	5	2.57	21.42	0.119
Kuolajдrva synclinorium				
3rd sedimentary stratum				
Magnetite-bearing greywacke gravelstones and metapsammites	9	1.19	8.54	0.139
4th sedimentary stratum				
Volcanomicticmetapsammites with carbonaceous matter	4	2.59	11.60	0.223
Volcanomicticmetaaleuropelites with carbonaceous matter	10	2.10	16.71	0.126
Ultra-basic metatuffs and metatuffites	6	1.06	10.53	0.101

albitophyres. And the weathering crust developed along them at the base of the sequence. Here the TiO_2 content is 4–5 %. This high titanicity is inherited by the overlying sandy sediments [12, p. 1695]: "*Products of eroded weathering crust and underlying effusive rocks, although mixed with granitoid clastic material, significantly enrich the sediments of the Pechenga deltaic and flow facies with titanium in comparison with deposits of a similar type*".

TM as a possible indicator of the *first cycle* arkoses. One of the petrogenic deposits signs may be the *reduced titanicity of sandstones compared to siltstones*, while lithogenic deposits, as a rule, are characterized by the opposite. An example is the Iotnian (Middle Riphean) red–colored arkoses of the Tersk series of the Kola Peninsula, studied by A.V. Sochava [245]. We obtained a similar result by processing of terrigenous rocks analyzes of the Middle Riphean Shatak Formation in the South Urals [202, p. 51]. Here, the TM of sandstones is also reduced in comparison with the TM of siltstones and argillites, which, apparently, makes it possible to classify these deposits as petrogenic arkoses.

TM variations in weathering crusts and their derivatives. The different titanium content of the substrate is inherited by the weathering crust formations. For example, among kaolinite clays there are two groups – with low and high titanicity, which indicates acidic and basic substrates of kaolinite. The most striking example of low-Ti kaolinite is interlayers of *tonsteins* – products of alteration of acidic pyroclastics in the aggressive environment of a peat bog [295, p. 34].

As shown by the careful studies of C. Weaver [359], kaolinite contains titanium in the form of anatase, and most of the TiO_2 is represented by spherical particles with a diameter of only 0.05–0.10 µm. The TiO_2 balls were formed from Ti^{4+} ions in the octahedral layers of biotite and other dark-colored minerals.

In the kaolinite structure, the balls are either isolated (individually and in the form of spherical and layered aggregates of irregular shape), or they form whole layers. They contain impurities of Al and Si – as it is assumed, in amorphous compounds that act as cement. It is assumed that the initial form of anatase balls was an amorphous $Ti(OH)_4$ gel, and only a small part of anatase in kaolinite is represented by larger tabular anatase pseudomorphs by ilmenite, several microns in size.

Anatase particles of so different in size should behave differently under the conditions of the weathering crust erosion: in more massive plates of apoilmenite anatase; more chances of separating and accumulation in the sandy sediment. On the other hand, micron-sized anatase beads should be easier to dissolve with the titanium removal in reducing media.

According to G.I. Bushinsky, in the parent rocks – a substrate for the weathering crust formation – titanium is present in three main forms [38, p. 215]: ... *"1) grains capable of giving placers, 2) small crystals, and 3) an isomorphic impurity in other minerals. The last two forms predominate quantitatively and give, during weathering, fine particles, which are carried by water together with clays. Some of the fine particles included in the fragments of the weathering crust are transferred in coarse dispersions, for example, during the accumulation of sedimentary bauxite. In the process of rocks chemical weathering, titanium, like aluminum, accumulates as a residual product. In this case, no significant titanium removal is observed*".

Thus, TM of bauxite is inherited from the substrate, and G.I. Bushinsky can be understood so that TM will not change significantly, even if bauxites undergo epigenetic processes [38, p. 216]: "*During the aluminum chemical removal, titanium is also removed from bauxite. The iron removal is most often not accompanied by the titanium removal. This fact makes us assume the existence of some relatively mobile titanium–aluminum complexes*".

In fact, as numerous data show, the mobility of titanium and aluminum during bauxite epigenesis is different, and this must necessarily change the TM value. As emphasized by N.M. Strakhov, "*when TiO_2 and Al_2O_3 go in an acidic solution, they inevitably separate very quickly. The alumina precipitate* *becomes titanium-free. This process is inevitable, since* TiO_2 *settles at pH < 2, and* Al_2O_3 *– at pH 4.5–5*" [249, p. 251].

Materials on weathering crusts reveal both trends – TM inheritance of the substrate and changes in HM in epigenetic processes.

For example, N.A. Lisitsyna and M.V. Pastukhova, who processed 1500 analyzes of Paleocene–Eocene bauxites in Kazakhstan, note that the TM value in them is stable: *"... as* Al_2O_3 *increases, the* TiO_2 *content proportionally increases."*

However, titanium is removed more vigorously than aluminum in reductive epigenesis. If among the Amangeldy group of deposits in the upper member of red bauxites and clays the average TM value is 0.061, then in the middle member of grey "lignitic bauxites and clays" it decreases to 0.017. In this regard, the authors write [157, p. 243]: *"<...> in a highly reducing environment, there is a significant iron, titanium and partly aluminum removal. The latter, apparently, becomes mobile at low pH values. These elements are removed to varying degrees, which is the reason for the permanent violation of the* TiO_2 *and* Al_2O_3 *ratio. At the same time, the* TiO_2 *content falls to 0.16–0.5 %, while the* Al_2O_3 *content does not fall below 12–25 % <...>*". Indeed, according to the D. Carroll's calculations of [325], at Eh = –0.3 V and in an acidic medium at pH = 3 (in the field of pyrite existence) 84 % of the total Ti should be reduced to the migration-capable form Ti^{3+}. However, the titanium migration can also lead to an increase in TM [157, p. 244]: "*It can be assumed that titanium, coming from rocks rich in* C_{org}, *moving over short distances under the influence of reducing conditions, enriches the neighboring areas of bauxite*".

Under the conditions of peat bogs, tetravalent Ti (IV) can acquire mobility either upon reduction to Ti (III), or which is no less important, under conditions of abundance of complexing agents in the solution: ligands of humus acids – humic (HA) and fulvic (FA). Calculations show that under the conditions of peat bogs, the formation of Ti–HA and Ti–FA complexes containing 1.5–2.0 % of titanium is possible [307, p. 75]. These data are directly related to the formation of those weathering crusts that were overlapped by bog deposits. "*The reality of Ti leaching from terrigenous suspension in an aggressive environment of peatlands has been reliably proven by experiments <...> and indirectly confirmed by a number of mineralogical observations on titanium migrations in the OM presence...*" [307, p. 78].

In the normal laterite profile of the ancient WCr (weathering crust) on the ferrous quartzites of the KMA (Lebedinskoe deposit), loose martite-marshallite eluvium occurs on the substrate and, higher, loose rich iron ores composed of martite, hydrogematite, and hydrogoethite [34]. These ores have a TM of 0.052. When the epigenetic sideritization process is applied to the WCr column, the TM values clearly increase to 0.109 and even 0.235.

However, further development of this process, with the transformation of Fe-hyperhydrolysates into Fe-carbonatolites, is accompanied by a strong TM dispersion, so that, on average, it even decreases. Thus, the ***reduction of iron and its involvement in migration is accompanied by the titanium migration.*** When aluminum is immobile, this can lead to both an increase in TM (titanium input) and its decrease (titanium output).

With the accumulation of data, it became clear that even in the absence of epigenetic processes, the TM value changes during bauxite formation. Thus, the processing of materials by Yu.G. Tsekhovsky on the Cretaceous-Paleogene humid red-colored deposits of Kazakhstan [268] suggests that in zonal weathering crusts without significant manifestation of superimposed processes, the development of the bauxite process (AM increase from 0.20 to 0.80) is accompanied by a *decrease in TM* (decrease in TM from 0.080 to 0.010). All deviations from this trend show either more ferrous formations or the products of epigenetic changes – re-silicification.

The decrease in TM in the ancient laterite process is also evidenced by the data of A.P. Nikitina et al., who studied the Lower Visean laterite WCr on carbonaceous KMA Karelian shales. The processing of these data shows a decrease in TM from the original rocks (0.031) to kaolinized and further to bauxite (0.023–0.026). A similar picture is observed in the laterite WCr of the same age on the substrate of amphibole-chlorite schists (pseudosiferlites) in the North Onega region: from the original rocks to montmorillonitized and kaolinized and then to gibbsite TM decreases from 0.047 to 0.035–0.038 [185, p. 210–211].

The picture of TM changes in bauxite-bearing variegated deposits of Central Kazakhstan (Paleocene–Middle Eocene) is even more complex. We processed 13 analyzes, of which 12 belong to the Arkalyk bauxite deposit (104, p. 178]. All these laterite formations are certified as titanium hydrolysates. According to the HM value, the following can be distinguished among them: Ti-normohydrolysates, represented by kaolinite clays; Ti-superhydrolysates, represented by dried bauxite; Ti-hyperhydrolysates, represented by stony bauxite.

At the same time, in the genetic series “clays ⇒ crunchy bauxites ⇒ stony bauxites” the titanium module TM first decreases and then increases, reaching the initial values (on average, about 0.065). However, there are also more titanium bauxites, in which both the TiO_2 content and the titanium module TM value are almost doubled. This difference can have two explanations: either the selective accumulation of titanium in comparison with aluminum, or the primary more titanium substrate. Note that it is these bauxites that are closest to clays (AM 2.28–2.32 versus 0.75–1.31 in clays), apparently representing the initial stage of bauxite formation, for which the assumption of the differential titanium and aluminum mobility is quite acceptable.

The study of *young laterites* also provides numerous evidences that the TM value in the laterite process is subject to a noticeable change. Judging by A.D. Slukin's data, who studied young Indian laterites, in the series of lateritic WCr from dolerite to kaolinized dolerite and further to laterite, the *TM value clearly decreases*: 0.129 ⇒ 0.106 ⇒ 0.052. This process, i.e., the anticipatory accumulation of alumina against the background of stationary or even outgoing titanium, continues in bauxite as well. In the richest bauxite with 71.9 % $A1_2O_3$, TM drops to 0.008. On the contrary, in epigenetic formations such as cuirass (about 40 % Fe_2O_3) or in iron-enriched kaolinite-goethite formations, in gibbsite-goethite crusts ("gingerbread") TM can again increase to 0.189. It can be assumed that at the stage of kaolinization (with a relatively weak silica removal), titanium accumulates (but weaker than alumina), and with intensive silica removal, it begins to output and, entering migration, can accumulate together with iron.

Processing of Yu. Yu. Bugelskiy's eleven analyzes on Cuba young laterite weathering crusts [32, p. 95–122] makes it possible to construct a series of increases in the average titanicity: *WCr for gabbro (TM 0.019) ⇒ WCr for andesites (TM 0.034) ⇒ WCr for andesite tuffs (TM 0.036) ⇒ WCr for shales (TM 0.052)*.

Outside of this series, there are several high Ti compositions of WCr in gabbro (TM 0.058–0.109). It is difficult to interpret these data otherwise than as an indication of the titanium removal possibility in the crust formation process over the gabbro substrate. Otherwise (since the initially gabbro substrate is more titanium), one would expect the most titanium WCrs for this substrate. Another (weaker?) assumption is about the heterogeneity of the gabbro substrate in Cuba, about its initially different titanium content.

Let us add that the laterite process can develop on any substrate, for example, on a phosphate one. An example is the Cambrian pellet phosphorites of Queensland in Australia [326]. Undergoing superimposed laterite weathering, these rocks lose phosphorus and alkalis. At the initial stage of this process, the TM sharply increases (0.036 → 0.246), possibly due to the relatively higher inertness of TiO_2 compared to Al_2O_3.

Thus, the accumulated data indicate that the TM value in the laterite weathering crust does not remain stable even in the normal course of the process not complicated by epigenesis, and most often TM decreases with bauxite formation. If the processes of epigenesis (cuirass formation, sideritization, chamositization, kaolinization) are superimposed on the WCr, then the fluctuations in the TM value can acquire an irregular, "chaotic" character, which greatly complicates the judgment of the WCr substrate's primary titanicity.

A.I. Pak specially investigated the titanium behavior in weathering crusts, having at his disposal materials for both Phanerozoic and more ancient WCrs. He calculated the input–output coefficients (K_{io} of titanium in 54 sections of different age WCrs and concluded that the behavior of titanium in WCrs underwent a characteristic evolution [200, pp. 122–123]: *Early Proterozoic, Early and Middle Riphean weathering crusts differ from their younger counterparts in a generally negative titanium balance <...> Obviously, this is due to the predominance of migration (removal) processes in the weathering zone <...> In the weathering crusts of the Mesozoic and Cenozoic, there is a titanium accumulation and removal from all zones of the weathering crust <...> The intensity of these processes in the Mesozoic and Cenozoic is greater than in the Precambrian. This is apparently due to the development of weathering crusts in the Mesozoic and Cenozoic in both oxidative and reducing conditions*".

Incomplete similarity of the titanium and aluminum behavior in WCr could lead to some regular fluctuations of the titanium module in time. Aluminum ..."*at the beginning of the Proterozoic did not experience any noticeable migration <...> From the Middle Proterozoic to the Middle Riphean, there is a slight removal of it from the weathering crusts (from 2 to 12 %) <...> Starting from the Middle Riphean, the behavior of aluminum in the weathering crusts is unstable; both accumulation and removal are noted. However, the weighted averages of the input–output <...> in the weathering crusts of the Middle and Late Riphean are relatively small (*K_{pw} *from 0.70 to 1.20) <...> There is evidence of an aluminum weak accumulation (6–8 %) in the weathering crusts from the Middle Riphean to the Silurian. Since the Devonian, the intensity of this process in weathering crusts has increased on average to 160 %*" [200, p. 118].

Unfortunately, A.I. Pak himself did not calculate the TM values and did not trace their fluctuations; not having the materials he has collected, it is impossible to do this. Nevertheless, based on the above, it can be assumed that ***throughout the history of the Earth, the TM value should not have remained stable in the weathering crusts – it probably fluctuated depending on the Eh of the medium, since low Eh values increase the titanium mobility, but do not affect the Al mobility. Therefore, weathering in reducing media should have led to a decrease in TM due to the predominant titanium removal.***

Since it is highly probable that the media with low Eh were at the same time carbon dioxide-bearing, iron removal should be expected in such a *gley process*. This could lead to a positive correlation between TM and FerM in the weathering crust derivatives. However, if, following A.I. Pak, we admit the possibility of mass aluminum removal in the gley process (in the form of salts such as dawsonite), then all our reasoning becomes doubtful. ***The conclusion is obvious: to understand the evolution of ancient hydrolysates, it is very important to systematically study the distribution of the TM value in the weathering crusts depending on the WCr age.***

TM in rare types of weathering crusts

The rare ones include high-titanium WCrs, which usually develop over a titanium-rich substrate. For example, in the Mesozoic WCr on ore-bearing troctolites[5] of the Korosten pluton of the Ukrainian crystal shield [26], TM clearly decreases in the series of initial and intermediate decomposition – clayization of the substrate: 0.429 (initial rocks) ⇒ 0.360 (leached troctolites) ⇒ 0.224 (essentially kaolinite – montmorillonite zone). In the same series, the content of TiO_2 also decreases, in%: 6.14 ⇒ 5.77 ⇒ 5.41. However, in the rear kaolinite-goethite WCr zone (where there is almost no additional leaching of the substrate – only hydrolysis), the TiO_2 content again increases to 8.97 % and simultaneously TM rises to 0.328. It is obvious that in this zone the accumulation of titanium occurs faster than the accumulation of aluminum.

In the Cretaceous–Paleogene sediments of the Zaisan Depression, variegated clays are described, which are the product of a peculiar, *ferrous-silica* type of weathering and soil formation. This process developed over the substrate of silty-clay deposits and led to the appearance in the section of powerful monotonous members of ferrous-silica variegated strata, often associated with peculiar quartz sandstones – "*with very dense silica and ferrous cement*" [104, p. 137]. The ferrous-silica profile usually has three zones: lower variegated flowers (0.3–0.5 m), upper variegated strata (from 1 to 7 m), above, rather gradually turning into a clay-stony silica-ferrous cuirass, composed mainly of goethite and hematite. Clear traces of dissolution of detrital quartz are visible in it, and the kaolinite of the original rocks undergoes the dispersion-allophanization process.

Data processing by V.S. Erofeev and Yu.G. Tsekhovsky shows that, as the profile of the ferrous–silica crust develops, there is a decrease in HM caused by silicification (which is very unusual for WCr, in which the opposite usually occurs) *with a significant increase in TM*: from 0.055 to 0.081. This increase reaches its maximum during the formation of "ferrous argillites" containing twice as much iron and even less alumina than the cuirass. It is easy to see that the increase in TM is not explained by the titanium input (the content of which in the cuirass does not change or even slightly decreases), but rather the *aluminum strong output* as ferruginization-silicification occurs (23.63 ⇒ 14.00 ⇒ 10.70 % Al_2O_3). The aluminum output is accompanied by an intense supply of iron. Concerning the genesis of the ferrous-silica weathering profiles, V.S. Erofeev and Yu. G. Tsekhovsky compare them with the

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[5] Gabbro-anorthosites, containing on average about 14% ilmenite.

"*ferrsiallite type of the fulvoferrallite family of modern soils*" (according to M.A. Glazovskaya), which develop in areas with a subtropical or tropical humid climate under forest tracts. However, they believe that "*intensive silicification or ferruginization of the studied ancient soils is associated not only with the* SiO_2 *and* Fe_2O_3 *release in the soil profile itself, but also with the lateral input of these compounds by soil-ground waters<…>*" [104, p.145].

This interpretation means that the soil formation process took place in an acidic environment with an abundance of fulvic acids. Consequently, these were the conditions for the aluminum removal from the substrate (and the addition of iron) against the background of immobility or very weak titanium removal. In the same deposits V.S. Erofeev and Yu. G. Tsekhovsky described another rare type of ancient soils – *weathering crust with alunite cuirass.* The alunitization process developed along the substrate of silty clays of the floodplain facies, which are dominated by kaolinite with an admixture of hydromica or smectite. The profiles with a thickness of 3 to 4 m have a two-member structure: variegated strata develop on the parent rocks, above which there is an alunite cuirass horizon of variable thickness, from 1.8 to 0.1 m, up to complete wedging out. The formation of alunites occurs instead of bauxites and is due to the abundance of pyrite in the substrate [104, p. 149]: "*If the parent sedimentary rocks of the alunite weathering horizon did not contain significant amounts of iron sulfides in their initial composition, the process would end with the formation of not alunite, but bauxite cuirass*".

The researchers believe that sulfate and potassium were introduced into ancient soils by the lateral flow of soil groundwater and that these formations resemble modern acidic alum soils. Data processing by V.S. Erofeev and Yu.G. Tsekhovsky shows that as the soil profile develops from parent rocks – green clays-normosiallites to variegated clays-hypersiallites and further to alunite cuirass (hypohydrolysate) – an unusual process of K_2O growth occurs (usually in the WCr profile, the K_2O content decreases) with an insignificant increase in alumina and a decrease in the titanium content. Accordingly, TM decreases markedly: $0.049 \Rightarrow 0.038 \Rightarrow 0.025$.

So, relying on this example, we can assume that the ***process of sulfuric weathering is characterized by a decrease in TM.***

Some examples of Migdisov law. The Migdisov law is observed in terrigenous strata of different regions, different ages and different formational affiliation. This means that everywhere the elutriation process of alumina pelitic suspension and the accumulation of heavy titanium-bearing accessories in the sandy sediment proceeded in the same type. The *modern model* of the Migdisov law can be alluvial sandy deposits, such as the Holocene arkose sands of California, in the analyzes of which we find the presence of anomalous compositions (with increased titanicity (Fig. 10, sample 7). Less distinctly, but also noticeably, the ferruginosity is increased in these sands. It is obvious that we have here a natural schlich process – the accumulation of titanium-containing minerals. Indeed, anomalous titanium samples are coarse-grained (0.5–1.0 mm) and contain 5 % of heavy minerals [356, p. 198–199]. We can see a clear negative correlation on the NKM–HM graph; it is created precisely due to the "schlich" samples with an increased TM. Obviously, in the schlich process, a change in the "feldspars/mica" ratio occurs and the most alkaline is the most titanium coarse–grained sand with a minimum HM (sample 7: $TiO_2 = 1.98$ %, TM = 0.156) In this case, this means not the accumulation of feldspars, which would be little is clear, but the loss (washing) of micas.

This assumption is confirmed when processing analyzes of B.S. Lunev, made for the chemical characteristics of three alluvium genotypes [161, p. 128]. If these analyzes are plotted on module diagrams, then in the series of alluvium "mountain ⇒ mountain-plain ⇒ plain" one can notice a regular decrease in HM (due to an increase in the proportion of quartz) and an increase in the values of TM, as well as FerM and NKM. Obviously, as the dynamic sorting of sediments increases, not only the content of iron-titanium concentrate increases, but also the feldspar/mica ratio, due to the washing of light micas from the sands.

In *modern oceanic lithogenesis*, the Migdisov law can be masked by an admixture of titanium volcaniclastics. However, it is clearly manifested in the settings of the *continental slope*, where this factor can be neglected. For example, the study of the bathyal sediments of the Bengal Cone showed that TM values increased from the Late Miocene to the modern period. This is explained by the increase in time of the bottom gravity flows velocity, which transported clastic material from the slope and shelf towards the abyssal basin of the Indian Ocean. The reason for this evolution was the rise of the Himalayas – this led to an increase in the rate of land denudation [350].

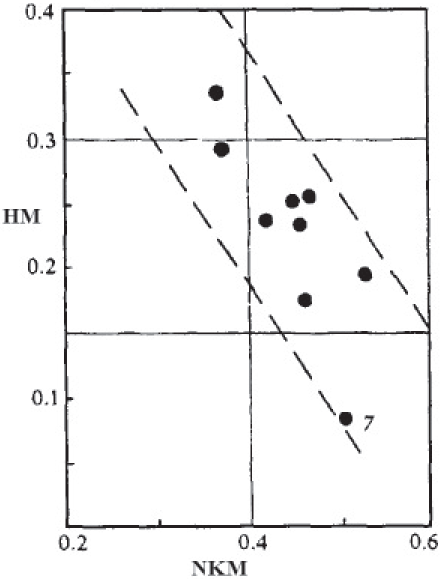

Fig. 10. Module diagram for the Holocene arkose sands of California, Salt Lake area. *Compiled according to P. Van de Kamp and others* [356, p. 199]

The Migdisov law is perfectly manifested in the strata of the flysch type, for example, in the Paleogene of the northern slope of the Ukrainian Carpathians. Sandy-silty rocks of this flysch reveal hyperferrous and hypertitanicity in half of the compositions given by I.M. Afanasyeva [10]. Since the gross contents of iron and titanium are low, this picture is due to the removal of alumina by vigorous elutriation of the clay suspension from the clastic material containing heavy Fe-Ti minerals. A similar picture is revealed when processing a sample of 68 sandstones analyzes from the Cretaceous–Paleogene flysch of the Inner Carpathians [11]: out of 13 hypertitanium compositions (TM > 0.085), 12 were Paleogene and only one was Lower Cretaceous. Since among the Paleogene sandstones, quartz varieties dominate here [11, p. 62, 74], then we can think that these are lithogenic formations of the *second cycle* type.

On the contrary, flysch *clay deposits*, in contrast to sandy ones, should be distinguished by extremely low TM values due to the depletion of clay suspension with titanium during its elutriation in a turbid flow. Indeed, the processing of siltstones and argillites analyzes of the Gissar-Alai Carboniferous flysch [271] reveals the presence among them of compositions with a strikingly low TM, up to TM = 0.001. This feature can be considered as a lithochemical "visiting card" of flysch.

A remarkable contrasting picture is revealed when processing R.A. Mandalyan's data for two types of Callovian sandstones of the Lesser Caucasus: acid greywackes of the Somkheto-Karabakh anticlinoric zone and calcareous quartz sandstones of the Vayksk anticlinoria [166, p. 23, 33]. The first are normotitanium, with TM values of 0.057–0.037 and 0.024–0.026, which reflects their acidic petrofund. Indeed, according to the R.A. Mandalyan's description, greywackes contain on average 22 % plagioclase, 12 % inheriting epidote, 39 % fragments of acid effusive rocks and 8 % quartz [166, p. 22]. On the contrary, calcareous sandstones are characterized by hypertitanium values: TM from 0.318 to 0.410. It turns out that the carbonate cement of quartz sandstones is not chemogenic. It is represented by "*a mixture of micro–grained and fine detrital (sludge) material. It also contains fragments of crinoids, corals, pelecypods and oolites*" [166, p. 32].

These features clearly indicate the process of natural sizing of the carbonate–quartz sediment. Therefore, the high TM values of calcareous sandstones are most likely due to dynamic sediment sorting. Thus, two lithotypes of Callovian sandstones seem to belong to different genotypes: *first cycle* and *second cycle*.

Almost all sub-platform Famennian-Tournaisian quartz sandstones and quartzites of the Lesser Caucasus, described by M.A. Satian et al. [230, p. 112–113] are characterized by hypertitanium values: with an average value of 0.139, TM reaches such unusual values as 2.213. Obviously, as for the Callovian sandstones described above, here we are dealing with well sorted (and, most likely, recycled, lithogenic) clastic material, from which the clay impurity was removed during numerous washings. This process is most pronounced in quartzites – rocks, the least clay and most titanium.

TM anomalies in glauconite sands. So, the Migdisov law is most clearly manifested in quartz sandy rocks of the *second cycle* type. However, there is an important exception to this rule – quartz sands with glauconite. As V.N. Shvanov points out, glauconite can be considered syngenetic only in a very broad sense – as a mineral approximately synchronous with the formation of sandy sediment. "*Glauconite sandstones are most often composed of glauconite, formed from the washing of clay glauconite-containing silts, since this mineral is formed in clay silts with a certain organic content and pH, Eh of the medium. Silty sediment in the geological sense can be almost synchronous with the forming sand, it can be weakly lithified, and its destruction can be associated with local consedimentary erosion. The resulting glauconite grains are not detrital components by their nature; strictly speaking, they are not authigenic components of the sand containing them*" [276, p. 123].

Processing of 11 analyzes of Cenomanian quartz sands of the Kaluga and Smolensk regions [140, p. 123] showed low TM values: from 0.022 to 0.038 on average (for three clusters), and for individual samples – even such low values as 0.012. Actually at low TiO_2 contents at the level of 0.03–0.10 %, glauconite makes the sands abnormally aluminous (up to 5 % Al_2O_3 in some samples), which leads to a decrease in the TM value (and to an increase in the AlkM module).

Thus, anomalously low TM values in quartz sands or their metamorphic analogs (in combination with increased AM) can serve as an indicator of the presence (or former presence) of glauconite in them.

TM anomalies in silicious rocks. If an alumina content increased against the norm leads to a decrease in TM, then an abnormally low alumina content, on the contrary, will increase the TM value. Such a picture is typical for some silicious rocks in which the values of TM, NKM and FerM are increased, i.e., all three modules with alumina in the denominator. This may be due to the incorporation of alkalis into low–alumina silicates, where the place of Al^{3+} is occupied by Fe^{3+} [295, p. 32]. For example, in the Upper Cretaceous jasper of Kamchatka [193], the TM values exceed 0.060, while the TM values in silica argillites and phtanites are much lower. Actually, even with comparable TiO_2 contents, jasper are much less alumina rocks than phtanites, and even more so argillites.

In addition, the TM of some silicious rocks can be increased due to *biogenic accumulation of titanium*. Such facts were noted for spongolites, biomorphic silicites formed from the remains of silicious sponges [295, p. 128; 327]. For example, according to the analyzes of J. Martin and G. Knaurer (1973), we calculated the TM values for the silica plankton of the Pacific Ocean and obtained high TM values– about 0.120 and 0.140. "*These calculations show that the increased titanium module of silica rocks can be created not only due to silica sponges, but partly due to silica phytoplankton*" [306, p. 72].

TM of tonsteins as an indicator of their genesis. In coal seams, kaolinite interlayers – tonstein (German *Tonstein*: clay stone) have been known for a very long time. At low thickness (centimeters and fractions of a centimeter), they are often traced in the coal basin for tens of kilometers, which allows them to be used as excellent stratigraphic benchmarks. The most convincing version of their volcanogenic genesis is that they are interpreted as interlayers of acid ash that underwent kaolinization in the aggressive environment of ancient peat bogs. Nevertheless, the genetic link between tonsteins and kaolin weathering crusts cannot be excluded. Actually, the existence of the latter is beyond doubt – this is precisely the nature of the "underclay" – kaolinite interlayers in the bottoms of many coal seams. For example, the famous Ukrainian lithologist prof. P.V. Zaritsky spoke ambivalently about the Donbass tonsteins [109, p. 186]: "<...> *the initial material of the tonsteins is mechanically introduced into a peat bog (most likely by aeolian route) either material of weathering crusts or volcanic ash".*

It seems to us that the use of TM allows us to resolve this issue unambiguously. According to P.V. Zaritsky's data for Donbass, the average TM values fall within a narrow range of 0.010–0.017, which is characteristic only of rhyolites [315]. According to our data [295, p. 34], the scatter of individual TM values in tonsteins of several basins, although wider (0.005–0.050), still does not overlap with significantly higher TM values in kaolinite clays of weathering crusts (0.050–0.120). As a result, in the coordinates TM–TiO_2 (which are equivalent to the coordinates TiO_2–Al_2O_3), two fields of points are clearly distinguished, corresponding to low-titanium low-module clays and high-titanium high-module clays [295, p. 35]: *"It is remarkable that among kaolinite clays there is a group of low-module clays. All Donetsk tonsteins fall here. This is in very good agreement with only one hypothesis of their origin – as a product of acid leaching of acid volcanic ash*".

TM of carbonate rocks. After A.A. Migdisov's work on the sedimentary cover of the Russian Platform, it became clear that the TM of carbonate rocks is by no means inherited from the TM of the non-carbonate admixture contained in them. As a rule, the TM of carbonates is significantly higher not only the TM of clays, but often higher than the TM of sandstones.

Subsequently, we paid serious attention to the study of carbonate rocks TM during regional geochemical studies of the Paleozoic strata of the Pechora

Urals [295, p. 120–124]. In the carbonate strata of the Carboniferous, studied in detail by our graduate student T.I. Ivanova, the TM values fall within the range of 0.070–0.090. The higher titanicity of carbonates was confirmed by a detailed study of the Ordovician strata. It is characteristic that, all other things being equal, even in terrigenous rocks, TM very often turns out to be the higher, *the more carbonate admixture is in them* [130]. The study of the literature convinces us that the increased TM of most carbonate rocks is the rule, not the exception. For example, the Upper Jurassic "organogenic limestone" of Gissar [1] shows TM = 0.098, Cambrian limestone gravelite of Primorye [93] has TM = 0.148, siderite iron ore of the Lebedinsky KMA deposit [34] – 0.084, etc.

Of course, among the factors of the increased TM of carbonate rocks may be the Migdisov law, since many of them (detrital limestones) are shallow-water formations, formed during vigorous movements of water, which created the possibility of not only elutriation of clay impurities, but even sizing of heavy minerals. It was in such deposits that unique *chromium deposits* in insoluble residues were found - up to 1% of Cr_2O_3 [73]. Nevertheless, there are carbonate rocks with an increased HM, for which calm water conditions of sediment formation are more likely; for them it is necessary to look for *other factors* of increasing TM. At one time (1981) we assumed [295, p. 124] that such a factor may be the incorporation of a part of titanium into the carbonate substance[6]. Unfortunately, this idea has not yet been tested by anyone.

On the use of TM as a climatic indicator. Since in the A.A.Migdisov's works, the TM value in sedimentary strata showed a rather clear dependence on their climatic affiliation. This makes it possible to use TM as a climatic indicator. Siberian lithologists, especially E.P. Akulshina [2], widely practiced the use of the value Al_2O_3/TiO_2 (i.e., 1/TM) in this capacity. The Yakutsk geologist V.A. Amuzinsky interprets the change in the Al_2O_3/TiO_2 value along the almost seven-kilometer section of the Verkhoyansk complex C_1–P_1 in terms of climate. Following the E. P. Akulshina's methodological recommendations, he plotted the change in this value along the section (9 points corresponding to the formations) and concluded [4, p. 164]: "*The rocks of the lower part of the section <...> were formed in humid conditions* ($Al_2O_3/TiO_2 < 20$)*, and upper – in transition from humid to arid* ($30 > Al_2O_3/TiO_2 >$ 2Q)*. Thus, during the Upper Paleozoic, there was a steady change in climate from humid to humid-arid, which, accordingly, led to a decrease in the intensity of chemical weathering and an increase in the role of physical weathering*".

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[6] This idea was prompted by the presence of a free term (i.e., some extrapolated titanium content in pure carbonate matter) in the regression equations of titanium on the insoluble residue.

It is difficult to dispute this rather trivial conclusion, sufficiently reliably substantiated by other (in particular, paleontological and lithological) data. However, it should be noted that such use of TM (in this case, the inverse value of 1/TM) can be correct under the indispensable condition: unchanged titanicity of the petrofund during accumulation of the Verkhoyansk complex sediments. It is hard to believe that the average composition of a folded structure (Paleo-Verkhoyansk mountains) could remain the same for a hundred million years (this is the duration of only one Carboniferous). Therefore, it is important to emphasize that the difference between the TMs of humid and arid sediments has a diagnostic meaning (for diagnosing the climatic conditions of sedimentation) only other things being equal. ***The climatic factor influences the TM value much weaker than two other powerful factors: dynamic facies and petrofund composition.***

Sometimes the Migdisov law is observed in red-colored deposits, but it is important that *such red–beds are not arid, but humid.* We processed a statistical sample of 20 analyzes of Paleocene–Eocene ferrous-carbonate red beds, of which 15 belong to the Zaisan trough and 5 to the Chuya depression of Gorny Altai [104, p. 179–180]. It turned out that in the series of clusters formed on the module diagrams “sandstones and siltstones ⇒ aleurites and siltstones ⇒ clay and siltstones ⇒ clay”, the TM value monotonically decreases from 0.100 to 0.037. Since during the entire Paleogene the petrofund for these humid formations remained unchanged (the mountain uplifts of the Southern Altai and Sur-Tarbagatai were eroded [104, p. 55]), such a change in TM should be attributed only to the factor of dynamic sorting of clastic material, i.e., Migdisov law.

Other examples of high TM values in red sediments have a similar explanation – they are also due to the Migdisov law. Thus, at the Rudaevsk ocher deposit (Poltava Series of the Lower Neogene, Voronezh anteclise), judging by the given analyzes [13], quartz sands, kaolinite clays, and ocher proper are characterized by hypertitanicity (TM = 0.100–0.144). The extreme values of TM reach 0.256; probably, such sands formed in the delta facies, next to the eroded weathering crust on land. In such conditions, sizing of the sediment occurs, which we observed, for example, in the Visean deposits at the Voja whetstone deposit (Komi Republic) [316].

Probably, the given data can be “inverted” for diagnostic purposes: ***the manifestation of the Migdisov law in red-colored strata serves as an indirect indication of their humid (rather than arid) nature***.

Titanium-zirconium module as an antipode of TM. As the Portuguese researchers have shown, the titanium-zirconium module TiO_2/Zr can act as a kind of antipode of the titanium module. The point is that the titanium-zirconium module is controlled by the same two factors as TM: a) the composition of rocks in the source area, because the TiO_2/Zr module does not change during weathering; b) dynamic sorting of material, in which psammitic sediments acquire minimum module values, and pelitic sediments – maximum. This effect is due to the different forms of titanium and zirconium occurrence. Titanium is present both in the accessory mineral form and in the composition of clay minerals, while zirconium is almost exclusively in the form of accessory zircon. Since the latter accumulates in psammites, this also decreases the magnitude of the module [332].

Probably, the titanium–zirconium module could be used for diagnostics of isochemical metamorphites.

Short issues

1. The titanium module TM is one of the most effective tools in lithochemistry, which makes it possible to obtain information on the composition of rocks in the source area, on the dynamics of the sedimentation environment, and on the epigenetic processes of aluminum and titanium redistribution.
2. The higher TM of siltstones, rather than sandstones, may be a diagnostic sign of petrogenic arkoses of the first cycle rock type.
3. Contrary to the widespread opinion about the inheritance of TM in weathering crusts from their substrate, several examples have shown that in the normal laterite process there is a persistent tendency for TM decreasing during the substrate bauxitizing.
4. The previous data on irregular fluctuations of TM were confirmed when epigenetic processes were superimposed on the weathering crust column. These fluctuations are due to variations in the rate of aluminum and titanium removal. In this case, in the formation processes of ferrous weathering products (including Fe-hydrolysates), titanium follows iron, because of which TM increases.
5. In the Precambrian weathering crusts formed in reducing media, TM most likely tended to decrease in mature WCr horizons, due to the reduction and removal of titanium in the form of Ti^{3+} against the background of relative stability (or less weak removal) of aluminum.
6. Lithogenic clastic rocks are characterized by the *Migdisov law* – an increase in TM due to natural schlich process, i.e., the separation of the alumina clay fraction from the titanium-containing accessory minerals. The Migdisov law is one of the most reliable empirical patterns of lithochemistry.
7. Glauconite sands, even if they have a mono-quartz composition, are characterized by decreased TM values, and not increased due to the Migdisov law implementation. The reason for this anomaly is the abnor-

mally high alumina content of such sands. This can be a useful feature in the diagnosis of metamorphic metapsammites.

8. Deep–water silicon rocks (jasper, phtanite) are characterized by increased TM values, due to two factors: a) the presence of titanium pyroclastics, b) biogenic accumulation of titanium by silicious organisms (sponges and radiolarians).

9. Low values TM of coal kaolinite tonsteins are the most reliable indication of their pyrogenic nature, i.e., that these rocks are a product of bog weathering of acid volcanic ash.

10. Most carbonate rocks are characterized by increased TM values. But if for detrital (shallow) carbonates this can be explained in terms of the Migdisov law, for others this explanation is not suitable and the idea of the possible presence of a part of titanium in the carbonate phase gains the right to exist.

11. The use of TM as a climatic indicator requires caution, since it is associated with the need to consider other, more powerful factors affecting the TM value.

12. The use of the titanium-zirconium module value can be a useful adjunct and means of independent control of the TM outputs.

3.6. Ferrous module (FerM)

The ferrous module expresses the ratio between ferrous and aluminous hydrolysis products. But if for rocks-hydrolysates the FerM value is of service value (specifies genetically similar classes), then for siallites it is much more significant, since among normal sedimentary rocks of moderate hydrolysate high-iron rocks are not found. Consequently, if a rock has a HM within the range of 0.30–0.55, but at the same time shows an abnormally high FerM value, then this means that we are dealing either with a pyrogenic sedimentary rock, or simply with volcanic. Therefore, the value of the ferrous module $\text{FerM} = (FO_3 + FeO + MnO) / (TiO_2 + Al_2O_3) > 0.75$ was adopted by us for the separation of siallites and siferlites [302]. It is quite possible that this border, which is oriented towards the average FerM value for the main effusive rocks of the continents, is overestimated. Perhaps, experience will show that it is more expedient to lower it to 0.70 or even to 0.60. For now, we keep it in force, using gradations of chemotypes by iron content (Table 17a). Higher (relative to the siallite standard) iron content of siferlites is given by definition; the increased FerM of hydrolysates is also understandable since there are many Fe-hydrolysates among them. The increased FerM of carbonatolites and phosphatolites can be explained by the admixture of carbonate or sulfide iron, and the decreased FerM of alkalites – by their alumina content. The establishment of an increased iron content of silites can be considered a nontrivial result.

Table 17a

Chemotype gradations by FerM module

Chemotype	Hypo-	Normo-	Super-	Hyper-
Silites and pseudosilites	< 0.20	0.20–0.70	0.71–1.00	> 1.00
Siallites and pseudosiallites	< 0.30	0.30–0.55	0.56–0.70	0.70–0.75
Siferlites and pseudosiferlites		0.75–1.75	1.76–3.50	> 3.50
Hydrolysates and pseudohydrolisates	< 0.30	0.30–1.00	1.01–2.00	> 2.00
Alkalites	< 0.10	0.10–0.40	0.41–0.50	> 0.50
Carbonatolites	< 0.20	0.20–3.00	3.01–7.00	> 7.00
Phosphatolites	< 0.20	0.20–2.00	2.01–3.00	> 3.00

The frequency distribution of FerM in siallites and silites is similar to that for TM: in siallites it is close to normal (see Ch. 5, Fig. 48), and in silites it is similar to lognormal (Fig. 11).

Of great interest is the FerM value of sandy rocks, where it partly depends on *diagenetic processes*. As Middleton notes, the contents of Fe_2O_3 and FeO in sandstones depend at least on four factors: 1) the presence of terrigenous iron-bearing minerals; 2) the presence of terrigenous fragments of iron-bearing rocks, both sedimentary (especially jasper) and igneous, and metamorphic (especially basic effusive rocks); 3) the presence of authigenic

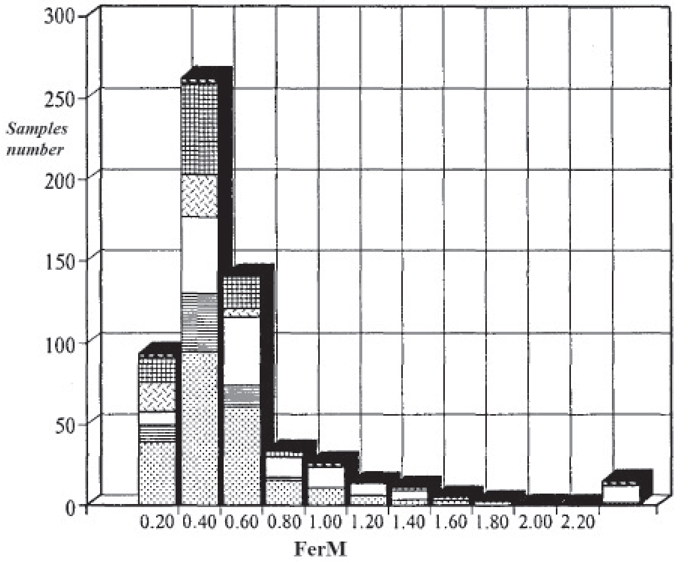

Fig. 11. Frequency distribution of FerM value in silites (630 samples, 11 735 analyzes). See the legend in Fig. 4.

oxides, sulfides, and iron carbonates; 4) the presence of glauconite [343, p. 1014].[7]

The first two factors are petro- and lithogenic, and the last two are aquagenic. Therefore, as in TM, quartz glauconite sandstones are anomalous in FerM. For example, the above-mentioned Cenomanian quartz sands of European Russia [140, p. 23] in 7 analyzes out of 11 showed an FerM of more than 0.65, and in some samples, the richest in glauconite, up to 1.05.

Table 18 summarizes the FerM values calculated for the average compositions of continents' sedimentary rocks, estimated by A.B. Ronov et al. [229].

Table 18

Average FerM values in the sedimentary shell

Rocks	Riphean + Vendian			Paleozoic			Mesozoic + Cenozoic		
	1	2	3	1	2	3	1	2	3
Sandy	0.45	0.39	0.28	0.37	0.36	0.38	0.36	0.34	0.40
Clay	0.32	0.41	–	0.33	0.37	0.49	0.23	0.38	0.38

Continents: 1 – platforms, 2 – geosynclines, 3 – orogens

Below are the FerM values for sediments of the oceans' first seismic layer and in the sedimentary shell:

Sediments	**FerM**
Sandy-silty	0.45
Clay	0.45
Carbonate-clay	0.51
Carbonate	0.70
Silica	0.59
Volcanomictic	0.52
Sedimentary shell (no effusive)	
Continental block	0.38
Ocean block	0.48
Sedimentary shell total	0.38

Thus, all terrigenous sedimentary rocks, except for the Mesozoic platform clays, are, on average, normal-ferrous according to the siallite standard, the silica sediments of the ocean are superferrous, and the carbonate sediments are hyperferrous. Since the hyperferrous platform clays are characterized by an increased HM and a decreased NKM, we can assume that these are rocks with kaolinite, formed predominantly from an acidic low ferrous substrate.

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[7] There are even five of them since the presence of jasper fragments in Middleton is a separate factor.

The hyperferrous values of carbonates can probably be attributed to the $FeCO_3$ phase, while the superferrous values of the silica sediments can be explained by the admixture of basic pyroclastics. Such an admixture can also be of an exhalative nature (ferrous gel coagulates), as was shown for the D_3 silicious sequence at Pai-Khoi [297].

The data on the composition of metapelitoids, compiled by A.B. Ronov and A.A. Migdisov in 1970, according to A.A. Beus, indicate that in the Katarchean the iron values of the shales was "andesitic" and not "basaltic". however, at the Karelian/Riphean border, their Fe content reached a maximum. On this basis, A.A. Beus concludes that "*a significant increase in the amount of basic volcanic rocks on the surface of continents in the Early Proterozoic time compared with the early Archean, when the role of andesitic effusive rocks, in all likelihood, was predominant*" [18, p. 296]. However, this conclusion is not confirmed if one uses not the absolute iron content, but the FerM. The FerM value calculated by us from the figures of A.B. Ronov and et.al [228] in the “shales” of the continents decreases noticeably by the beginning of Karelian, and then stabilizes: 0.53 (Katarchean) ⇒ 0.46 (Upper Archaean) 0.42 (Karelian) ⇒ 0.41 (Riphean).

Despite the importance of the FerM module for classification purposes (separation of siallites from siferlites), it is most often used not independently, but in tandem with other modules – usually with TM, FM or NKM. However, there are situations when the variances of other modules are small, and the variance is characteristic only of the FerM value. For example, the Lower Jurassic clays of the greywacke-shale formation in Armenia consist, according to I. Kh. Petrosov, of hydromica of the $2M_1$ polytype, close to muscovite, and in the detrital fraction, in addition to quartz (up to 50–60 %), volcanic glass is noted (up to 40 %), fragments of effusive and sedimentary rocks (up to 10 %), intensively altered feldspars (up to 5 %) [205, p. 63–64]. Against the background of the relative constancy of the bulk composition of these clays, the FerM is almost the only variable parameter, sensitively reflecting the admixture of chlorite that develops along volcanic glass and fragments of volcanic rocks. If, on the other hand, an increased FerM value is combined with an increased alkalinity (NKM), then this directly reflects the contribution of volcanogenic matter (dark-colored, glass, and feldspars).

A positive correlation of the FerM value with TM and/or with FM is characteristic of petrogenic deposits, since such a correlation reflects the “endogenous” relationship in the Fe–Ti–Mg triad. For example, for the Silurian metabentonites of Ireland [324], the minimum FerM and TM values are very characteristic – this sharply differs from the host shale-turbidites. The compositions of the Paleogene arkoses of Southern California [356], when plotted on the module FerM–FM diagram (Fig. 12), reveal a

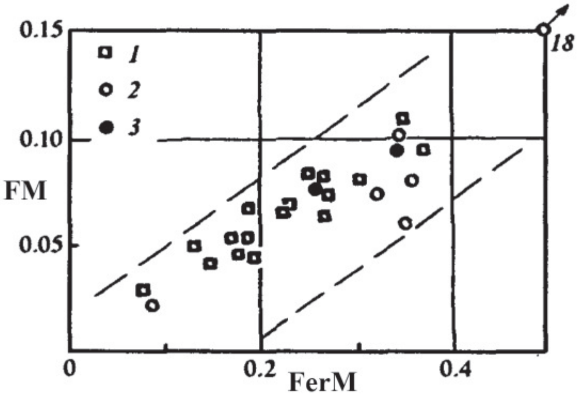

Fig. 12. Positive FerM–FM correlation for Paleogene arkoses of Southern California. *Compiled according to P. Van de Kamp et al., 1976* [356, p. 199]. 1 – arkoses proper, 2 – siltstones, 3 – gravel stones

single band of positive correlation, which includes the arkoses, siltstones, and gravel stones themselves. This correlation, among other things, serves as evidence that these rocks belong to the first cycle type. It is possible that this feature should help distinguish paragneisses (apoarkose rocks) from orthogneisses (apogranitoid rocks).

Sometimes a directed change in the FerM value can serve as an indicator of the epigenesis processes. Thus, when comparing the compositions of the initial Permian red flowers with their gleyed varieties [25], one can see a noticeable decrease in the FerM value: on average, from 0.50–0.30 to 0.30–0.20. This sitution is explained by the reduction and removal of a part of iron during gleying, against the background of relative immobility of aluminum.

3.7. Other modules

At the beginning of our lithochemical studies [295, p. 33] we envisaged the use of the *plagioclase module* PM = $(CaO + Na_2O)/K_2O$, the idea of which was taken from R. Garrels and F. Mackenzie [68]. Perhaps, in some special cases, the use of this module is justified, for example, it was used by G. V. Ivensen, who studied the thick terrigenous strata of the Verkhoyanye [114]. As noted by V. N. Shvanov, "*only in the case of washing basic and middle effusive rocks can specific basic arkoses and tuffs be formed* (? – Ya. Yu.)*, almost entirely composed of plagioclases fragments*" [276, p. 139]. Obviously, such rocks should show an abnormal PM module, which would help distinguish them from other siallites.

However, in most situations, the PM use has serious limitations. The point is that for the correct calculation of the plagioclase CaO_{pl} itself, it is necessary to consider CaO not only in the carbonates and apatite composition, but also in the sulfate composition, which is a common case for arid formations. Moreover, in the main greywackes, CaO can also be included in dark–colored silicates: epidote, amphiboles, and pyroxenes [276, p. 146]. All this means that the value of the plagioclase module PM calculated without corrections will have a persistent tendency to overestimate due to the inclusion of non–plagioclase components in CaO. The introduction of numerous amendments does not make sense, because it turns a simple procedure of module classification–diagnostics into a kind of normative recalculation. As a result, it turns out that PM does not have any advantages over AlkM (or its inverse value 1/AlkM = $K_2O:Na_2O$, used in many works).

Difficulties with the use of CaO content for diagnostic purposes are of fundamental nature. Actually, such leading CaO carriers as carbonates, sulfates, and phosphates are aquagenic formations. Meanwhile, the idea of using modules is to minimize the influence of sedimentary rock heterogeneity on its diagnostics. For example, when we calculate the NKM value for a carbonate rock, the amount of carbonate matter is not significant, since, as a rule, neither alkali nor aluminum is included in it.

In addition to plagioclase, we tried to use the *redox module* RM = FeO/Fe_2O_3. This value (either its inverse or normalized to the sum $FeO + Fe_2O_3$) is widely used in petrology. For example, intrusive rocks, as a rule, have a RM higher than effusive ones, which reflects significantly different oxygen fugacity (fO_2) during the formation of both. However, soon it became clear that the RM value has too large a dispersion without any clear regularities: it is heavily influenced by the diagenesis and metamorphism processes, leading to the iron reduction (and less often to its oxidation). For example, as noted above, in the presence of a sufficient C_{org} amount, all the original ferrous iron can be reduced to ferrous [300, p. 16] with the corresponding growth of RM "to infinity").

We know only one example of the RM successful application in lithochemistry – this is the work of E. Z. Gareev on the geochemistry of the South Ural stratotype of the Riphean [63]. Only with a very large averaging of the data the researcher revealed a rather clear pattern– an abrupt decrease in RM at the border between the Late Riphean and Vendian, which the author linked with an increase in the free oxygen content in the atmosphere.

CHAPTER 4

LITHOCHEMICAL DATA PROCESSING

4.1. Module diagrams

The rock composition can be represented by a point plotted on the graph in the coordinates of any petrochemical modules' pair. Such plots are called *module diagrams* [206]. Most often, we used module diagrams of the type NKM–HM, (Na_2O + K_2O)–HM, HM–TM, TM–FerM, FerM–NKM and, less often, some others. These diagrams are unequal: the first three are the most informative (since the HM module and alkalinity bear the main classification load), while the others are used for additional characterization of rocks. Since module diagrams NKM–HM and (Na_2O + K_2O)–HM are used much more often than others, we will call them *basic*, or main.

Yet no module diagram is universal, that is, suitable for any set of analyzes. For example, for aquagenic silica rocks, it is more convenient to use the diagram (Na_2O + K_2O)–HM instead of NKM–HM, as well as HM–TM. In addition, geosynclinal silicites are characterized by extremely high HM and FerM values, due to the deficiency of alumina. A strong dispersion of these modules with a small dispersion of HM often forces researchers to use the TM–FerM module diagram for clustering. For pyrogenic and some petrogenic rocks, it is preferable to use an aluminum-silicon module (AM) for acidic rocks and a femic module (FM) for basic rocks instead of HM.

At the initial stage of lithochemical studies, the calculations of the modules and the plotting of points on the module diagrams were performed manually, and later with the help of a computer according to the following algorithm.

1. One enters analytical data into a specially prepared matrix of the QUATTRO PRO (or EXCEL) spreadsheet processor, where petrochemical modules values, the sum of alkalis and the sum of all analysis components are calculated. The latter serves as a control of the technical procedure correctness: a “suspicious” amount of the amount allows one to quickly detect an error in data entry.

2. According to HM and other components' values (CO_2, Na_2O + K_2O, P_2O_5, SO_3, etc.), the samples are classified. Thus, all the original lithotypes receive a second, lithochemical, name – they are qualified. For example, "clay shale" is qualified as "alkaline hypohydrolyzate", feldspar-quartz sandstone – as "normosilite", etc.

3. Module diagrams are built on a computer, where the initial lithotypes are denoted by a conventional sign.

4. From the whole set of module diagrams, the one is selected that satisfies two conditions better than others: a) minimal lithotypes mixing; b) maximum resolution, i.e., differentiation of a set of points into separate subsets-clusters. Within each cluster, rock compositions (in given coordinates!) should be closer to each other than to any composition from any other cluster.

More often than others, one uses basic diagrams NKM–HM and (Na_2O + K_2O)–HM, less often – HM–TM, TM–FerM, and even less often – others. For example, the choice of the diagram (Na_2O + K_2O)–FM for distinguishing metaarcoses from metariolites in ancient metamorphic strata of the Subpolar Urals proved to be successful [315].

In general, we can recommend a universal four-ray diagram, in which the upper half (with HM) is more suitable for lithogenic and aquatic rocks, and the lower (with FM) for pyrogenic and petrogenic rocks. The right quadrants (with alkalis) are basic, the left ones are additional (Fig. 13).

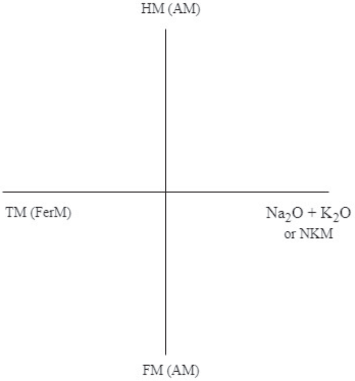

Fig. 13. Universal four-ray diagram (in brackets – modules that are used less often) [301]

After that, averaging is performed on a computer for close compositions that form clusters. **The cluster average composition is nothing more than a certain rock type (chemotype) composition.**

In a statistical sense, the difference between the averages for clusters and individual compositions that did not fall into the contour of clusters (or were excluded from them by additional parameters, for example, by the CO_2 content), lies only in the fact that for the former we know the natural variance (on the graph it is clearly reflected in the clusters size), and for the latter, we do not know. Here the researcher faces with the characteristic "Clark-Washington problem", that is, the problem of the analyzes set *representativeness* [252, p. 139—140]. One doesn’t know in advance whether the individual compositions are more rare rocks, or this is a random feature of the statistical sample – the different representativeness in relation to the natural set of lithotypes.

Often, the initial data were already *averages*. It is clear that the clustering of such data leads to the production of very compact clusters on the plots, since the natural dispersion of the compositions is already largely reduced at the first averaging of the analyzes.

As a result, any initial analytical data set falls into two parts: a) clusters, that is, average compositions calculated from at least two analyzes;

b) individual compositions that did not fall into clusters either due to a rebound (large variance) of their parameters, or exclusion from clusters for other features, for example, an abnormally high (for a given cluster) carbonate content.

Thus, the described procedure combines formal operations with non-formal (expert) ones. The latter include the formation of clusters (groups of close points are simply outlined on the graph) and the decision to remove one or another analysis result from the cluster, even if it formally falls there.

Let's show the application of module diagrams with several examples.

4.2. Choice of the right diagram

The variance of the modules itself suggests which diagram is more convenient to use for clustering. Obviously, if the modules values vary slightly, then the set of analyzes cannot be divided into separate subsets-clusters. However, if the variance of the modules is too high, then clustering also becomes a questionable procedure.

For example, Fig. 14 shows the compositions of six metasandstones samples of the Middle Riphean Kuvash Formation of the Southern Urals [202]. The main diagrams feature is the strong variances of the modules. At the best case, one cluster (dashed contour) can be distinguished on the HM–NKM graph, but this procedure is also questionable, since the compositions that fall into it still differ greatly in FerM, HM, total alkalinity and AlkM. The reason for these variances is the heterogeneity of the statistical sample made up of samples from

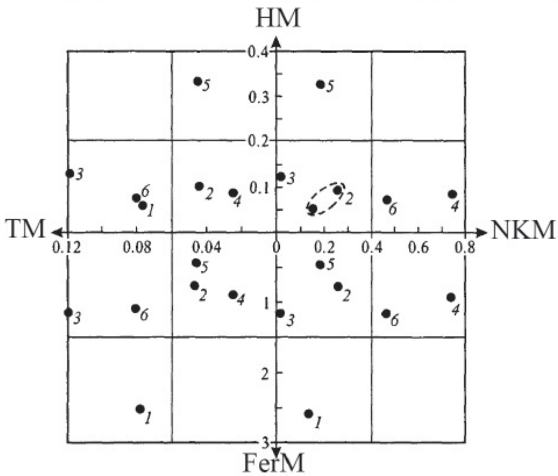

Fig. 14. Module diagrams for metasandy rocks of the Middle Riphean Kuvash Formation of the South Urals.

Compiled according to the data of V.P. Parnachev et. al. [202, p. 76] different regions. Probably, this heterogeneity refers both to the metasands of terrigenous material and to the facies environments of sedimentation.

All other things being equal, it is desirable to use a diagram where the parameters values are correlated, forming trend bands – positive or negative correlation. The location of the points in such bands usually indicates that the rocks belong to the same set – the one that in petrology has long been called a "series". On the contrary, the exit of individual points or entire clusters outside the trend band usually suggests that we are dealing with a mixed population.

Table 19 and Fig. 15 show the compositions of 26 Iotnian (Middle Riphean) siltstones and sandstones of the Tersk series (Kola Peninsula) [245, p. 96]. In this case, the boundary between siltstones and sandstones exactly corresponds to the HM value = 0.30, which confirms the siltstones proximity to clay, rather than to sandy rocks. Thus, all arkose siltstones are qualified as *siallites*, and sandstones – as *silits*. A negative correlation is observed on the module diagram of the NKM–HM: the lower the clay content of the detrital rocks (i.e., the higher the feldspar/mica ratio), the more acidic these rocks are.

A similar picture is observed in the Upper Cretaceous red-colored rocks of Mongolia, where clay rocks contain a noticeable impurity of arkose composition [245, p. 101].

Note that the Tersk "sandstones" of *cluster Id* have "siltstone" NKM values. All three analyzes represent "member IV" of the Tersk series section

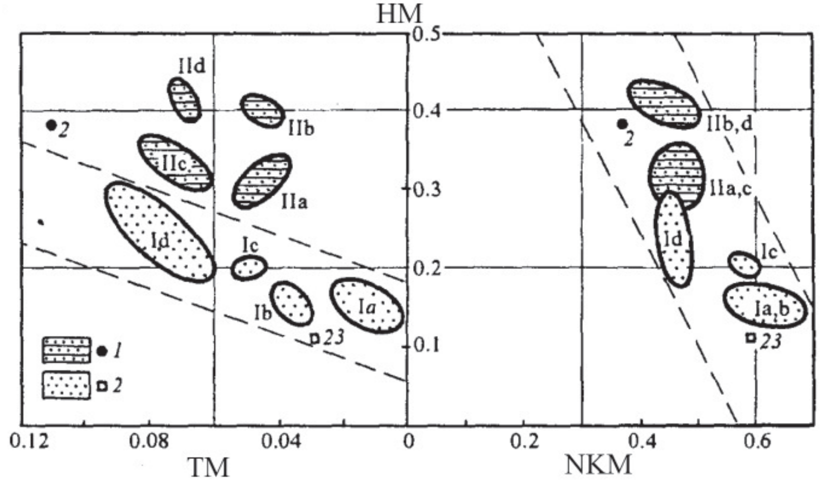

Fig. 15. Module diagrams for red-colored siltstones (*1*) and sandstones (*2*) of the Tersk series of the Middle Riphean of the Kola Peninsula.
Compiled according to the A.V. Sochava's data [245, p. 96]

Table 19

Chemical composition of red-colored siltstones and sandstones of the Tersk series of the Middle Riphean of the Kola Peninsula. *Compiled according to the data of A.V. Sochava, 1979* [245, p. 96]

Oxides	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId	2	23
	Sandstones				Siltstone				Siltstone (alkaline normosiallite)	Sandstone (normosilit)
	Alkaline normosilit	Alkaline myosilit			Alkaline hyposiallite	Alkaline normosiallite	Alkaline hyposiallite	Alkaline normosiallite		
n	3	5	2	3	3	2	4	2		
SiO_2	79.75	80.09	75.63	71.66	64.33	61.19	64.87	61.03	62.42	85.38
TIO_2	0.12	0.35	0.54	0.86	0.64	0.76	0.97	1.09	1.64	0.20
Al_2O_3	10.55	9.39	10.61	11.49	13.75	16.57	13.71	15.57	14.79	6.73
Fe_2O_3	1.15	1.84	3.27	3.92	3.82	5.78	4.93	7.04	5.86	1.49
FeO	0.24	0.42	0.69	0.81	1.66	1.09	1.52	1.19	1.60	1.06
MnO	0.02	0.03	0.05	0.08	0.07	0.08	0.09	0.08	0.07	0.02
MgO	0.22	0.53	1.12	1.18	1.55	1.74	2.32	2.67	2.26	0.15
CaO	0.44	0.61	0.67	2.74	3.44	1.87	1.64	1.17	2.55	0.23
Na_2O	4.29	3.42	3.17	2.60	2.57	2.17	2.69	1.96	2.00	1.91
K_2O	2.10	2.50	3.02	2.62	3.72	5.26	3.69	4.59	3.48	2.08
P_2O_5	0.04	0.10	0.17	0.15	0.17	0.15	0.25	0.22	0.25	0.02
CO_2	–	0.40	0.65	1.51	1.91	0.03	0.13	0.61	0.78	–
SO_3	–	0.18	0.09	0.01	–	–	0.12	0.07	–	–
LOI	0,83	0,62	0,50	0,86	2,76	3,64	2,18	2,83	2,22	0,76
Total	99.75	100.47	100.14	100.50	100.39	100.32	100.09	100.09	99.92	100.03
HM	0.15	0.151	0.20	0.24	0.31	0.40	0.33	0.41	0.38	0.11
FM	0.02	0.03	0.07	0.08	0.11	0.14	0.14	0.18	0.16	0.03
AM	0.13	0.12	0.14	0.16	0.21	0.27	0.21	0.26	0.24	0.08
TM	0.011	0.037	0.050	0.075	0.047	0.046	0.070	0.070	0.111	0.030
FerM	0.13	0.24	0.36	0.39	0.39	0.40	0.45	0.50	0.46	0.37
NKM	0.61	0.63	0.58	0.45	0.46	0.45	0.47	0.42	0.37	0.59
AlkM	2.00	1.40	1.00	1.00	0.70	0.40	0.70	0.40	0.60	0.90

and, apparently, are carbonate siltstones. It is very curious that on the NKM–HM diagram the rocks form a single correlation field, while on the HM–TM diagram the correlation (and, moreover, positive) is observed only for sandstones, while the HM of siltstones does not in any way correlate with their titanium value. Let us note two more features of these red-colored arkoses (Table 19).

1. High total alkalinity: among siltstones, all are alkaline (Na_2O + + K_2O = 5.8–6.8%, there is even one alkalite), and among sandstones – 12 alkaline out of 14. According to the normalized alkalinity, 25 out of 26 compositions are super- and hyper-alkaline (NKM = 0.40—0.67). This situation is due to the abundance of feldspars.

2. The titanity of siltstones is not only not lower, but in general, even noticeably higher than the titanity of sandstones, both in absolute (TiO_2) and in relative (TM) terms. In some sandstones, which one can call quartz (SiO_2 > 80 %), TM is even lower than 0.010. Apparently, in the initial acidic substrate (granitoids or gneisses), the predominant dimension of Ti-bearing minerals was precisely silty rather than sandy (accessory minerals), and the dynamic sorting of clastic material was weak.

Table 20 and Fig. 16 processed 22 analyzes of the Riphean black shales of the Udereisk Formation of the Yenisei Ridge (cluster III) and the concretions occurring in them: silica (clusters Ia, b and II, samples 7, 10, 12), sulfide and silica-siderite (cluster IV and sample 16, 18) [92, p. 71] Characteristically, the silica concretions fall into the same correlation field with the host shales, while the sulfide and silica-siderite concretions are far beyond the correlation band. Note also that sample 10 (alkaline normosiallite) can in no way be a “silica concretions”, as indicated in the original source.

4.3. Basic diagrams (Na_2O + K_2O)–HM and NKM–HM

We have hundreds of statistical samples that have been clustered on basic module diagrams. We presented many such diagrams in our regional works [98, 111, 297, 304], dozens of others will be presented in the subsequent chapters of this book. Therefore, here we will restrict ourselves only to an example of *a complex set* clustering: uneven-aged weathering crusts of Ukraine [233]. Even though in Fig. 17 and Tab. 21 rocks from different WCr profile zones (from the most mature zone III to the least mature zone I) are combined; they form clear substrate-age clusters.

A series of *clusters Ia-Id* corresponds to the Krivoy Rog Karelians and includes amphibolites (*Id*), a weathering crust developed on them (*Ib, c*), and overlying arkose sandstones of the Skelevat Formation (*Ia*). Amphibolites are qualified as *pseudosiferlites* (*Id*), WCr I–II zones as *pseudosiallites* (*Ib*), and WCr II–III zones — as *siferlites* (*Ic*). It is remarkable that the lower layers of the Skelevat sandstones are still very

Table 20

Chemical composition of black shales and concretions of the Udereisk formation of the Riphean, Yenisei ridge.

Compiled according to the V.M. Datsenko's data, 1983 [92, p. 71]

Oxides and modules	Ia	Ib	II	IV	III	7	10	12	13	16	18
	Siliceous concretions				Black shales	Siliceous concretions				Sulfide and siliceous-siderite concretions	
	Normosilit		Myosilit	Carbonic pseudo-hydrolisate	Normo-siallite	Myosilit	Alkaline normo-siallite	Myosilit	Normo-siallite	Sulfurous siferlite	Sulfurous super-hydrolysate
n	5	2	3	2	4						
SiO_2	84.70	85.21	76.01	39.77	58.32	78.37	60.52	64.89	82.00	59.90	19.22
TIO_2	0.37	0.53	0.42	0.49	1.02	0.29	1.01	0.42	0.70	0.24	0.34
Al_2O_3	6.09	5.25	9.29	11.20	18.21	4.45	22.10	7.79	7.40	4.70	6.05
Fe_2O_3	3.03	2.63	3.75	19.22	6.69	3.63	3.26	7.40	4.00	1.38	2.57
FeO	1.45	2.93	2.48	3.68	0.72	8.37	0.27	0.10	1.32	18.51	40.45
MnO	0.02	0.02	0.09	0.98	0.07	0.04	0.04	0.17	0.02	0.02	0.02
MgO	0.45	0.24	0.88	3.52	1.53	0.27	0.83	2.21	0.47	0.11	0.38
CaO	0.36	0.30	0.95	1.37	0.41	0.30	0.30	4.48	0.40	0.30	1.07
Na_2O	0.24	0.23	0.70	0.69	0.50	0.25	1.05	0.42	0.84	0.10	0.18
K_2O	0.92	1.05	1.29	1.79	3.50	0.74	4.65	2.50	1.24	0.90	0.89
P_2O_5	0.16	0.05	0.10	0.90	0.17	0.12	0.05	0.09	0.15	0.69	1.78
LOI	1.70	1.40	3.41	16.83	8.05	2.84	5.98	9.05	1.66	11.59	23.84
Total	99.50	99.82	99.37	100.41	99.19	99.67	100.06	99.52	100.20	98.44	96.79

CO_2	0.11	0.20	1.05	10.00	2.32	0.32		6.36	0.16	0.10	1.11
S	0.14	0.05	0.05	0.08	0.26	0.05	0.05	0.21	0.05	13.23	34.64
HM	0.13	0.13	0.22	0.90	0.46	0.21	0.44	0.24	0.16	0.41	2.57
FM	0.06	0.07	0.10	0.66	0.15	0.16	0.07	0.15	0.07	0.33	2.26
AM	0.07	0.06	0.12	0.28	0.31	0.06	0.37	0.12	0.09	0.08	0.31
TM	0.062	0.100	0.044	0.043	0.056	0.065	0.046	0.054	0.095	0.051	0.056
FerM	0.68	0.98	0.63	2.06	0.39	2.54	0.15	0.93	0.66	4.03	6.74
NKM	0.19	0.24	0.22	0.22	0.22	0.22	0.26	0.37	0.28	0.21	0.18
AlkM	0.30	0.20	0.70	0.40	0.10	0.30	0.20	0.20	0.70	0.10	0.20

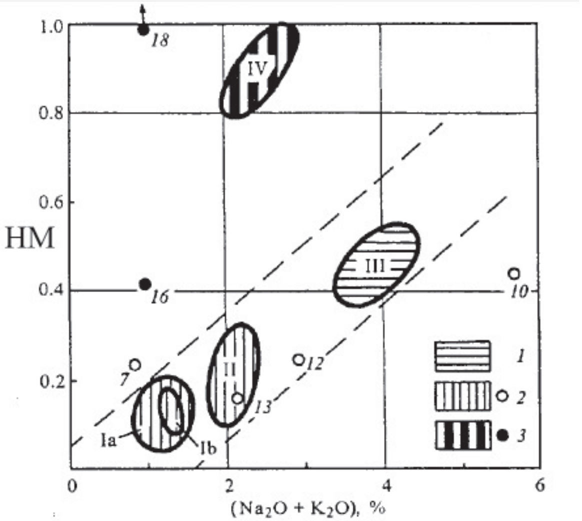

Fig. 16. Module diagram for black shales and concretions of the Udereisk Formation. *Compiled according to the data of V.M. Datsenko et. al.* [92, p. 71].
1 — shale; 2, 3 — silica concretions (2), sulfide and silica-siderite (3)

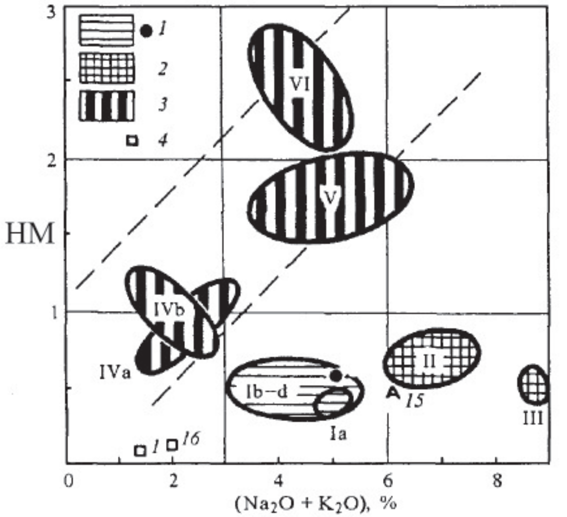

Fig. 17. Module diagram for uneven-aged weathering crusts of Ukraine for different substrates. *Compiled according to the data of A.D. Savko and A.D. Dodatko* [233, p. 26–29, 102–103].
1–3 – weathering crust over amphibolites *(1)* porphyrites, *(2)* and tuffs *(3)*; *4* – sandstones, *A* – amphibolites

close in composition to the WCr formations and are enriched with quartz only up the section (*sample 1* outside the clusters).

Clusters II and III correspond to the ancient WCR along the porphyrites of the Middle Riphean Zbrankov Formation of the Ovruch Ridge, which are overlain by sandstones of the Tolkachev Formation of the Middle Riphean (*sample 16*). All these formations are part of the Ovruch series. The weathering crust formations correspond to II–III zones of the profile, have a hydromica-montmorillonite composition, and

Table 21

Chemical composition of uneven-aged weathering crusts of Ukraine for different substrates.
Compiled according to the data of A.D. Savko and A.D. Dodatko, 1991 [233, p. 26—29, 102—103]

Oxides and modules	Ia	Ib	Ic	Id	II	III
	Source rocks					
	Amphibolites				Porphyrites	
	Sandstones (normo-siallite)	Qu-Chl-Bt-Act shales (pseudo-siallite)	Qu-Chl-Bt-Ser shales (siferlite)	Amphibolites (pseudo-siferlite)	Hsl-Mont shales (alkaline hydrolysate)	Porphyrites (alkalite)
n	2	4	2	4	5	2
SiO_2	63.65	53.79	61.32	51.68	49.82	53.62
TIO_2	0.90	0.79	0.69	0.96	1.60	1.30
Al_2O_3	16.51	14.90	13.15	13.62	22.29	18.13
Fe_2O_3	2.82	1.94	2.32	2.25	7.16	4.33
FeO	4.99	9.83	11.19	11.69	1.96	4.54
MnO	0.05	0.12	0.16	0.13	–	–
MgO	2.33	8.83	2.63	6.65	1.69	2.59
CaO	0.11	2.04	1.03	5.98	2.23	2.17
Na_2O	4.70	3.05	4.10	2.59	0.01	2.99
K_2O	0.15	1.17	0.20	2.14	6.69	5.75
P_2O_5	0.14	0.10	0.10	0.10	–	–
LOI	4.21	4.12	3.55	2.69	5.82	3.80
Total	100.53	100.36	100.44	100.48	99.28	99.19
HM	0.40	0.51	0.45	0.55	0.66	0.53
FM	0.16	0.38	0.26	0.40	0.22	0.21
AM	0.26	0.28	0.21	0.26	0.45	0.34
TM	0.055	0.053	0.052	0.071	0.072	0.072
FerM	0.45	0.74	0.99	0.97	0.38	0.46
NKM	0.29	0.28	0.33	0.35	0.30	0.48
AlkM	31.30	2.60	20.50	1.20	<0.10	0.50

are qualified as *super-titanium alkaline hypohydrolysates* (cluster II) and as *alkalites* (III). Obviously, the latter correspond to the substantially hydromica zone of the weathering crust.

A series of clusters IV—VI corresponds to the WCr by the tuffs of the Antontaran Formation of Donbass, underlying the Frasnian deposits. This young WCr strongly differs from the ancients considered above in greater hydrolyzability and high accumulations of titanium in the form of anatase, reaching 13.38 % TiO_2 in the hematite-hydromica formations of zone II (cluster VI). In addition, the altered tuff breccias of cluster IV are sharply differ by their high magnesium content and are qualified as *pseudohydrolysates.*

Thus, the clustering of analytical data by A.D. Savko and A.D. Dodatko [233] makes it possible to note the WCr composition dependence on two factors: (a) the WCr substrate, (b) the WCr age.

4.4. HM–TM diagram

Such a diagram must be applied in the case of low rocks alkalinity or in the absence of a noticeable total or normalized alkalinity dispersion. In particular, a low alkali content is characteristic of substantially kaolinite rocks, often adjacent to coal beds. It is known that near-coal rocks do not belong to bog, but to lacustrine-bog (or lagoon) facies; they formed in water reservoirs that were no longer peat bogs, but contained a lot of dissolved humic acids, strong weathering agents [293].

In the Carboniferous period of Canada, such rocks in the top of coal beds are represented by carbon-bearing “overclays” on which carbonate siltstones or non-carbonate argillites occur. The soil of the strata contains carbonaceous “underclays”, and under them there are massive or slated argillites [363, p. 306–307] proved to be hydrolysates (due to the high content of

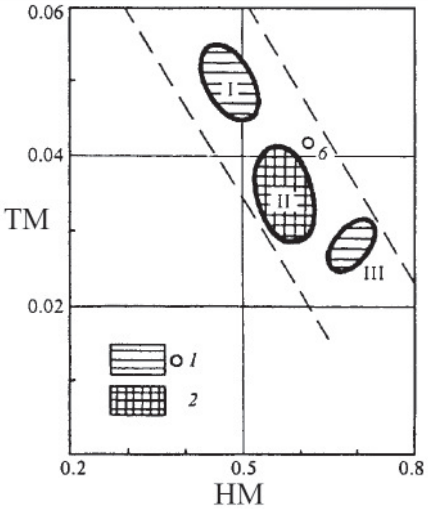

Fig. 18. Module diagram for the average compositions of the near-coal rocks of Nova Scotia (Canada). *Compiled according to the data of E. Zodrow, 1983* [363, p. 306–307]. Rocks: *1* – in the roof of coal beds (overclays), *2* – in the roof and bottom of coal beds (mixed cluster: overclays and underlays)

kaolinite), four are related super siallites (HM 0.47–0.54), one is carbonatolite (sample 6). All of them form a correlated set, in which *clusters I and III*, represented by overclays, and *cluster II* is a mixed one. Noteworthy is the negative correlation HM–TM. It turns out that during lacustrine-bog lithogenesis, the alumina accumulation (the kaolinite formation) is accompanied by the titanium loss. This can be explained by the reduction of Ti^{4+} to Ti^{3+} with its subsequent removal in soluble humate complexes [293]. Consequently, the negative HM–TM correlation can be used to diagnose hydrolysates of this (reductive) type.

Since TM values are informative themselves, TM diagrams often provide non-trivial genetic information. Table 23 and the module diagram (Fig. 19) show the compositions of the Devonian-Carboniferous shales of the Near-Araksin zone of Armenia – kaolinite-hydromica (*clusters I–III*) and pyrophyllite paragonite-bearing (*IV*) ones. According to I.Kh. Petrosov, the latter are metamorphosed equivalents of the former: "*There is no doubt that paragonite*

Table 22

Chemical composition of Nova Scotia near-coal rocks.
Compiled according to E. Zodrow, 1983 [363, p. 306-307]

Oxides and modules	I	II	III	6
	Carbonic normosiallite	Carbonic hypohydrolysate		Carbonatolite
n	3	6	2	
SiO_2	57.97	52.37	45.70	28.90
TIO_2	0.95	0.85	0.71	0.55
Al_2O_3	18.97	24.27	25.15	13.10
FeO	7.23	5.16	5.33	4.03
MnO	0.20	0.07	0.04	0.17
MgO	1.58	1.35	1.33	1.22
CaO	0.40	0.31	0.51	27.70
Na_2O	0.43	0.39	0.40	0.42
K_2O	3.27	3.81	3.98	2.00
LOI	8.22	10.71	15.35	21.40
Total	99.22	99.29	98.50	99.49
HM	0.47	0.58	0.68	0.62
FM	0.15	0.12	0.15	0.18
AM	0.33	0.46	0.55	0.45
TM	0.050	0.035	0.028	0.042
FerM	0.37	0.21	0.21	0.31
NKM	0.20	0.17	0.17	0.18
AlkM	0.10	0.10	0.10	0.20

and pyrophyllite develop on a clay base, that is, on monoclinic kaolinite with a disordered structure, or on hydromica $2M_1$” [205, p. 52]. The module diagram allows to significantly clarify this diagnosis: it turns out that clays with pyrophyllite form a single series (*clusters II ⇒ III ⇒ IV*) not with all, but only with a part of kaolinite-hydromica clays; the most titanium-bearing clays of *cluster I* from this series clearly fall out. That’s why one can think that hydrolysate formations in *clusters II and III* were kaolinite WCr on acidic low-iron rocks of different maturity – less (*cluster II*) and more mature (*cluster III*). Less hydrolyzed rocks in *cluster I*, judging by their hypertitanium value (TM 0.106—0.128), were formed based on the basic rocks’ substrate.

Table 23

Average clays chemical composition in the Near-Araksin zone of Armenia. *Compiled according to I. Kh. Petrosov’s data, 1983* [205, p. 30, 32]

Oxides and modules	I	II	III	IV
	Kaolinite-hydromica clay			Pyrophyllite clay
	Titanic normosiallite	Normosiallite	Hypohydrolysate	
n	3	2	6	3
SiO_2	62.62	58.26	53.77	49.60
TIO_2	2.01	0.90	0.78	0.90
Al_2O_3	17.36	15.88	20.77	31.91
Fe_2O_3	5.75	6.01	8.27	5.08
FeO	0.61	1.21	1.24	1.05
MnO	0.02	0.05	0.04	0.22
MgO	0.70	1.43	0.64	1.05
CaO	0.77	3.07	0.87	1.46
Na_2O	0.78	1.52	0.65	0.27
K_2O	2.90	1.67	2.44	3.87
P_2O_5	0.18	0.49	0.42	0.19
H_2O^-	0.96	1.74	1.68	0.32
LOI	5.51	7.53	8.46	4.28
Total	100.18	99.73	100.02	100.20
HM	0.41	0.41	0.58	0.79
FM	0.11	0.15	0.19	0.14
AM	0.28	0.27	0.39	0.64
TM	0.116	0.056	0.037	0.028
FerM	0.33	0.43	0.44	0.19
NKM	0.21	0.20	0.15	0.13
AlkM	0.30	0.90	0.30	0.10

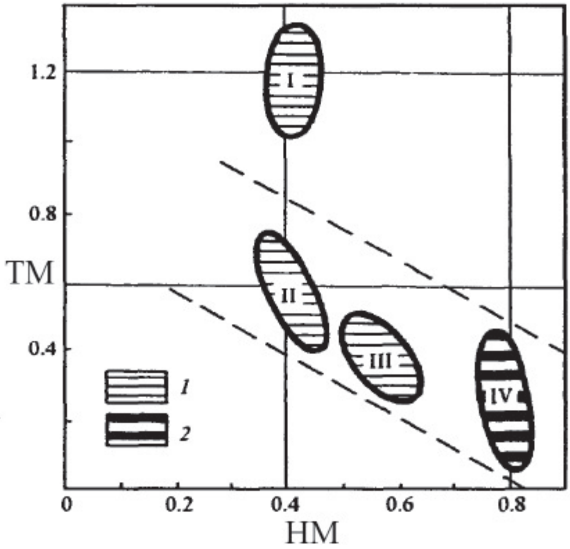

Fig. 19. Module diagram for kaolinite-hydromica (*1*) and pyrophyllite (*2*) clays of the Near-Arakhsin zone of Armenia.
Compiled according to I.Kh. Petrosov's data [205, pp. 30, 32]

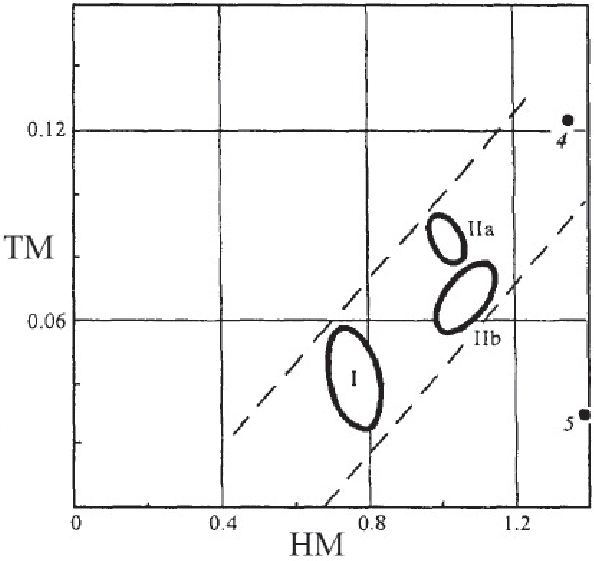

Fig. 20. Module diagram for clay rocks of the bauxite-bearing weathering crust of Armenia (C_2–C_3). *Compiled according to I. Kh. Petrosov's data* [205, p. 39]

I. Kh. Petrosov suggests that the bauxite-bearing Middle-Upper Carboniferous WCr in Armenia was formed on the substrate of sedimentary and metamorphic rocks, which is not specifically indicated [205]. However, as can be seen in the module diagram (Fig. 20) and in Table 24, these rocks compositions form three clusters and two separate compositions, which correspond to at least three substrates. One can assume that the least hydrolysate, least titanium and ferruginous clays of *sample 5* were formed by an acidic substrate, clays of *cluster I* – by an andesite substrate, cluster II with some intermediate HM and TM values – by the sedimentary rocks' substrate, and the hypertitanium composition of *sample 4* – by the basic rocks' substrate.

Table 24

Chemical composition of clay rocks of the bauxite-bearing weathering crust of Armenia. *Compiled according to I. Kh. Petrosov's data, 1983* [205, p. 39]

Oxides and modules	I	IIa	IIb	4	5
	Hypohydrolysate	Titanium normohydrolysate	Normohydrolysate	Titanium normohydrolysate	Normohydrolysate
n	2	2	2		
SiO_2	52.99	44.26	40.67	36.51	36.19
TIO_2	0.99	2.12	1.83	3.12	0.70
Al_2O_3	25.50	25.16	27.20	25.37	23.06
Fe_2O_3	13.20	17.01	11.57	19.79	25.65
FeO	0.70	0.85	2.63	1.15	0.92
MnO	0.00	0.02	0.00	0.00	0.03
MgO	0.20	0.50	0.45	0.61	0.27
CaO	0.61	0.48	1.05	0.70	0.60
Na_2O	0.13	0.13	0.21	0.30	0.06
K_2O	0.18	0.18	1.52	0.70	0.15
P_2O_5	0.04	0.08	0.22	0.32	0.12
LOI	5.41	9.61	12.27	12.06	11.26
Total	99.94	100.35	99.59	100.63	99.01
HM	0.76	1.02	1.06	1.35	1.39
FM	0.27	0.41	0.36	0.59	0.74
AM	0.48	0.57	0.67	0.69	0.64
TM	0.039	0.084	0.067	0.123	0.030
FerM	0.52	0.66	0.49	0.73	1.12
NKM	0.01	0.01	0.06	0.04	0.01
AlkM	0.70	0.70	0.10	0.40	0.40

4.5. Diagram with AM instead of HM

One must apply such diagrams in cases where the use of the hydrolysate module HM becomes questionable, for example, if the rock contains noticeable amounts of iron and manganese in the carbonate form. Such, for example, are the Aptian-Albian phosphorites of NW Germany, the carbonate varieties of which are distinguished by high manganese and iron contents (Table 25). German geologists distinguish among them the proper phosphate and carbonate-phosphate concretions. The former are dominated by apatite with an admixture of quartz, siderite, calcite and with minor admixtures of

Table 25

Chemical composition of the Aptian-Albian manganese phosphorites of NW Germany. *Compiled according to W. Zimmerle et al., 1982* [362, p. 235-243]

Oxides and modules	I	IIa	IIb	4	5	
	Carbonate phosphatolite	Carbonate Mn-P super-hydrolysate	Mn-P carbonatolite	Carbonate Mn-P super-hydrolysate	Carbonate phosphatolite	
n	5	8	12	5		
SiO_2	19.64	18.83	6.30	4.56	4.43	11.79
TIO_2	0.18	0.29	0.12	0.09	0.07	0.10
Al_2O_3	3.72	5.73	2.50	1.73	1.53	2.40
Fe_2O_3	4.33	16.37	13.85	7.75	2.58	3.12
MnO	0.11	4.92	5.58	3.32	0.34	0.09
MgO	0.89	1.82	1.09	0.71	0.31	0.72
CaO	35.15	19.48	31.24	38.73	46.12	41.35
Na_2O	0.81	0.33	0.33	0.56	0.84	0.80
K_2O	1.32	0.97	0.33	0.25	0.19	1.11
P_2O_5	20.88	9.24	10.97	19.26	29.25	25.42
SO_3	1.08	0.41	0.39	0.26	0.82	1.29
LOI	11.26	19.95	25.12	19.06	12.80	11.40
Total	99.37	98.44	97.98	96.54	99.28	99.59
HM	0.42	1.45	3.50	2.83	1.02	0.48
FM	0.27	0.97	2.37	1.86	0.65	0.33
AM	0.19	0.30	0.40	0.38	0.35	0.20
TM	0.048	0.051	0.048	0.052	0.046	0.042
FerM	1.14	3.54	7.42	6.08	1.83	1.28
NKM	0.57	0.23	0.26	0.47	0.67	0.80
AlkM	0.60	0.30	1.00	2.20	4.40	0.70

Note. In the rocks of clusters II–IV, the average content of Ba and Sr is 0.015-0.031 and 0.085-0.226%, respectively.

hydromica, kaolinite, dolomite, and feldspar. The latter are dominated by apatite, calcite, siderite and kutnagorite (Mn-dolomite), while quartz and clay minerals are present as impurities, among which, in addition to hydromica and kaolinite, chlorite and montmorillonite are also noted [362].

Due to the significant proportion of Fe-Mn carbonates in the phosphorites composition, the use of the HM module becomes doubtful in the sense that it will no longer reflect the hydrolysate nature of the silicate substance. Therefore, for the compositions clustering in this case, we used the AM–NKM module diagram (Fig. 21), which can show four clusters.

Cluster I is formed by phosphorites proper, which are qualified as carbonate phosphatolites. The small scatter of AM values reflects the constancy of the aluminosilicate composition, while the hyperalkaline NKM values reflect the presence of feldspar in these concretions.

Clusters II and III are carbonate phosphorites with the highest average Fe and Mn contents. At the same time, in cluster II, concretions were taken from only two mines (Otto Gott and Sarstedt), which emphasizes some individuality of these rocks. Cluster III includes 7 carbonate and 3 proper phosphorites. An increase in AM values (from 0.30 to 0.40 compared to cluster II) reflects an increased proportion of kaolinite in the clay matter of these concretions. They contain a few more manganese and less iron than in cluster II.

Finally, loose *cluster IV* represents carbonate phosphorites with a wide range of AM values: from 0.32 to 0.45. Of course, the selection of such a cluster can be challenged, but the higher alkalinity (NKM 0.47) and noticeably lower Mn and Fe

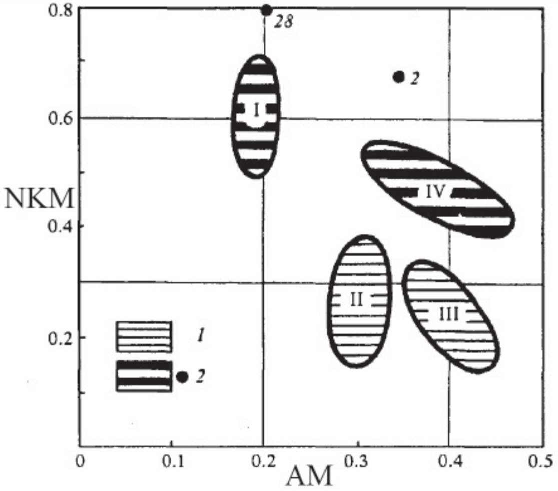

Fig. 21. Module diagram for the Aptian-Albian manganese phosphorites of NW Germany. *Compiled according to W. Zimmerle et al., 1982* [362].
1 – phosphate-carbonate concretions, *2* – phosphate concretions

contents as compared to the concretions of clusters II–III indicate that this is a kind of intermediate type of rocks – between the proper phosphorites (cluster I) and carbonate phosphorites (clusters II–III).

4.6. Diagram with FM instead of HM

The use of the femic module is preferable in all cases when we deal with magnesian silicate rocks, in particular, with montmorillonite rocks. Among the latter, as Ukrainian geologists have shown [197], one can recognize two genetic types: a) formed from acidic volcanic ash, b) formed in the weathering crust along the basic rocks substrate.

These types differ in contrast in the fixation nature of potassium by montmorillonite upon boiling in a IN solution of KCl. Apo-ash montmorillonites during the KCl processing in just 15–20 min reduce the d_{001} to 9.81–10.59 Å. "*The relatively easy contraction of the montmorillonite lattice to 10 Å upon saturation with potassium indicates that it has a relatively large interlayer charge inherited from the primary micaceous mineral*" [197, p. 30]. Montmorillonites from the weathering crusts, even after six hours of KCl treatment, are characterized by only a partial reduction in d_{001} to 11.51–12.91 Å. "*The difficulty of reducing the interlayer distance <...> allows us to believe that they were formed by staged changes in amphiboles, pyroxenes, chlorites in the weathering crust of crystalline rocks*" [197, p. 31].

This data is of great value to us. They will suggest the idea that montmorillonites of two genotypes can be distinguished by their chemical composition. Apparently, montmorillonites from weathering crusts by the basic substrate should have higher FM module values and lower NKM module values than montmorillonites from typical bentonites. It can also be expected that the former should partially inherit the high titanium value of the substrate and, therefore, have higher TM values. On the contrary, acidic pyroclastic rocks are distinguished by minimal TM values, which is also inherited by bentonites.

Since magnesium and iron are contained not only in montmorillonites, but also in chlorites and hydromicas, it can be assumed that the *FM module can be used universally* for diagnostics of polymineral clays, in which four common clay minerals (hydromica, chlorite, montmorillonite, and kaolinite) form a mixture of two or three, and often of all four minerals.

One knows that there were repeated attempts at chemical typification of clay rocks; one of the latter belongs to Norwegian scientists.

J.-O. Englund and P. Jorgensen constructed a petrochemical classification of clay rocks based on statistical processing of analyzes in a triangle with vertices (in mol %): ($MgO + FeO_{total}$)–Al_2O_3–($K_2O + Na_2O + CaO$) [330]. When forming the array of initial data, the compositions with the content of $CO_2 > 10$ % and $SiO_2 > 70$ % were rejected. In addition, the amount of CaO included in $CaCO_3$ was preliminarily subtracted by the normative recalculation. In this triangle, five fields (concentration of points) are outlined, the coordinates of which can be set using two parameters M1 and M2: M1 = (FeO + + MgO + Al_2O_3)/(K_2O + Na_2O + CaO); M2 = (Al_2O_3)/(FeO + MgO).

The authors believe that parameter M1 reflects the ratio (chlorite + kaolinite): (hydromica + kaolinite), and parameter M2 reflects the ratio of kaolinite: chlorite. Both parameters are a measure of chemical weathering, but they do not change in the same way as this process develops: "*Unweathered sediments have low values of M1, and M2, while more weathered sediments have higher values. In going from the most unweathered to somewhat more weathered sediments, the M1 value is gradually increased, while the M1 value remains approximately constant.* [On the contrary]*, For the more weathered sediments the M1 value will change very little, while the M2 value will greatly increase, and a sediment rich in alumina is the final product*" [330, p. 94].

It is easy to see the analogy of the Englund–Jorgensen triangle with the AKM triangle ($A1_2O_3$–K_2O–MgO) used in Russian literature (for example, in the works of V. K. Golovenok). We believe that there is no necessity either the molecular form of data presentation, or the representation of the composition in a triangle (which requires bringing the sum to 100 % and not the simplest graphical constructions), or, finally, the need to amend CaO in order to include it in the constructions. A completely satisfactory lithochemical systematics of clays can be constructed much easier in the FM–NKM coordinates. Indeed, the processing of about 500 collected by us analyzes of clay rocks (siallites and hydrolysates) shows that the FM value monotonically increases in the series:

kaolinite ⇒ montmorillonite ⇒ hydromica ⇒ chlorite
0.03 (0.004–0.25) 0.11 (0.07–0.19) 0.12 (0.03–0.33) 1.5 (0.7–2.4)

The NKM value gives another increasing series:

chlorite ⇒ kaolinite ⇒ montmorillonite ⇒ hydromica
0.01 (0.002–0.16) 0.02 (0.0–0.07) 0.04 (0.02–0.12) 0.26 (0.12–0.38)

Thus, the alkalinity and femicity of clays are practically independent, which makes it possible to construct a module diagram with a rather good resolution. It makes it possible to distinguish six main lithochemical types of clay rocks, differing in the mineral composition of the clay fraction and therefore, undoubtedly corresponding to some real lithotypes (Fig. 22).

Type I: kaolinite dominates in the composition of clay matter. The minimum FM and NKM values are characteristic in the intervals 0.02—0.12 and 0.03—0.13, respectively.

Type II: montmorillonite dominates in the composition of clay matter, less kaolinite, and hydromica may be present in subordinate amounts. The characteristic FM and NKM values are in the ranges 0.06–0.25 and 0.06–0.22, respectively. Such clay rocks may contain rather rare mixed-layer min-

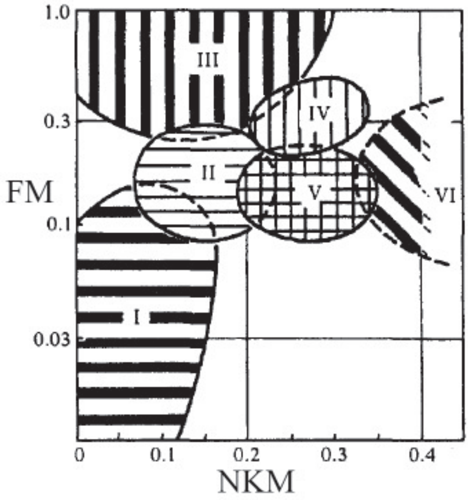

Fig. 22. Module diagram for the taxonomy of clay rocks. More than 500 analyzes were used. The scale for FM is logarithmic. Explanations in the text

erals of the kaolinite-montmorillonite series. As L. Schulz et al. [351] have shown, these minerals are obtained by stagewise weathering of volcanic ash in an acidic medium. Initially, as they believe, montmorillonites with H–Al interlayers, partly gibbsite-like, are formed, and then they are transformed into kaolinite layers.

Type III: chlorite dominates in the composition of clay matter, with a subordinate admixture of ferruginous hydromicas. The characteristic FM and NKM values are 0.25–0.65 and 0.02–0.30, respectively.

Type IV: "standard two-component mixture of chlorite + hydromica", characteristic of clay strata that underwent catagenesis and early metagenesis. The characteristic FM and NKM values lie in the ranges 0.25–0.45 and 0.20–0.35, respectively. An increase in the proportion of chlorite raises the FM, and in the proportion of hydromicas – the NKM. As shown by Norwegian lithologists, an increase in the proportion of chlorite is characteristic of some clay rocks associated with carbonates. These are the interlayers of dark clays in the Ordovician of Sweden and Norway, as well as in the Upper Riphean–Vendian shale of Biri, Southern Norway. *"Due to the intimate association of shale and carbonate it is reasonable to assume that the terrigeneous part of these sediments was deposited at fairly high pH"* [330, p. 91–92].

Type V: "standard three-component mixture of chlorite + montmorillonite + hydromica" (± mixed-layer minerals of the montmorillonite–hydromica series and the rarer chlorite–hydromica series). Fig. 16 shows that the characteristic FM and NKM values for this type lie in the range 0.10–0.24 and 0.20–0.38.

As noted by Norwegian lithologists, when drawing points of 50 compositions of mixed-layer illite-montmorillonite minerals per the above-mentioned triangle, two separated fields are obtained. The first corresponds to compositions less aluminous and more ferrous-magnesian (~50–60 mol % Al_2O_3).

This field is practically overlapped by fields of illites and montmorillonites. It is obvious that these mixed-layer minerals were formed by hydromica formation of montmorillonites. The second field corresponds to compositions of more alkaline, low iron and high alumina (~70–80 mol % Al_2O_3) and partially overlaps with the field of dioctahedral micas. One believes that these mixed-layer minerals were obtained by degradation of micas (partial K loss) [330].

Fields IV and V in Fig. 22 contain most of the real clay rocks compositions of the sedimentary shell – those that are not directly related to the weathering crusts and, therefore, do not belong to the types dominated only by kaolinite or only montmorillonite and chlorite.

Finally, ***type VI*** is clay rocks, most often refers to hydromica rocks, but containing a significant admixture of dispersed feldspar particles, which leads to an abnormally high NKM value. Such rocks are characteristic of arid weathering crusts and are widely developed in the sediments of the Middle (Karelian) and Upper (Riphean) Precambrian [298].

4.7. Diagram with a given correlation

These are all diagrams in which the parameters have the same (or almost the same) normalization: HM–AM, HM–FM, AM–FM (normalization to SiO_2) or NKM–FerM, NKM–TM, FerM–TM (normalization to Al_2O_3 or $Al_2O_3 + TiO_2$ in the FerM module). Typically, such diagrams show a positive correlation, which is predetermined by the modules' shape. It is also clear that AM (alumina in the numerator) can show a negative correlation with NKM, TM and FerM (alumina in the denominator).

At the same time, the HM–AM (FM) diagrams are almost not informative, while the diagrams of the NKM–FerM, NKM–TM and FerM–TM types can be very useful for clustering. Obviously, in the presence of a strong correlation, the TM–FerM diagram can be replaced by a graph with unnormalized values: TiO_2–($FeO + Fe_2O_3 + MnO$), and the NKM–FerM diagram – by a graph ($Na_2O + K_2O$)–($FeO + Fe_2O_3 + MnO$). However, in Ch. 3 it was already noted that such a replacement in most cases is undesirable since it deprives us of important information.

Table 26 contains twenty-six processed analyzes of glauconites from the Cretaceous and Paleogene deposits of the Russian Platform [182]. For clus-

Table 26

Average chemical composition of glauconites from Cretaceous and Paleogene deposits of the Russian Platform.
Compiled according to V.I. Muraviev's data, 1983 [182, p. 96—97]

Oxides and modules	I	II	III	IV	V	VI	VII	VIII
	Diatomites (hypohydrolysate)	Gaize (alkaline hypohydrolysate)	Sandstone and diatomite (alkaline hypohydrolysate)	Gaize and sandstone (alkaline pseudohydrolysate)	Sands with zeolites (alkaline pseudohydrolysate)	Sands with zeolites (alkaline pseudosiferlite)	Different sands (alkaline pseudohydrolysate)	Gaize and sandstone (alkaline pseudohydrolysate)
n	2	3	2	2	8	2	5	2
SiO_2	48.34	47.12	48.98	49.62	47.72	49.36	47.69	50.23
TIO_2	1.02	0.61	0.52	1.06	1.32	0.34	0.34	0.30
Al_2O_3	8.43	9.10	6.76	11.35	10.24	9.87	9.46	7.96
Fe_2O_3	18.55	22.12	23.08	14.04	18.03	14.97	17.31	18.71
FeO	0.32	0.66	0.41	1.61	1.11	1.73	1.53	1.32
MnO	0.11	0.02	0.02	0.03	0.07	0.05	0.01	0.02
MgO	2.96	2.61	2.89	3.61	3.30	3.67	3.48	3.52
CaO	1.16	0.81	0.82	1.42	1.34	3.03	2.61	2.15
Na_2O	0.20	0.10	0.09	0.18	0.11	0.18	0.13	0.14
K_2O	3.69	5.59	5.70	5.93	5.83	6.72	6.83	6.76
P_2O_5	0.14	0.42	0.18	0.22	0.32	0.52	0.55	0.19
H_2O^+	6.92	5.71	5.19	5.69	5.22	5.17	6.30	5.60
H_2O^-	7.98	4.58	5.40	4.82	5.29	4.04	3.43	2.78
LOI	0.10	0.56	0.31	0.45	0.38	0.23	0.32	0.50
Total	99.82	99.71	100.20	99.90	100.14	99.80	99.82	99.97
HM	0.59	0.69	0.63	0.57	0.65	0.55	0.60	0.56
FM	0.45	0.54	0.54	0.39	0.47	0.41	0.47	0.47
AM	0.17	0.19	0.14	0.23	0.21	0.20	0.20	0.16
TM	0.122	0.069	0.079	0.092	0.128	0.034	0.035	0.037
FerM	2.02	2.35	3.24	1.27	1.67	1.64	1.92	2.43
NKM	0.46	0.63	0.86	0.54	0.58	0.70	0.74	0.87
AlkM	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

Note. Diatomites and other lithotypes are host rocks, chemotypes (in brackets) are glauconites.

tering, the NKM–FerM diagram was used (Fig. 23), which allows reflecting an important characteristic of glauconites – the content of the ferruginous hydromica component in them. An increase in this component fraction should simultaneously increase FerM and NKM values, and an increase in the smectite component fraction should decrease them. Therefore, one can observe a positive correlation on the module diagram, in which two lines can be distinguished: relatively more ferruginous glauconites from opokas and diatomites (clusters I ⇒ II ⇒ III) and relatively less ferruginous glauconites mainly from sandy rocks (clusters IV ⇒ (V, VI) ⇒ VII ⇒ VIII).

Glauconites belong to hydrolysates and alkaline hydrolysates *(clusters I and II*), to alkaline pseudohydrolysates (*clusters III–V ⇒ VII ⇒ VIII*) and to alkaline pseudosiferlites (*cluster VI*). It is natural that the most ferruginous glauconites from diatomites (*cluster I*) and opokas *(cluster II, partly cluster III*) are characterized by the lowest magnesiality.

Table 27 contains the analyzes published by S. McLennan et al.: nine analyzes of the Upper Archean metapelitoids of South Africa, over the Swaziland series (age from 3.5 to 3.3 Ga, as part of the Fig-Three and Modis series) and five – of the Ponrola superseries (older than 2.9 Ga) [340]. These

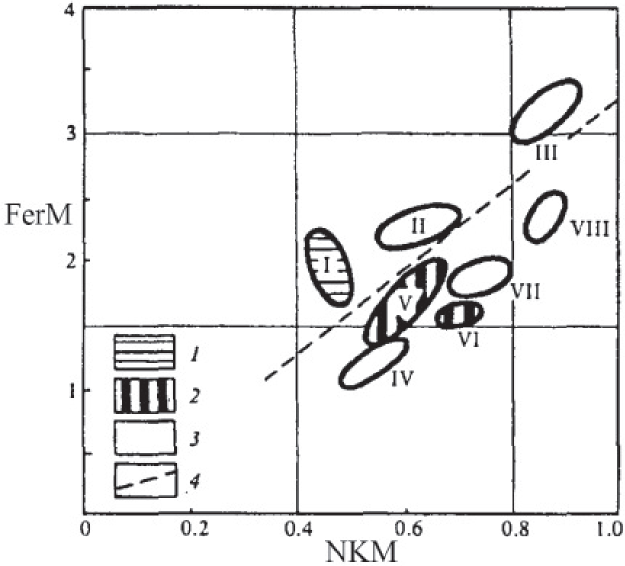

Fig. 23. Module diagram for glauconites from Cretaceous and Paleogene deposits of the Russian platform. *Compiled according to V.I. Muraviev's data, 1983* [182, pp. 96–97].

Glauconites from: diatomites (*1*), sands with zeolites *(2*), various – from opokas, zeolite-free sands and sandstones (*3*); *4* – line dividing glauconites of different iron content

Table 27

Chemical composition of the Upper Archean metasedimentary rocks of South Africa. *Compiled from the data of S. McLennan et al., 1983* [340, p. 102—105]

Oxides and modules	I	II	III	I	4	14
	Superseries and chemotype (in brackets)					
	Pongola (alkaline normosiallite)	Fig-Three (pseudosiallite)	Modis (alkaline pseudosiallite)	Fig-Three (pseudosilite, alkaline pseudosiferlite)		Pongola (alkaline normosiallite)
n	4	2	5			
SiO_2	58.89	54.51	59.32	74.49	58.46	64.20
TIO_2	0.79	0.61	0.44	0.26	0.58	0.66
Al_2O_3	21.69	15.23	13.93	3.56	13.46	16.33
FeO*	5.00	10.13	7.36	2.09	11.88	7.88
MnO	0.05	0.09	0.13	0.09	0.15	0.11
MgO	2.80	6.94	5.09	4.57	4.84	1.20
CaO	0.03	0.39	1.29	7.20	1.61	0.01
Na_2O	0.44	0.95	1.76	0.31	1.95	0.86
K_2O	5.75	2.58	4.87	0.50	4.14	4.42
LOI	4.47	8.60	5.76	6.62	2.95	3.09
Total	99.89	100.00	99.94	99.69	100.02	98.76
HM	0.47	0.48	0.37	0.08	0.45	0.39
FM	0.13	0.31	0.21	0.09	0.29	0.14
AM	0.37	0.28	0.23	0.05	0.23	0.25
TM	0.036	0.040	0.031	0.073	0.043	0.040
FerM	0.22	0.65	0.52	0.57	0.86	0.47
NKM	0.29	0.23	0.48	0.23	0.45	0.32
AlkM	0.10	0.40	0.40	0.60	0.50	0.20

*Total iron

strata correspond best of all to the clusters identified on the FerM–NKM module diagram (Fig. 24).

Cluster II includes two analyzes of the Fig-Three series, super-ferruginous high-magnesian rocks *pseudosiallites* and *pseudhydrolysates*. Obviously, these are some tuffoids, and, judging by the low titanium value, the volcanogenic material in them is rather hyperbasic than basic. *Alkaline siferlite* (*sample 4*) is also similar to these rocks. The composition of *sample 1* is quite peculiar: it is qualified as *silit* but it contains a lot of CaO and MgO and an increased TM value. Maybe it's dolomitic flint. In the Modis series, in terms of iron content, one can distinguish *cluster III*, which is represented by *pseudosiallites* with increased alkalinity (one composition even corresponds to

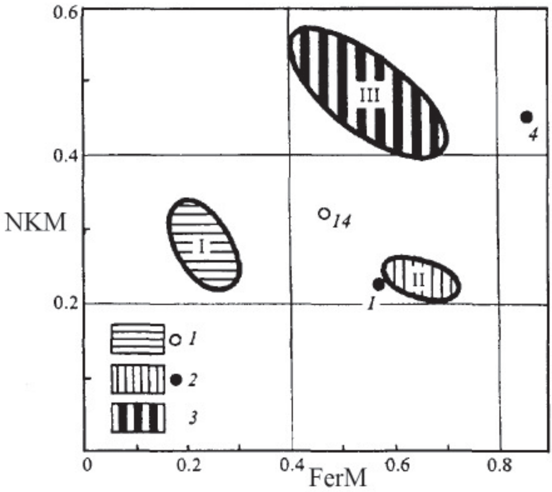

Fig. 24. Module diagrams for the Upper Archean metasedimentary rocks of South Africa belonging to the Ponrola superseries *(1)*, Fig-Three *(2)* and Modis *(3)* series. *Compiled according to S. McLennan et al., 1983* [340, p. 102—105]

alkalite), with a low TM value. Judging by these data and considering the information on minor elements (TR, Cr, Ni), we can assume that two contrasting substrates took part in the formation of metapelites of the Swaziland superseries: hyperbasitic (source of Mg and Fe) and acidic (source of alkalis) [340]. It is obvious that the acidic substrate participation was more significant during the formation of the Modis Series sediments.

The metapelites of the Pongola superseries (*cluster I*) noticeably differ from those considered in their reduced iron content (FerM 0.20–0.47 versus 0.43–0.86, except for anomalous siltstone? – sample 14) and increased alumina content (AM 0.25–0.39 versus 0.18–0.35). And although the influence of the magnesian substrate is still quite noticeable (three compositions –pseudosiallites), it can be thought that essentially potassium metapelites of the Pongola superseries were formed mainly on the granitoids substrate, in an arid climate [298].

A positive correlation is seen on the TM–FerM module diagram for the aspid Middle Ordovician formation of Gorny Altai (Fig. 25), which may be evidence of volcanogenic-sedimentary rocks. One can also be consider the predominance of magnesian rocks-pseudosiallites (four analyzes out of six – Table 28) as an indirect confirmation of this. Indeed, as I.A. Vyltsan notes, "*episodic outbreaks of volcanic activity should be considered a very curious fact that took place at the beginning of Llandeilo* <…>" [58, p. 139]. Apparently, these episodes fell precisely on the forming period of the aspid formation.

Table 28

Chemical composition of the main lithotypes of the Middle Ordovician aspid formation in Gorny Altai.

Compiled according to I.A. Vyltsan's data, 1978 [58, p. 117]

Oxides and modules	1	2	3	4	5	6
	Greywacke (alkaline myosilit)	Siltstone (pseudosiallite)			Clay shale	
					Normosiallite	Pseudosiallite
SiO_2	68.67	58.86	59.00	61.40	65.00	65.34
TIO_2	0.40	0.94	0.71	0.79	0.71	0.63
Al_2O_3	14.56	17.57	19.64	17.27	16.08	17.19
Fe_2O_3	0.41	1.58	3.18	1.58	3.98	1.00
FeO	4.50	6.28	4.67	5.21	3.23	4.31
MnO	0.08	0.22	0.11	0.08	0.14	0.08
MgO	1.88	3.69	3.00	3.84	2.73	3.33
CaO	0.91	1.47	0.90	1.50	0.30	0.40
Na_2O	5.10	3.33	1.17	1.18	0.47	0.79
K_2O	0.31	1.36	2.13	2.44	2.40	3.08
H_2O	0.14	0.96	0.20	–	0.16	––
P_2O_5	0.10	0.11	0.07	0.08	0.13	0.09
LOI	2.42	3.06	5.48	5.34	4.96	4.32
Total	99.49	99.43	100.27	100.73	100.32	100.57
HM	0.29	0.45	0.48	0.41	0.37	0.36
FM	0.10	0.20	0.18	0.17	0.15	0.13
AM	0.21	0.30	0.33	0.28	0.25	0.26
TM	0.027	0.054	0.036	0.046	0.044	0.037
FerM	0.33	0.44	0.39	0.38	0.44	0.30
NKM	0.37	0.27	0.17	0.21	0.18	0.23
AlkM	16.50	2.40	0.50	0.50	0.20	0.30

Note. The average S content is 0.01—0.03 %

4.8. Rare diagram types

Sometimes one must resort to "non-standard" diagrams, due to the unusual nature of the original data. As an example, in Table 29 the author processed 17 analyzes of lower Carboniferous kimberlites (Eastern Siberia) and the Early Triassic weathering crust developed along them, from which only the lower horizons have survived – the leaching zone [37, p. 156—157]. Since the kimberlites composition is characterized by the presence of noticeable titanium and alkalis contents, it is possible to apply a non-standard module diagram in the coordinates ($Na_2O + K_2O$)–TM (Fig. 26). It turns

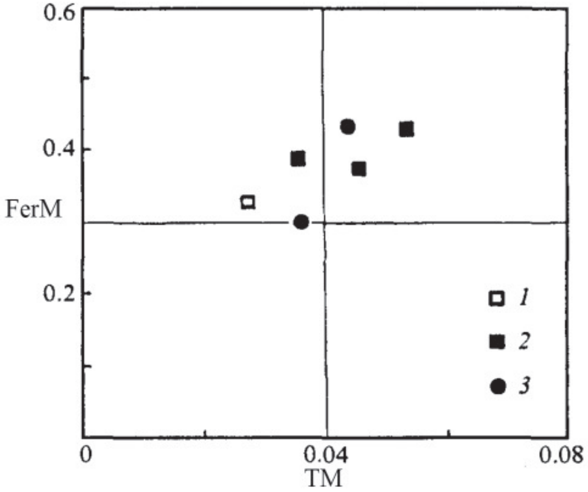

Fig. 25. Module diagram for the main lithotypes of the aspid formation O_2 in Gorny Altai. *1* – greywackes, *2* – siltstones, *3* – shales. *Compiled according to I.A. Vyltsan's data, 1978* [58, p. 117]

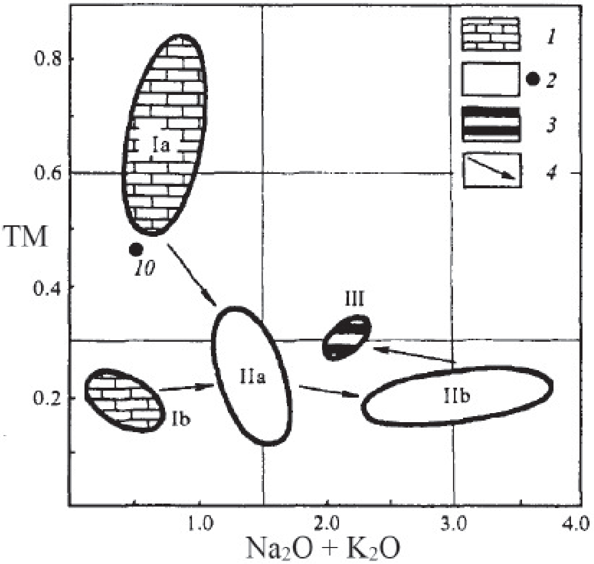

Fig. 26. Module diagram for the weathering crust over the kimberlites of Eastern Siberia. *Compiled according to Yu.A. Burmin's data, 1987* [37, p. 156–157]. *1* – kimberlites, *2, 3* – zones of the weathering crust: initial (*2*), leaching (*3*); *4* – the assumed direction of the weathering processes

Table 29

Chemical composition of kimberlites and weathering crust over kimberlites, Eastern Siberia.

Compiled according to Yu.A. Burmin's data, 1987 [37, p. 156–157]

Oxides and modules	Ia	Ib	IIa	IIb	III	10
	Carbonatolite			Siferlite	Titanium pseudohydrolysate	Carbonatolite
n	4	3	3	2	2	
SiO_2	14.51	16.29	24.57	42.55	36.06	14.00
TIO_2	1.94	0.88	1.00	1.43	2.27	1.44
Al_2O_3	3.11	4.56	4.23	7.22	7.28	3.10
Fe_2O_3	5.81	4.91	4.86	5.91	12.43	3.34
FeO	1.68	1.32	1.13	1.04	0.90	1.52
MnO	0.17	0.13	0.23	0.18	0.27	0.19
MgO	11.43	7.72	7.79	7.88	8.06	7.54
CaO	29.94	30.53	26.32	12.03	10.50	33.98
Na_2O	0.04	0.05	0.07	0.14	0.10	0.05
K_2O	0.73	0.37	1.37	2.90	2.10	0.50
P_2O_5	0.91	0.30	0.47	0.58	0.77	0.63
H_2O	1.06	3.61	3.89	4.17	7.12	2.75
LOI	27.75	28.43	23.86	13.16	12.11	29.98
Total	99.07	99.10	99.79	99.16	99.95	99.02
F	0.24	0.09	0.11	0.10	0.12	0.17
HM	0.88	0.72	0.47	0.37	0.64	0.69
FM	1.30	0.86	0.56	0.35	0.59	0.89
AM	0.21	0.28	0.17	0.17	0.20	0.22
TM	0.625	0.193	0.237	0.198	0.311	0.465
FerM	1.52	1.17	1.19	0.82	1.43	1.11
NKM	0.25	0.09	0.34	0.42	0.30	0.18
AlkM	0.10	0.10	0.10	<0.10	<0.10	0.10

out that at the early stage of leaching, titanium is removed much stronger than alumina, because the TM value sharply decreases from 0.625 in *cluster Ia* to 0.193 in cluster Ib. With the further development of leaching, apparently, titanium and alumina are relatively immobile – the TM value fluctuates insignificantly. Simultaneously, with leaching (*clusters I ⇒ IIa*), the alkali content (and the HM value) increases, which indicates the hydrolysis onset – the appearance of clay minerals. This process is intensified when carbonate also begins to dissolve (*IIb*). Further hydrolysis development (with decomposition of clay minerals as well) is represented only by the very initial stage (*claster III*), marked by a decrease in total alkalinity and a weak increase in TM.

Thus, a non-standard module diagram ($Na_2O + K_2O$)–TM turned out to be a convenient tool for analyzing the weathering of kimberlites[1].

A very remarkable picture is shown by clay and sandy rocks of the Lower Cretaceous flysch of Kamchatka (Ilpinsky semi-island)[2]: lithotypes identified by P.V. Markevich – "sandstones" and "aleuro-argillites" [169] – can hardly be discriminated on module diagrams. For example, on the diagrams HM–TM, TM–FerM, there is an almost complete overlap of fields. In the graphs with NKM and $Na_2O + K_2O$, discrimination is better, but still 40–50% of sandstone points do not differ from clay rocks. Undoubtedly, such a similarity in the clay and sandy rocks compositions can be considered typical for flysch greywackes, in which there is no significant mechanical differentiation of the pelitic and psammitic fractions. Therefore, greywackes with a high content of clay matrix give transitions to argillites through intermediate varieties of "aleuro-argillites". The only module by which it is possible to distinguish these lithotypes was the *alkaline module AlkM*.

For example, on a non-standard module diagram AlkM–HM one can see that in "aleuro-argillites" the AlkM value is stable and on average does not exceed 1 ± 0.1 (normosodium compositions). On the contrary, in sandstones, the AlkM value is, firstly, higher, and secondly, it shows significant variability: on average, from 1.7 to 6.5 (super- and hypersodium compositions). At the same time, several clusters of increasing sodium content can be identified: aleuro-argillites ⇒ sandstones ⇒ sandstones ⇒ sandstones. Obviously, in this series, the proportion of clay matter (potassium carrier) decreases. In order for the HM to remain at approximately the same level (0.40 on average) with such a change, it is necessary that the composition of the detrital material is substantially feldspar (with its substantially quartz composition, the HM will inevitably decrease as the proportion of clay matter in the rocks decreases).

In the book by A.V. Maslov et al. [170], devoted to the description of the South Uralian stratotype of the Riphean, the diagram of J. Maynard et al. [339] is promoted in the coordinates SiO_2/Al_2O_3–K_2O/Na_2O, which, as believed, allows to determine the formational (geodynamic) characteristics of sandy rocks. Obviously, in terms of our modules, this is the 1/AM–1/AlkM diagram. Unfortunately, we have no experience in using such a diagram and therefore cannot judge its merits.

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[1] A similar picture can be seen on the standard HM–TM diagram; however, the use of the HM module for igneous rocks is undesirable. Note that the original kimberlites are formally qualified either as titanium pseudohydrolisates or as carbonatolites.

[2] A similar picture is observed for the statistical sample of analyzes on the Kronotsky Peninsula [169, p. 64–65]

V. I. Silaev, who studied in detail the mineralogy of phosphate-bearing weathering crusts of the Polar Urals, used a non-standard graph HM–FerM, which outlined a band of positive correlation covering about 75% of all points [237].

4.9. "Module spectra" by G. V. Ivensen. Module curves

The Yakut researcher G. V. Ivensen, who studied the Upper Permian-Cretaceous terrigenous strata of the Peripheral Verkhoyansk Depression, widely used petrochemical modules and module diagrams for diagnostic purposes. At the same time, in addition to the usual diagrams in the coordinates of a pair of modules, she used the "spectra" favorite by geologists – broken curves, where *all* petrochemical modules are plotted along the abscissa in a certain order, and their values along the ordinate (for which, however, it was necessary to resort to a logarithmic scale). She built "module spectra" on such diagrams, as a rule, for *average compositions.* The coincidence of the configuration of module spectra for different rocks was interpreted as their material and genetic similarity.

The researcher made this conclusion, for example, for the Lower Triassic strata of the Nedzhelinsk formation: "*In Fig. <...> the module curves are given for different types of the Nedzhelinsk formation rocks. Here, the relationship between the petrochemical parameters of sandstones, argillites and diabase is clearly visible. The module curve of argillites almost coincides with the module curve of diabase, and the module curve of sandstones has some differences, but the relationship between them is very clearly manifested. Based on these data, argillites of the Nedzhelinsk formation can be attributed to tuffs, and sandstones to tuffites, at least*" [114, p. 47].

An equally important conclusion was made based on module curves plotted for the Jurassic and Cretaceous lithotypes: "*The average values of the modules for Jurassic and Cretaceous argillites are practically the same <...>, but just as for sandstones, the KM of Jurassic argillites* (0.20) *is higher KM of chalk argillites* (0.16) <...>. *The same graphs show petrochemical modules values calculated for the average composition of dacites. The module curves plotted for various types of Jurassic and Cretaceous rocks are remarkably accurate to follow the module curve of dacites. Moreover, sandstones are closest to dacites in terms of their petrochemical characteristics, and argillites are farther away, but genetic links are well traced*" [114, p. 51].

In our work on the regional geochemistry of the Paleozoic strata of the Pechora Urals, we used the traditional for geology *average values distribution curves* of the petrochemical modules *over the stratigraphic section* [295, p. 208–210]. In the Paleozoic column from the Lower Ordovician to the Upper Permian inclusive, 11 *lithostratigraphic units* were identified, corresponding to the formations or stages of the stratigraphic scale. For each lithostratigraphic unit, based on a significant number of chemical analyzes, the average (median) values of petrochemical modules were calculated. Drawn next to the schematic stratigraphic column (on a conventional scale – without considering thickness of the subdivisions) and connected by straight segments, the corresponding points form broken lines – module curves. The analysis of such curves allowed to reveal nontrivial regularities, for example, for carbonate rocks – the tendency of an increase in the alkaline module (AlkM) and sodium module (NM) up the section.

A similar methodological technique was applied by E.Z. Gareev, who studied the geochemistry of the South Uralian stratotype of the Riphean [170]. In the column of the stratotype section, covering the interval from the Lower Riphean to the Upper Vendian, inclusive, he identified from 13 (sandstones) to 28 (clay rocks) lithostratigraphic units corresponding to formations and subformations. For example, in the sandstones of Burzyanian (Lower Riphean) from the bottom up the section in the series Aisk ⇒ Bolsheinzersk ⇒ Yushinsk HM values decrease, while in the section Yurmatinian (Middle Riphean) in the series of formations (from bottom to top) Mashaksk ⇒ Zigalginsk ⇒ Zigazino-Komarovsk ⇒ Avzyan HM reaches a minimum in Zigalginsk, then sharply increases in the Zigazino-Komarovskaya and decreases again in the Avzyan formations. The HM distribution is even more complex in the sandstones of the Karatavian (Upper Riphean), giving two minima (the deepest in the extraquartz sandstones of the Lemezin Subformation of the Zilmerdak Formation).

E.Z. Gareev believes that the Lower Riphean picture “*reflects the maturation of the clastic that entered the basin from the beginning to the end of the sedimentation cycle*” [170, p. 130], while the ramp change in HM values for the Middle and Upper Riphean “*could be caused by a number of factors, the most real of which was the expansion over time of the water collecting area and the involvement of material from more distant and less transformed areas in the sedimentation processes*” [ibid. p. 131].

4.10. Lithochemical standard YuK

The lithochemical standard YuK (based on the initial letters of the authors' surnames) is intended for uniform computer processing of any sample of silicate analyzes and is a system of five documents. Our experience allows us to recommend the standard for mass use. Text documents are executed in LEXICON or WORD format, and tabular documents – in QUATTRO PRO or EXCEL format.

Document-1: a table of initial data (in the author's original version) with the addition of calculated modules and rocks attestation according to the chemical classification.

Since this and the following tables must be printed on a double sheet (A4 x 2), it is useful to keep in mind its length: three display screens plus three five-digit columns. Since the table often turns out to be longer, one can hide columns that are not very necessary when printing (command *Hiden*).

Document-2: a table for calculating clusters, which shows (and can always be checked and corrected) in which cluster any analysis is located. Clusters previously marked on the graph should be carefully checked in the table on the display. With such a review, samples are easily identified that have pop-up values of other parameters that are not considered by this module diagram. For example, in a sandstones cluster highlighted on the NKM–HM diagram, there will be a sample with anomalous TM value or carbonate content (CO_2), etc. Such a sample, of course, should not be averaged with the rest. If the cluster volume is more than two, then in addition to the average values, standard deviations are also calculated.

Document-3: summary table. It shows averages for clusters (whether to provide standard deviations is a matter of the authors' choice) and residuals from averaging are individual analyzes that cannot be averaged for some reason (for example, the same carbonate sandstone). Tables 1–3, as already mentioned, in addition to the original traditional rocks names (lithotypes), contain rocks names according to the chemical classification – *chemotypes.* Sometimes the lithochemical qualification procedure alone is sufficient for the diagnosis. For example, titanium pseudohydrolyzate is usually basite or metabasite. Table 1 and 2 are saved in the data bank, and the final Table 3 with minimized information can be used for publishing.

Document-4: a graph, i.e., a module diagram. As a rule, the most informative one is enough but sometimes it makes sense to give two or even three diagrams. On the selected graph, clusters are first distinguished to compile a Table 2, and they are further corrected as described above.

Document-5: a text file that provides a geological description and lithochemical interpretation of information (documents-3 and 4). Of course, when interpreting, one must refer not only to the final Table 3, but also to Table 12.

Document-5 is a ready-made material for editing any logically coherent texts. In this regard, the technology of compiling this book may also be of interest: a significant part of its text (starting with Chapter 3) is actually assembled from *documents-5* accumulated over the years, i.e., the results of interpreting statistical samples of silicate analyzes, accompanied by processed factual material in form of *documents-4* (graphics) and *3* (summary table).

CHAPTER 5

LITHOTYPES AND CHEMOTYPES: THE PROBLEM OF INFORMATION

5.1. Iterative MT procedure

As noted in Ch. 2, the use of chemical classification in some cases leads to a "collision" with tradition – the boundaries of chemotypes may not coincide with the boundaries of traditional lithotypes. However, if the classifier is convinced of his boundaries' validity, then they must be defended even when a contradiction with a long tradition is found. Logic and, most importantly, successful practice should gradually change the minds of the conservative scientific community. For example, at one time V. D. Shutov revolutionized the concept of "greywacke" by proposing to consider any sandstone, which contains more than 25 % of rock fragments, regardless of their composition, as greywacke. Strictly following this principle, he was compelled to consider greywackes such rocks, in which fragments are represented by granites. This was very unusual for lithologists and caused, for example, sharp objections from A. A. Predovsky [211, p. 24]. Nevertheless, the term by V. D. Shutov has become generally accepted in modern Russian lithology. Even more indicative are the numerous terminological innovations of N. B. Vassoevich (*bitumoids, micro-oil, polymer lipoidins, kakhites, sedikahites, amikagins, etc.*). At first they were extremely unusual, but the logic behind them has done its job, and now they are widely used and perceived as quite natural.

At first glance, the situation is different with chemical classification. Due to its narrow geochemical, “target” purpose, it seems that the classifier has no right to “encroach” on the boundaries of lithological taxa. So, A.V. Sochava, plotting the points of the compositions of the red-colored Cretaceous argillites of Central Asia on the A.N. Neyelov’s graph, fell into the field of "siltstones" [245, p. 98–99]. Strictly following the classification by A.N. Neyelov, he had to certify the rocks as siltstones, and not as argillites. However, this was not done.

A theoretical analysis of such examples allows one to discover what in classiology (the science of classifications) is called “iterative meronomic-taxonomic ($M \Rightarrow T$) procedure” [173]. For example, starting the classification of phosphate rocks, we first have a vaguely defined set – a set of some sedimentary rocks that have the sign of "high phosphorus content." Having made this feature quantitative and setting the *meron* equal to 21.5 % P_2O_5 (which corresponds to the content of 50 % normative fluorine apatite), we form a subset – the taxon “phosphatolites”. Thus, we performed the $M_1 \Rightarrow T$ procedure (meron-1 $\Rightarrow$ taxon). Now changing the meron for some reason and setting, for example, M_2 = 20 % P_2O_5, we form a new taxon, thus performing an iterative process $(M_1 \Rightarrow T_1) \Rightarrow (M_2 \Rightarrow T_2)$ [136, p. 37].

In the literature, one can find many analyzes of vaguely defined and poorly characterized “tuffogenic rocks” (i.e., in our terms, rocks with a pyrogenic admixture). Having set ourselves the goal of forming a taxon of *tuffoids* (T_0), i.e., rocks with a substantial (for example, > 10 %) pyrogenic admixture, we are looking for a suitable meron and stop, for example, at the NKM module. For some meaningful reasons (suppose, relying on the reference statistical sample of exactly known tuffs analyzes), we set the meron M_1: NKM = 0.50. Now we will classify all analyzes of specific rocks with NKM > 0.50 as tuffoids, although they were not named so in the original source. In this example, we have performed the procedure $T_0 \Rightarrow (M_1 \Rightarrow T_1)$. If the meron was chosen successfully, then the resulting classification will acquire a significant heuristic value. With its help we will now be able to recognize rocks with a pyrogenic admixture.

Since the assignment of new merons is necessarily associated with some change in the old taxa, ***it becomes clear that if the chemical classification does not at all "encroach" on the boundaries of the old taxa, then this is not its advantage, but a disadvantage.*** In the above example with the Cretaceous argillites of Central Asia, the contradiction between the content of the initial taxon (T_0) “argillite” and chemical merons could be resolved in two ways:

– either by adaptation of merons to the old lithological taxon T_0, i.e., by changing the boundaries of "argillites" in the classification by A.N. Neyelov according to the scheme: T_0; $(M_1 \Rightarrow T_1) \Rightarrow (M_2 \Rightarrow T_0)$.

– or by changing the old taxon according to the scheme: $T_0 \Rightarrow (M_1 \Rightarrow T_1)$.

The second route is riskier since it requires changing the boundary of the original lithological taxon. On the other hand, it can give more in a heuristic sense – under that non-variable condition, if the M_1 meron is defined in a certain sense “in a good way”.

Let's move on from these theoretical considerations to the analysis of specific examples illustrating the relationship between lithotypes and chemotypes.

5.2. Approximate coincidence of chemotypes with lithotypes

Such situations are most often encountered in the practice of lithochemistry, but nevertheless, some "subtleties" that have heuristic significance are often found. Below we will give a series of examples, in some of which there is an almost complete coincidence of lithotypes with the chemotypes highlighted on the module diagrams, and in others – certain discrepancies.

Table 30 and Fig. 27 processed 18 analyzes of Paleocene–Eocene silica-kaolinite (with hematite) red-colored rocks [104]. These deposits occured in the depressions of the Kazakh Shield, the West Siberian Plate and the orogenic region of Altai. The analyzes characterize the Zaysan trough (12), Gorny Altai (4), and the Semipalatinsk Pre-Irtysh region (2).

Clusters I–III exactly correspond to lithotypes: sands and sandstones (*I*), silts and siltstones (*II*), clays and argillites (*III*). The compositions of rocks outside the clusters correspond to rocks enriched in kaolinite or hematite, and, as a result, they are classified as hypersiallites (*sample 6*), hydrolysates (*samples 7, 9*), or siferlites (*sample 4*). However, clusters *IVa* and *b* correspond to a mixture of lithotypes: clay + siltstone (*IVa*) or

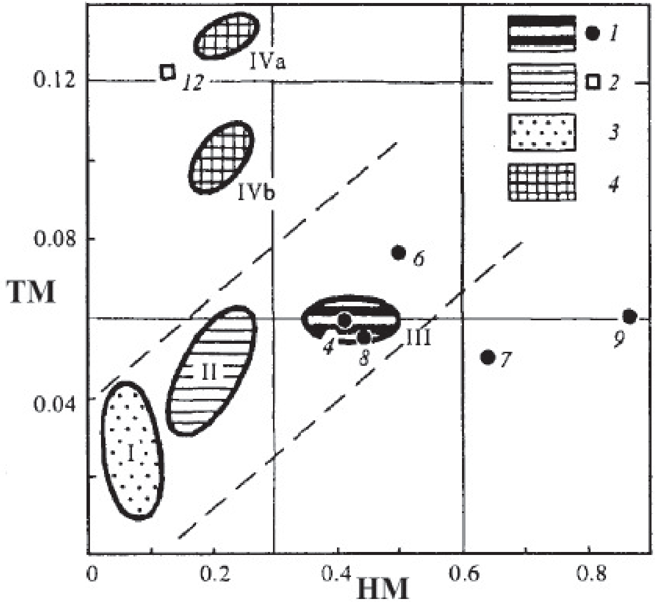

Fig. 27. Module diagram for silica-kaolinite red-colored rocks of the Cenozoic NW Asia. *Compiled according to V.S. Erofeev, Yu. G. Tsekhovsky, 1983 [104, p. 176–177].* 1 – clays and argillites, 2 – silts and siltstones, 3 – sands and sandstones, 4 – a mixture of lithotypes

Table 30

Chemical composition of silica-kaolinite red-colored rocks of the Cenozoic NW Asia.

Compiled according to V.S. Erofeev and Yu. G. Tsekhovsky, 1983 [104, p. 176–177]

Oxides and modules	I	II	III	IVa	IVb	4	6	7	8	9	12
	Sands and sandstones (supersilit)	Aleurites and siltstones (normosilit)	Clays and argillites (normosiallite)	Clays and Aleurites	Aleurites and sandstones	Clays and argillites					Aleurites and siltstones (normosilit)
				Myosilit		Siferlite	Supersiallite	Hypohydrolisate	Normosiallite	Normohydrolisate	
n	3	2	3	2		2					
SiO$_2$	89.16	76.23	63.19	73.10	75.69	61.00	58.82	54.30	62.66	47.84	82.60
TIO$_2$	0.13	0.61	1.08	1.19	0.86	0.73	1.72	1.30	1.18	1.23	1.10
Al$_2$O$_3$	5.04	12.64	18.11	11.69	6.51	12.15	22.34	25.52	21.07	20.13	9.00
Fe$_2$O$_3$	0.69	1.66	7.64	2.98	9.26	12.28	5.67	7.73	5.42	20.18	0.86
FeO	0.07	0.35	0.12	0.05	0.04	0.10	0.00	0.21	0.21	0.07	0.00
MnO	0.01	0.02	0.02	0.03	0.13	0.07	0.01	0.03	0.04	0.01	0.01
MgO	0.78	0.51	0.80	1.17	0.56	0.70	0.64	0.79	0.24	0.32	0.48
CaO	0.14	0.22	0.32	0.48	0.85	0.99	0.68	0.58	0.80	0.58	0.43
Na$_2$O	0.38	0.66	0.59	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00
K$_2$O	0.76	1.09	0.78	0.75	0.76	0.70	0.09	0.81	0.00	0.00	0.76
P$_2$O$_5$	0.02	0.12	0.09	0.04	0.10	0.07	0.05	0.10	0.23	0.04	0.01
LOI	2.64	5.42	7.82	8.67	4.43	9.60	10.00	9.04	8.20	10.10	4.14
Total	99.81	99.50	100.57	100.13	99.60	98.39	100.02	100.41	100.05	100.50	99.39
HM	0.07	0.20	0.43	0.22	0.22	0.42	0.51	0.64	0.45	0.87	0.13
FM	0.02	0.03	0.14	0.06	0.13	0.21	0.11	0.16	0.09	0.43	0.02
AM	0.06	0.17	0.29	0.16	0.09	0.20	0.38	0.47	0.34	0.42	0.11
TM	0.026	0.048	0.060	0.101	0.131	0.060	0.077	0.051	0.056	0.061	0.122
FerM	0.15	0.15	0.41	0.24	1.28	0.97	0.24	0.30	0.25	0.95	0.09
NKM	0.23	0.14	0.08	0.06	0.18	0.06	0.00	0.03	0.00	0.00	0.08
AlkM	0.50	0.60	0.70	0.00	0.60	0.00	0.00	0.00	-	-	0.00

sand + siltstone (*IVb*). In terms of the HM value, these mixtures correspond to the silty rocks of cluster II, but very much differ in their titanium value: TM 0.101–0.131 versus 0.048. It turns out that this difference is not accidental: only these clusters contain rocks from the depressions of the Altai and Pre-Irtysh regions. Obviously, the petrofund of these regions was different – more titanic.

Among the Permocarbonic tuffs of the Norilsk region (Table 31), four clusters are distinguished on the NKM–HM module diagram (Fig. 28), which practically coincide with the lithotypes described by T. A. Divina [94]. *Clusters I* (hypoalkaline siallites) and *II* (normalkaline siallites) are mostly "tuffs", and only one analysis corresponds to "tuffogenic sandstone". Clusters *III* and *IV* (alkaline hyposiallites and normosilites) are represented by “tuffosandstones” and “tuffogenic sandstones”. In this example, the rocks chemical composition allowed an error-free lithological rocks diagnostics. However, lithochemical information is richer than lithological: in Fig. 28, we find points of compositions with anomalous titanium value (*samples 4, 13*), carbonate and iron content (*sample 3*). This circumstance does not allow to combine the rocks, which are qualified by T.A. Divina as “tuffogenic microfelsites”, into one cluster, although such a combination suggests itself by their location on the graph. Consequently, one lithotype in this case cor-

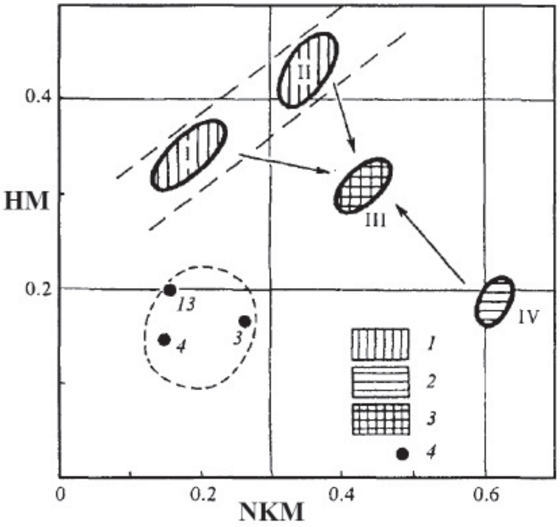

Fig. 28. Module diagram for tuffogenic rocks C_3–P_1 of the Norilsk region.
Compiled according to T.A. Divina, 1969 [4, p. 53].
1 – tuffs, 2 – tuffogenic sandstones, 3 – tuffogenic sandstones, 4 – tuffogenic microfelsites

Table 31

Chemical composition of tuffogenic rocks C_3–P_1 of the Norilsk region. *Compiled according to T.A. Divina, 1969 [94, p. 53]*

Oxides and modules	I	II	III	IV	3	4	13
	Normo-siallite	Alkaline normosiallite	Alkaline hyposiallite	Alkaline normosilite	Pseudo-silite	Normosilites	
n	2	3	4	2			
SiO_2	64.13	52.91	62.32	74.90	57.72	78.90	76.05
TiO_2	0.89	0.84	0.71	0.41	0.39	2.30	0.10
Al_2O_3	13.41	16.59	15.56	12.44	4.25	8.35	12.77
Fe_2O_3	0.76	0.90	0.40	-	1.11	0.05	0.73
FeO	6.64	4.38	2.38	1.12	3.60	1.08	1.79
MnO	0.19	0.09	0.10	0.04	0.48	-	0.01
MgO	2.42	2.70	1.20	0.32	4.11	0.37	0.21
CaO	1.06	6.00	4.81	1.21	11.42	0.15	0.80
Na_2O	0.52	3.05	4.43	3.33	0.22	0.37	0.12
K_2O	1.98	2.83	2.31	4.30	0.90	0.90	1.92
P_2O_5	0.46	0.33	0.23	0.03	0.08	0.04	0.02
S	0.23	0.21	0.06	0.01	0.45	0.01	0.01
H_2O	1.06	0.96	0.34	0.23	0.35	1.05	1.13
LOI	6.97	8.33	5.45	1.61	15.23	6.50	4.40
Total	100.70	100.13	100.30	99.93	100.31	100.07	100.06
HM	0.34	0.43	0.31	0.19	0.17	0.15	0.20
FM	0.15	0.16	0.06	0.02	0.15	0.02	0.04
AM	0.21	0.31	0.25	0.17	0.07	0.11	0.17
TM	0.066	0.052	0.046	0.032	0.092	0.275	0.008
FerM	0.53	0.32	0.18	0.09	1.12	0.11	0.20
NKM	0.18	0.36	0.43	0.61	0.26	0.15	0.16
AlkM	0.20	1.10	2.00	0.80	0.20	0.40	0.10

responds to two chemotypes. In addition, the “tuffs” of *clusters I* and *II* have a much lower alkalinity than the tuff sandstones of *cluster IV*. Obviously, the first are altered (clay) tuffs.

Thus, even with a good coincidence of the chemo- and lithotypes, the lithochemical information may turn out to be nontrivial – it prompts the lithologist to look for subtle differences in rocks that were not noticed in the standard lithological description.

It is known that flysch deposits are characterized by weak differentiation of sandy-silty and pelitic material, since material of different sizes is carried away by the turbid suspended current. As one can see from the table 32,

Table 32

Chemical composition of argillites and sandstones
of the Lower Ordovician flysch series Greenland, New Zealand.
Compiled according to S. Nathan, 1976 [346, p. 687]

Oxides and modules	Ia	Ib	IIa	IIb	8
	Myosilite		Alkaline hyposiallite	Alkaline pseudosiallite	Pseudo-siallite
n	4	2	2	2	
SiO_2	72.10	69.54	65.92	61.83	65.25
TiO_2	0.59	0.71	0.70	0.81	0.89
Al_2O_3	12.44	13.73	15.23	18.11	14.13
Fe_2O_3	0.85	0.91	0.44	0.48	1.54
FeO	3.55	3.97	4.91	5.68	5.64
MnO	0.12	-	-	-	-
MgO	2.36	2.82	2.90	3.22	3.91
CaO	0.85	0.55	1.15	0.24	1.39
Na_2O	1.45	2.09	1.27	1.04	1.68
K_2O	2.81	2.63	4.12	5.00	2.76
P_2O_5	0.16	0.20	0.17	0.16	0.29
LOI	3.19	2.79	3.93	3.83	3.25
Total	100.45	99.91	100.70	100.38	100.73
HM	0.24	0.28	0.32	0.41	0.34
FM	0.09	0.11	0.13	0.15	0.17
AM	0.17	0.20	0.23	0.29	0.22
TM	0.048	0.051	0.046	0.045	0.063
FerM	0.35	0.34	0.34	0.33	0.48
NKM	0.34	0.34	0.35	0.33	0.31
AlkM	0.50	0.80	0.30	0.20	0.60

the Lower Ordovician flysch "argillites" and "greywackes"[1] of New Zealand practically do not differ in normalized alkalinity, although the difference in total alkalinity is quite noticeable (Fig. 29). Also, there are no noticeable differences in lithotypes in titanium value, iron content, and even sodium content. This means that these rocks are close in terms of the “feldspar/clay matter” ratio, and the differences are mainly due to the quartz content, a mineral that is a diluent for alkali carriers. Nevertheless, even for these poorly differentiated sediments, the HM value serves as a reliable criterion for

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[1] The content of rock fragments in these "greywackes" does not exceed 6 %, so according to the classification by V. D. Shutov adopted in our country, they should be called simply polymictic sandstones.

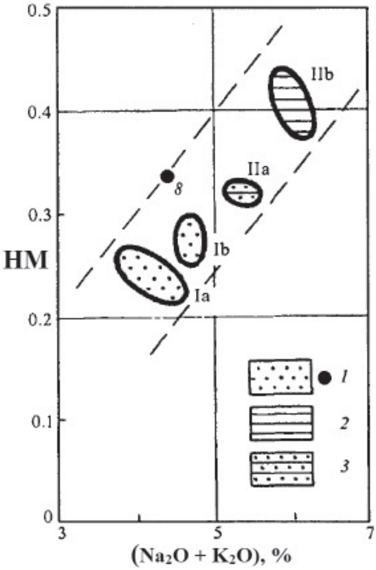

Fig. 29. Module diagram for greywacke (1) and argillites (2) of the Lower Ordovician flysch series, Greenland, New Zealand. 3 – supposed siltstones.
Compiled according to S. Nathan, 1976 [346, p. 687]

distinguishing clay from sandy lithotype: all "argillites" were siallites, and all "greywackes" were silites.

At the same time, lithochemistry is again more informative than lithology. Indeed, S. Nathan draws a boundary between macroscopically determined “argillites” and “greywackes” in terms of the SiO_2 content = 67 % [346]. However, it is difficult to agree to call a rock with 65–67 % SiO_2 "argillite". The rocks with HM in the interval of 0.30–0.35, as it seems to us, most likely correspond not so much to argillites as to *siltstones – cluster IIa* in Fig. 29.

The processing of analyzes of the Lower Jurassic sandstones and siltstones of the Greater Caucasus [272] showed that almost all sandstones are classified as silites, and all siltstones – as siallites. Thus, the composition classification according to the HM value gives a complete coincidence of lithotypes and chemotypes volumes. The difference in TM between lithotypes is less significant: TM in siltstones is in the range 0.014–0.027, and in sandstones, almost half of the compositions have TM > 0.027. The lower value of the ratio “feldspars/clay matter” determines the decreased alkalinity of siltstones: NKM = 0.24–0.36, while in half of the sandstones NKM is 0.35–0.51. In general, siltstones are more ferruginous: FerM = 0.34–0.42, while in sandstones FerM > 0.35 is only in two samples. Attention is drawn to the trend of positive correlation between HM–TM in sandstones, which is more clearly manifested in the Lower-Middle Jurassic sandstones of Svanetia. Such a correlation is possible in greywackes, in particular, biotite-bearing, which is quite consistent with the petrographic data given by G. A. Chikhradze [272]. However, even in this example, lithochemical information is richer than lithological one. Despite the coincidence of lithotypes with chemotypes, within the same lithotype of “sandstones”, three varieties-chemotypes can be defined, which gives the lithologist and geologist information for thought: it requires finding some lithological differences between sandstones.

Table 33 and Fig. 30 processed 21 analyzes of the Lower Cretaceous red-colored rocks of Fergana [245], of which 3 are carbonatic (*samples 3, 6, 13*). The fact that among argillites six compositions are formally classified as magnesian rocks – pseudosiallites, is explained by the presence of dolomite in them. *Sample 14* from the Yatan Formation, due to its iron content, is classified as siferlite; there is no additional information about this rock in the original source. On the HM–NKM diagram, the lithotypes "sandstones" and "argillites" are easily combined into clusters-chemotypes without overlapping. Argillites and sandstones form a single correlation field, and the titanium value of argillites is, on average, higher than that of sandstones, which we never observe in humid formations.

The peculiarity of the statistical sample is that, due to the presence of detrital impurities in argillites, the boundary between lithotypes does not pass along the HM value = 0.30 (i.e., not along the “silite/siallite” bound-

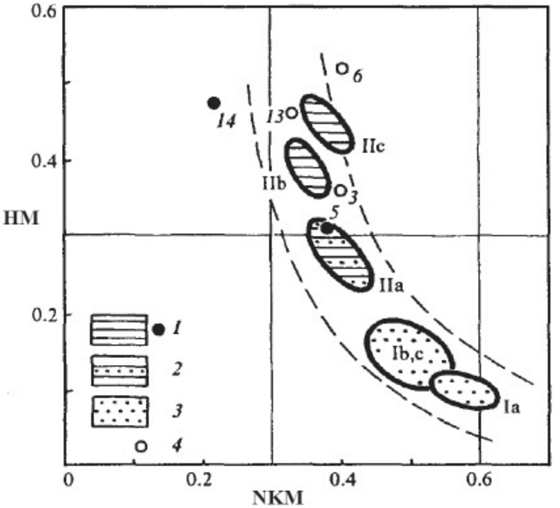

Fig. 30. Module diagram for the Lower Cretaceous reds of Fergana.
1 – argillites, 2 – siltstones (presumptive), 3 – sandstones, 4 – carbonate argillites.
Compiled according to the A.V. Sochava’s data, 1979 [245, p. 100]

Table 33

Chemical composition of the Lower Cretaceous red-colored rocks of Fergana.

Compiled according to the A.V. Sochava's data, 1979 [245, p. 100]

Oxides and modules	Ia	Ib	Ic	IIa	IIb	IIc	3	5	6	13	14
	Sandstones			Argillites							
	Normosiite			Alkaline myosilite	Alkaline pseudosiallite	Alkaline normosiallite	Carbonate pseudosiallite	Pseudo-siallite	Carbonate pseudosiallite	Pseudo-siallite	Siferlite
n	2	3	2	4	3	2					
SiO_2	83.60	74.01	79.53	68.88	59.14	58.84	41.03	60.59	32.66	44.17	59.65
TIO_2	0.25	0.37	0.39	0.69	0.76	0.95	0.52	0.88	0.56	0.61	1.06
Al_2O_3	7.78	8.68	9.60	13.49	15.90	16.74	10.03	12.39	10.36	14.12	14.70
Fe_2O_3	0.34	1.45	1.32	4.00	6.06	7.66	3.45	4.85	5.03	4.11	12.12
FeO	0.25	0.27	0.61	1.13	0.72	0.88	0.68	0.87	0.93	1.58	0.57
MnO	0.02	0.01	0.03	0.06	0.04	0.04	0.20	0.12	0.28	0.14	0.03
MgO	0.18	0.65	0.65	1.76	3.29	2.32	9.06	3.11	10.00	5.60	2.06
CaO	1.42	4.65	0.78	1.09	0.98	1.34	11.46	4.12	13.48	10.68	0.57
Na_2O	1.55	0.89	1.49	1.62	1.04	1.30	0.80	1.16	1.40	1.00	0.60
K_2O	2.92	3.43	3.21	3.82	4.58	5.10	3.24	3.62	2.80	3.70	2.64
P_2O_5	0.04	0.05	0.06	0.16	0.15	0.22	0.23	0.26	0.13	0.23	0.16
CO_2	0.57	2.94	0.37	0.50	0.98	0.27	12.32	4.35	18.30	7.83	0.20
LOI	1.08	2.25	1.69	2.61	5.91	4.36	6.98	3.27	4.07	6.46	5.21
Total	99.98	99.65	99.72	99.78	99.55	100.00	100.00	99.59	100.00	100.23	99.57
HM	0.10	0.15	0.15	0.28	0.40	0.45	0.36	0.32	0.53	0.47	0.48
FM	0.01	0.03	0.03	0.10	0.17	0.18	0.32	0.15	0.49	0.26	0.25
AM	0.09	0.12	0.12	0.20	0.27	0.28	0.24	0.20	0.32	0.32	0.25
TM	0.031	0.042	0.041	0.051	0.048	0.057	0.052	0.071	0.054	0.043	0.072
FerM	0.07	0.19	0.20	0.37	0.41	0.48	0.41	0.44	0.57	0.40	0.81
NKM	0.57	0.50	0.49	0.40	0.35	0.38	0.40	0.39	0.41	0.33	0.22
AlkM	0.50	0.30	0.50	0.40	0.20	0.30	0.20	0.30	0.50	0.30	0.20

ary), but along the HM of about 0.25 (i.e., within the subtype myosilites). If we give priority to chemotypes over lithotypes, then the rocks of the *IIa* cluster should be classified as *siltstones*, and not as argillites: their intermediate position between the explicit argillites-siallites (*cluster IIb*) and obvious sandstones-silites (*cluster I*) is evidence in favor of such a diagnosis. And indeed, as A.V. Sochava himself notes, "*the degree of matter's petrochemical differentiation in the Lower Cretaceous red-colored rocks is relatively low, which is associated both with the low "maturity" of the sedimentary material, and with the constant substantial silt impurity in the argillites*" [245, p. 97].

Thus, we again note a greater diversity of the "lithochemical reality" as compared to the lithological one: instead of two lithotypes (sandstones and argillites), six varieties of chemotypes have been defined: three for sandstones (*clusters Ia–c*) and three for argillites – proper argillites (*clusters IIb and IIc*) and siltstones (*cluster IIa*).

When considering the compositions of the four sandstone types described by F. Pettijohn [207, p. 277], it turns out that not 4, but 12 chemotypes – 6 clusters and 6 single compositions (Fig. 31) are distinguished on the module diagram.

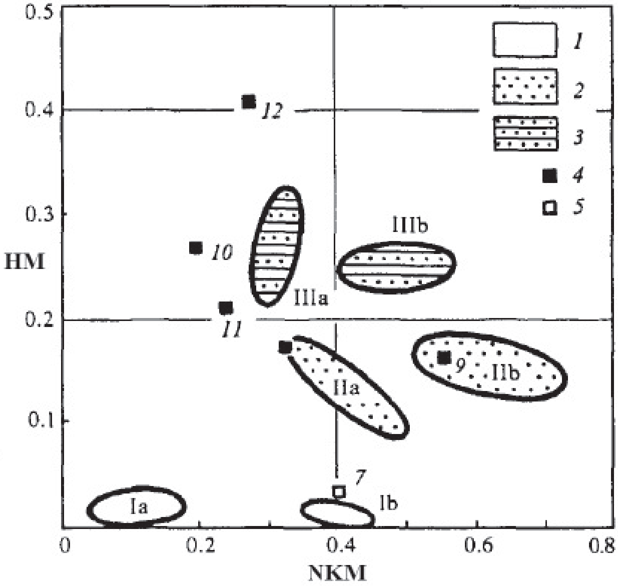

Fig. 31. Module diagram for typical sandstones.

Compiled according to F. Pettijohn, 1981 [207, p. 276–296].

1 – orthoquartzites, 2 – arkoses and subarcosis, 3 – greywackes, 4 – subgreywackes, 5 – protoquartzites

The orthoquartzite type differs in the minimum HM values, and in terms of alkalinity and titanium value it decomposes into two parts: low alkaline hypertitanium (*cluster Ia*) and alkaline relatively low titanium (*cluster Ib*). Obviously, the latter is genetically drawn towards subarcosis and "protoquartzites" – they should still retain feldspars and micas, and the mechanical differentiation of titanium and alumina mineral carriers has not yet manifested itself strongly. The first group of orthoquartzites, i.e., monomictic quartz sands and sandstones, are at least once recycled, washed residual products of humid chemical weathering. In them, silicates are almost completely decomposed, and TM is increased (Table 34) due to mechanical differentiation – separation of heavy titanium-bearing accessories from light clay minerals.

The arkoses and subarcosis type is even more heterogeneous: they form two mixed clusters – *IIa* and *IIb*. With wide variations in alkalinity (NKM from < 0.40 to 0.71), one can also notice the division of these rocks into groups of hypotitanium (TM < 0.30) and normotitanium (HM ~ 0.050). Such a difference can be a consequence of both the different titanium content of the petrofund and the different "maturity" of arkoses. The same strong heterogeneity is found in *greywackes*, giving two *clusters IIIa, b*. Finally, it is not possible to create clusters from *subgreywackes and protoquartzites*, and all of them (*an. 7–12*) act as individual compositions (or single clusters).

Thus, the chemototypes selection by clustering chemical compositions, on the one hand, allows to notice subtle differences in rocks that were not noticed during lithological typification, and on the other hand, to "deny individuality" to some lithotypes that were defined by the lithologist. These data should give him information for thought and encourage him to clarify the boundaries of the defined taxa.

Table 35 and Fig. 32 processed 12 analyzes of Cenozoic silica rocks of Sakhalin (Upper Oligocene–Upper Miocene) [91]. Silicites, opokas, and silica argillites (*clusters III, IIa, IIb*, respectively) on the module diagram are classified as normo- and supersilites, while more clay diatomites (*cluster I*) are already hyposiallites – at the very boundary of them with myosilitees (HM = 0.31 ± 0.03). Analysis of the diagram leads to two conclusions.

1. The loss of some silicites points (*an. 10*) from the line of positive parameters correlation indicates their belonging to some other set. In this case, such rocks can be interpreted as secondary (diagenetic) formations (the process of silicification, i.e., redistribution-input of silica).

2. The compositions similarity of the Lower Miocene opokas of the Kurasi Formation (*cluster IIa*) and the Upper Miocene silica argillites of the Pilenga and Kurasi Formations (*cluster IIb*) allows us to consider their formations closely related (the latter are simply more clay varieties of the

Table 34

Chemical composition of typical sandstones.
Compiled according to F. Pettijohn, 1981. [207, p. 276–296]

Oxides and modules	Ia	Ib	IIa	IIb	IIIa	IIIb	7	8	9	10	11	12
	Hypersilite		Normosiite	Alkaline normosilite	Myosilite	Alkaline myosilite	Hypersilite	Carbonate normosilite		Carbonate myosilite	Myosilite	Pseudo-siallite
n	2	2	2	4	3	4						
SiO_2	98.11	98.38	81.17	77.05	68.77	69.48	84.01	56.80	51.52	40.35	74.45	60.51
TIO_2	0.17	0.04	0.49	0.25	0.64	0.52	0.05	0.10	0.32	0.30	0.50	0.87
Al_2O_3	1.01	0.47	9.62	9.99	13.50	12.97	2.57	8.48	5.77	7.43	10.83	15.36
Fe_2O_3	0.20	0.32	0.75	1.32	0.75	1.19	0.17	1.67	2.43	3.27	4.62	0.76
FeO	-	0.14	0.20	1.01	3.67	2.96	0.26	-	-	-	-	7.63
MnO	-	0.01	-	0.10	0.07	0.07	0.04	-	0.14	-	-	0.16
MgO	0.02	0.01	0.71	0.65	1.75	2.07	0.67	1.24	0.95	10.28	1.30	3.39
CaO	0.02	0.03	0.45	1.42	2.83	1.42	5.41	15.25	16.96	12.00	0.35	2.14
Na_2O	0.02	0.08	0.73	1.89	2.63	3.91	0.17	1.31	1.32	0.54	1.07	2.50
K_2O	0.11	0.10	3.00	4.23	1.69	2.14	0.86	1.46	1.90	0.93	1.51	1.69
P_2O_5	-	0.01	0.11	0.25	0.13	0.09	0.04	1.01	0.10	-	0.01	0.27
SO_3	-	-	-	-	-	0.15			0.52	-	-	-
CO_2	-	-	-	1.34	1.23	0.11	4.65	12.95	13.34	17.80	-	1.01
LOI	0.27	0.65	3.82	1.17	2.76	2.97	0.75	0.50	4.79	6.75	4.95	3.95
Total	99.92	100.22	101.03	100.65	100.41	100.03	99.65	99.77	100.06	99.65	99.59	100.24
HM	0.01	0.01	0.14	0.16	0.27	0.25	0.04	0.18	0.17	0.27	0.21	0.41
FM	0.00	0.00	0.02	0.04	0.09	0.09	0.01	0.05	0.07	0.34	0.08	0.19
AM	0.01	0.00	0.12	0.13	0.20	0.19	0.03	0.15	0.11	0.18	0.15	0.25
TM	0.163	0.075	0.051	0.025	0.048	0.040	0.019	0.012	0.055	0.040	0.046	0.057
FerM	0.17	0.94	0.09	0.24	0.32	0.31	0.18	0.19	0.42	0.42	0.41	0.53
NKM	0.13	0.39	0.39	0.61	0.32	0.47	0.40	0.33	0.56	0.20	0.24	0.27
AlkM	0.20	0.80	0.20	0.40	1.60	1.80	0.20	0.90	0.70	0.60	0.70	1.50

Table 35

Chemical composition of the Cenozoic silica rocks of Sakhalin.
Compiled according to the data of R. V. Danchenko and G. L. Chochia, 1983 [91, p. 33]

Oxides and modules	I	IIa	IIb	III	10	11
	Diatomites (hyposiallite)	Opokas	Carbonate argillites	Silicites		Chalcedonolite
		Normosilite		Supersilite		
n	3	2	3	2		
SiO_2	65.19	79.69	73.77	87.78	85.60	92.30
TiO_2	0.63	0.37	0.35	0.16	0.23	0.12
Al_2O_3	15.33	8.87	8.97	4.29	5.15	2.28
Fe_2O_3	3.25	1.49	1.43	0.91	1.33	1.14
FeO	1.03	0.45	2.06	1.24	0.40	1.40
MnO	0.03	0.01	0.05	0.02	0.05	0.04
MgO	0.96	0.70	1.56	0.50	0.82	0.56
CaO	0.78	0.26	1.39	0.36	0.28	-
Na_2O	1.85	0.66	1.41	0.91	2.36	0.47
K_2O	2.48	1.45	1.43	0.60	0.78	0.39
P_2O_5	5.65	4.04	4.04	1.86	2.44	1.50
C_{org}	0.11	0.03	0.12	0.04	0.04	0.04
S	0.86	1.16	1.66	0.49	0.43	0.27
LOI	0.65	0.54	0.67	0.50	0.60	0.06
Total	98.82	99.68	98.90	99.64	100.51	100.57
HM	0.31	0.14	0.17	0.08	0.08	0.05
FM	0.08	0.03	0.07	0.03	0.03	0.03
AM	0.24	0.11	0.12	0.05	0.06	0.02
TM	0.041	0.041	0.039	0.036	0.045	0.053
FerM	0.27	0.21	0.39	0.49	0.33	1.08
NKM	0.28	0.24	0.32	0.35	0.61	0.38
AlkM	0.70	0.50	1.00	1.50	3.00	1.20

former), despite the noted by R.V. Danchenko and G. L. Chochia quite significant lithological differences between both [91, p. 37].

Considering the composition of the Carpathian clay rocks of the Cretaceous – Paleogene flysch strata, we notice three lithochemical features [Table 36, Fig. 33].

First, among the 42 analyzes [11] given by I.M. Afanasyeva, there are five compositions of "silica argillites", in which the HM value is below the siallite threshold of 0.30. Since these rocks are classified as myosilites (*clusters Ia, b*), their assignment to clay rocks is hardly legitimate.

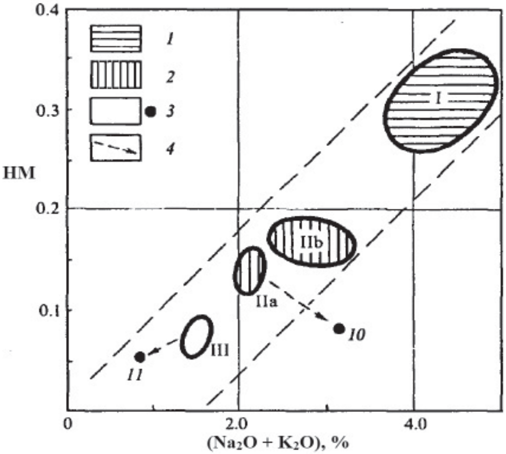

Fig. 32. Module diagram for the Cenozoic silica rocks of Sakhalin.

Compiled according to the data of R.V. Danchenko and G.L. Chochia [91, p. 33].

1 – diatomites, 2 – opokas and silica argillites, 3 – silicites. 4 – the assumed direction of the silicification process

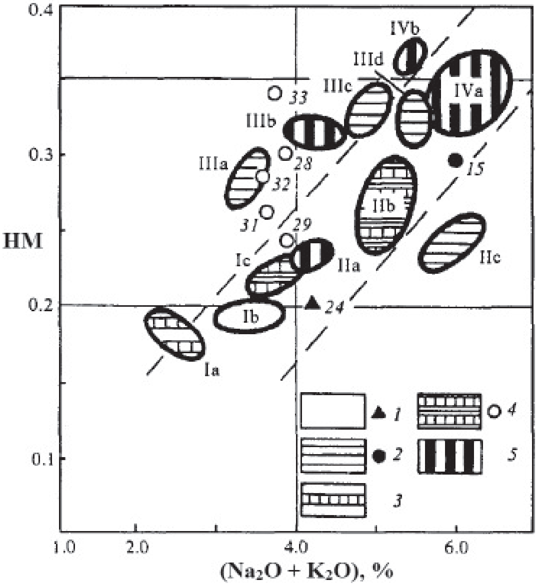

Fig. 33. Module diagram for Cretaceous and Paleogene flysch argillites on the southern slope of the Ukrainian Carpathians.

Compiled according to I.M. Afanasyeva, 1979 [11, p. 172–179].

Argillites: 1 – simple argillites, 2 – silty, 3 – silica, 4 – calcareous, 5 – tuffogenic and phyllitic

Table 36

Chemical composition of Cretaceous and Paleogene flysch argillites on the southern slope of the Ukrainian Carpathians.

Compiled according to I.M. Afanasyeva, 1979 [11, p. 172–179]

Oxides and modules	Ia	Ib	Ic	IIa	IIb	IIc	IIIa	IIIb	IIIc	IIId
	Silica (myosilite)		Calcareous (normo-siallite)	Silica (pseudo-siallite)	Aleurite	Silica	Argillite (normosiallite)	Tuffogenic (Mn pseudosiallite)	Argillites	
					Alkaline normosiallite				Hypohydro-lysate	Alkaline hyposiallite
n	2	2	2	2	7	2	2	2	4	3
SiO_2	62.27	65.93	56.09	61.77	57.39	60.93	54.47	53.13	52.82	53.13
TIO_2	0.64	0.48	0.57	0.95	0.62	0.56	1.08	0.89	0.90	0.90
Al_2O_3	11.63	14.45	13.76	15.63	18.08	17.13	18.69	19.16	21.00	20.35
Fe_2O_3	2.09	3.19	1.81	2.83	2.20	2.23	3.10	4.09	4.16	3.90
FeO	1.79	0.62	3.15	3.38	3.99	3.31	2.52	4.00	3.42	3.66
MnO	0.03	0.12	0.09	0.06	0.05	0.03	0.09	1.23	0.17	0.06
MgO	2.90	1.89	2.77	3.28	2.50	2.58	1.86	3.19	2.66	2.89
CaO	5.65	1.33	7.62	1.79	2.54	0.67	0.79	0.97	1.50	1.17
Na_2O	0.49	0.68	1.37	1.41	1.78	1.00	0.37	1.05	1.69	1.27
K_2O	2.06	2.78	2.41	2.76	3.34	5.02	3.06	3.21	3.27	4.25
P_2O_5	0.08	0.72	0.15	0.21	0.18	0.12	0.19	0.12	0.08	0.09
H_2O^+	2.93	7.18	4.18	4.41	3.41	5.65	9.70	6.60	5.10	4.96
CO_2	6.62	0.47	5.81	1.40	3.54	0.65	5.42	2.30	3.24	3.34
$S + SO_3$	1.41	2.76	0.14	0.21	0.72	0.46	1.61	0.10	0.22	0.26
Total	100.56	102.55	99.89	100.05	100.33	100.29	102.91	100.02	100.21	100.21
HM	0.26	0.29	0.35	0.37	0.43	0.38	0.47	0.55	0.56	0.54
FM	0.11	0.09	0.14	0.15	0.15	0.13	0.14	0.21	0.19	0.20
AM	0.19	0.22	0.25	0.25	0.32	0.28	0.34	0.36	0.40	0.38
TM	0.055	0.033	0.041	0.061	0.034	0.032	0.058	0.046	0.043	0.044
FerM	0.32	0.26	0.35	0.38	0.33	0.31	0.29	0.46	0.35	0.36
NKM	0.22	0.24	0.27	0.27	0.28	0.35	0.18	0.22	0.24	0.27
AlkM	0.20	0.20	0.60	0.50	0.50	0.20	0.10	0.30	0.50	0.30

Table 36 (continuation)

Oxides and modules	IVa	IVb	15	24	28	29	31	32	
	Phyllite argillites (alkaline pseudohydrolisate)		Aleurite argillite (alkaline pseudohydrolisate)	Silica argillite (myosiallite)	Calcareous argillites				
					Phosphate supersiallite	Normosiallite	Silica pseudosiallite	Normosiallite	Pseudohydrolisate
n	5	2							
SiO_2	52.12	49.39	54.18	67.02	44.16	51.85	44.02	49.02	44.72
TIO_2	0.86	1.18	0.68	0.90	0.79	0.20	0.72	0.54	0.53
Al_2O_3	22.31	22.59	19.63	14.30	15.60	14.61	13.28	17.34	17.29
Fe_2O_3	3.02	5.17	2.34	2.71	1.97	1.39	0.91	3.49	2.73
FeO	4.03	2.15	4.42	2.48	4.02	4.00	4.09	2.08	5.65
MnO	0.05	0.05	0.05	0.04	0.06	0.07	0.09	-	0.06
MgO	3.07	3.27	1.80	0.46	2.79	2.97	4.10	2.96	4.12
CaO	0.76	1.20	0.43	2.37	11.50	8.12	11.06	8.90	8.30
Na_2O	1.15	1.13	1.40	0.96	0.85	1.07	0.95	2.90	0.65
K_2O	4.97	4.33	4.63	3.26	3.04	2.83	2.69	0.70	3.17
P_2O_5	0.18	0.41	0.68	0.12	6.44	0.05	0.12	0.09	0.32
H_2O^+	6.29	6.65	6.22	4.23	3.91	5.26	5.12	3.48	3.38
CO_2	1.04	2.71	3.52	1.42	5.09	7.92	10.92	8.00	9.02
$S + SO_3$	0.68	0.05	0.29	0.01	0.23	0.03	0.75	0.03	-
Total	100.53	100.27	100.27	100.28	100.45	100.37	98.82	99.53	99.94
HM	0.58	0.63	0.50	0.30	0.51	0.39	0.43	0.48	0.59
FM	0.19	0.21	0.16	0.08	0.20	0.16	0.21	0.17	0.28
AM	0.43	0.46	0.36	0.21	0.35	0.28	0.30	0.35	0.39
TM	0.039	0.052	0.035	0.063	0.051	0.014	0.054	0.031	0.031
FerM	0.31	0.31	0.34	0.34	0.37	0.37	0.36	0.31	0.47
NKM	0.27	0.24	0.31	0.30	0.25	0.27	0.27	0.21	0.22
AlkM	0.20	0.30	0.30	0.30	0.30	0.40	0.40	4.10	0.20

Indeed, according to the description of I.M. Afanasyeva [11, p. 181], lithotypes from phtanite to silica argillite here form a "single row" as the content of free SiO_2 decreases. The boundary of "strong clay phtanites" and "silica argillites" performed according to the content of SiO_{2free} = 50 % in accordance with I. V. Khvorova's recommendation [264]. However, it is quite probable that there is no contradiction with this boundary: the SiO_{2free} value was not determined in the analysis of argillites [11, p. 172–179], therefore, when assessing its content, mistakes were possible. Indeed, as seen in Fig. 33, of all "silica argillites" silites were only rocks in clusters Ia, b, while the "silica argillites" in clusters *IIa, IIc* turned out to be siallites and pseudosiallites.

Secondly, among the remaining 37 compositions, 12 are hypohydrolysates and 7 related supersiallites with HM 0.50–0.55. In particular, all "phyllite-like argillites" turned out to be alkaline pseudohydrolysates (4 Lower Cretaceous, 2 Upper Cretaceous and 1 Eocene) – they form clusters *IVa, b.*

According to I.M. Afanasyeva, most of the Cretaceous clay rocks are composed of the mineral association "hydromica + chlorite", while in the Eocene kaolinite, montmorillonite, and mixed-layer montmorillonite-hydromica minerals appear (*clusters IIIa, c,* and *sample 15*). Nevertheless, the predominance of alkaline varieties ($Na_2O + K_2O > 5$ %) among hydrolysates and supersiallites shows that the main factor of hydrolysability is hydromica, and not kaolinite or chlorite.

Third, one in three of these compositions turned out to be magnesian (MgO > 3 %), which forces them to be attributed either to pseudosiallites (*clusters IIa, IIIb, sample 31*) or to pseudohydrolysates (*clusters IVa, b, sample 33*). At the same time, ten out of twelve magnesian rocks contain an appreciable carbonate amount: CO_2 1.44–10.92%.

If we call "carbonate-bearing" the rocks with $CO_2 > 5$ %, then they will be silites of *cluster Ia* and siallites of clusters Ic and IIb, as well as a series of separate compositions – *samples no. 28–29, 31–33.* Note that *sample 28* turns out to be phosphate-bearing. Obviously, magnesiality is associated with authigenic dolomite (or ankerite) and only in 10–15% of cases it can be attributed to chlorite. At the same time, one of the two analyzes of "tuffogenic argillites" also turned out to be pseudosiallite, and these rocks themselves were manganous (*cluster IIIb*).

All this gives reason to believe that among the Carpathian flysch clay rocks there are much more "tuffogenic argillites" than is established only by lithological methods. We believe that all magnesian varieties should be classified as tuffogenic. If I.M. Afanasyeva's statistical sample represents the clay rocks abundance in the section, it turns out that the share of tuffogenic argillites will account for up to 1/4 of all clay rocks of the Carpathian flysch. This is far from a trivial conclusion – the result of lithochemical research. So, the lithochemical processing of the I.M. Afanasyeva's data allows us to draw the following three conclusions.

1. Some of the chemotypes-clusters defined by us correspond to certain lithotypes: silica argillites (*Ia, b, IIa, c*), argillites (*IIId*), silty argillites (*IIb*), tuffogenic argillites (*IIIb*), phyllite-like argillites (*IVa*). In other words, these groups of lithotypes have a fairly distinct chemical identity.

2. Almost half of the clusters (5 out of 12) correspond to a mixture of lithotypes, which allows us to reasonably assume inaccuracies in identifying lithotypes.

3. There is a wide distribution of pyrogenic admixture in sedimentary strata, and, as one might think, its significant epigenetic change (dolomitization).

Table 37 and Fig. 34 shows the average compositions of the Lower Riphean dolomite, terrigenous-carbonate and terrigenous rocks of the Southern Urals, accompanying magnesites [258]. The need to reckon with the presence of carbonate iron forces the use of AM instead of HM for clustering. It turns out that pure dolomites (*clusters II, IV*) and calcareous dolomites (*V, VI*) have similar AM values (0.19–0.24) with significant differences in alkalinity (NKM 0.25–0.46). In general, the most alkaline rocks are in *clusters IV, V* and the most titanium.

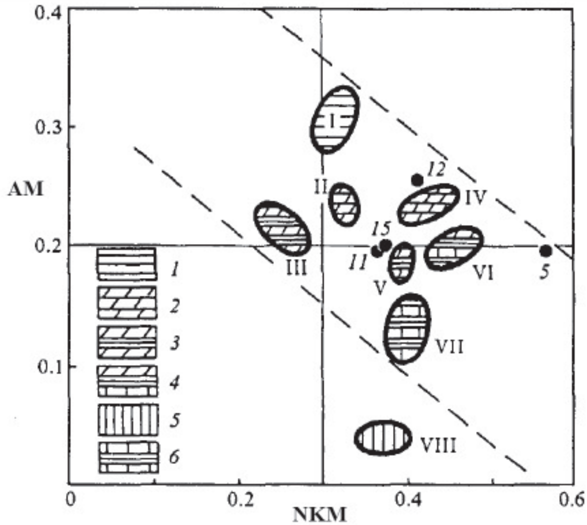

Fig. 34. Module diagram for the average compositions of carbonate and other rocks from the magnesite-bearing sections of the Riphean of the South Urals.

Compiled according to L.P. Urasina et al., 1993 [258, p. 104–105].

1 – aluminosilicate rocks, 2 – pure dolomites, 3 – dolomites with silicate admixtures, 4 – dolomites and limestones with silicate admixtures, 5 – silicate-carbonate rocks, 6 – carbonate-silicate rocks

Table 37

Average chemical composition of carbonate and other rocks from the lower Riphean magnesite-bearing sections, South Urals.

Compiled according to L.P. Urasina et al., 1993 [258, p. 104–105]

Oxides and modules	I	II	III	IV	V	VI	VII	VIII	5	11	12	15
	Alumino-silicate rocks (pseudosiallite)	Clear dolomites	Silica-bearing dolomites	Clear dolomites	Silica-bearing dolomites	Dolomites and limestones	Silicate-carbonate rocks	Carbonate-silicate rocks (carbonate pseudosilite)	Clear dolomites	Dolomites and limestones	Limestones	Silicate-carbonate rocks
		Carbonatolite							Carbonatolite			
n	348	181	64	133	87	97	507	104	73	38	7	14
SiO_2	57.83	1.45	2.70	1.45	3.70	4.75	12.42	48.30	1.50	6.50	7.70	14.20
TIO_2	0.79	0.02	0.03	0.02	0.06	0.04	0.09	0.12	0.02	0.04	0.09	0.10
Al_2O_3	17.83	0.35	0.60	0.35	0.70	0.95	1.74	2.10	0.30	1.30	2.00	2.90
Fe_2O_3	2.77	0.10	0.15	0.25	0.45	0.55	0.60	0.45	0.30	1.30	4.00	0.50
FeO	2.77	0.45	1.25	0.50	0.85	0.75	1.08	1.15	0.70	2.80	0.60	0.50
MnO	0.03	0.03	0.09	0.04	0.05	0.04	0.05	0.04	0.05	0.20	0.09	0.01
MgO	3.27	21.90	21.60	21.55	20.75	11.80	13.80	10.50	21.00	14.40	3.70	18.30
CaO	3.10	29.30	28.15	29.50	28.80	38.00	30.96	18.75	29.70	32.50	42.50	23.80
Na_2O	0.94	0.05	0.07	0.07	0.10	0.08	0.18	0.20	0.05	0.06	0.15	0.10
K_2O	4.66	0.07	0.09	0.09	0.19	0.35	0.51	0.59	0.12	0.42	0.68	0.99
P_2O_5	0.080	0.010	0.013	0.026	0.030	0.035	0.043	0.034	0.019	0.040	0.100	0.037
LOI	6.48	46.22	44.91	46.30	44.56	42.59	38.60	17.41	46.20	41.31	38.27	38.87
Total	100.56	99.95	99.63	100.15	100.22	99.93	100.07	99.62	99.96	100.87	99.88	100.31
HM	0.42	0.64	0.83	0.81	0.57	0.50	0.29	0.08	0.91	0.87	0.88	0.28
FM	0.15	15.63	8.68	15.54	5.96	3.25	1.23	0.26	14.67	2.85	1.08	1.36
AM	0.31	0.24	0.22	0.24	0.19	0.20	0.14	0.04	0.20	0.20	0.26	0.20
TM	0.045	0.054	0.044	0.088	0.086	0.043	0.049	0.055	0.067	0.031	0.045	0.034
FerM	0.30	1.49	2.67	2.10	1.77	1.37	0.97	0.75	3.28	3.21	2.24	0.34
NKM	0.31	0.33	0.25	0.43	0.40	0.46	0.40	0.37	0.37	0.37	0.42	0.38
AlkM	0.20	0.80	0.80	0.80	0.50	0.20	0.40	0.30	0.40	0.10	0.20	0.10

The difference between terrigenous-carbonate rocks (*clusters VII* and *VIII*) and clay rocks is interesting (I). They do not form a single row: carbonates contain silty or sandy impurities (low AM), and not clay. Note that this circumstance is very typical for ancient carbonate rocks, for example, for the Middle Riphean (?) Shchekurya and Upper Riphean Moroya formations in the Subpolar Urals [75, 95]. Abnormal NKM values, as in *an. 5* (average of 73 analyzes of the Urenga formation) may also be the result of analytical error (?!) since alumina contents is very low. But one cannot exclude the presence of some exotic alkali forms, for example, carbonatic.

But perhaps the most notable feature of Fig. 34 is that almost all average compositions of lithotypes defined by L.P. Urasina et al. [258, p. 104–105] by traditional lithological methods, correspond to individual chemotypes, that is, they are perfectly individualized on the NKM–AM module diagram. Only the compositions of the "silicate-carbonate rocks" of the Satkin deposit (*point 15*, n = 14) and "dolomite limestones" (*point 11*, n = 38) were indistinguishable here.

Table 38 and in Fig. 35 processed 18 analyzes of Cenozoic and Carboniferous palygorskite clays, given by O.S. Lomova [160]. Most of the compositions are characterized by high magnesium content (MgO = 3.5–

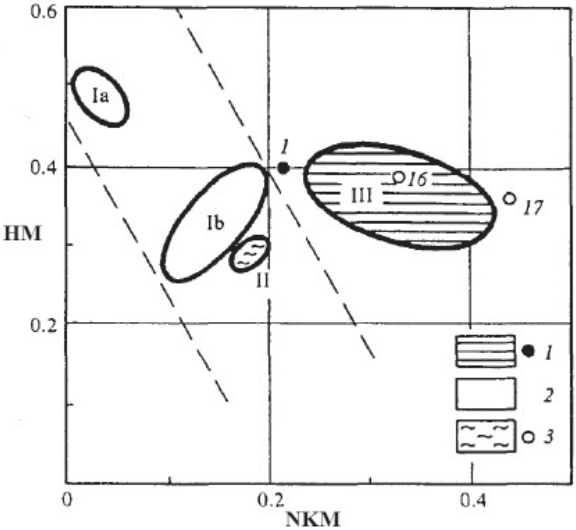

Fig. 35. Module diagram for palygorskite clays of two genotypes.
Compiled according to the O.S. Lomova's data, 1979 [160, p. 54–107].
1 – Eocene pelagic clays of the East Atlantic (camouflaged volcanogenic sedimentary type), 2 – Miocene clays of the Cherkassk deposit in Ukraine (the same type), 3 – Middle and Upper Carboniferous carbonate clays of the Moscow region (chemogenic-evaporite type)

12.1 %) and are classified as pseudosiallites and pseudosilites. If we neglect the markedly increased titanium value of two samples, then the Tertiary palygorskite clays form two rather distinct groups: the Eocene pelagic clays of the East Atlantic (*cluster III*) and the Miocene clays of the Cherkassy deposit in Ukraine (*Ia, b*). Compositional points of carbonic clays in the Moscow region are very close to cluster *Ib*, forming a small *cluster II*. In this

Table 38

Chemical composition of palygorskite clays of two genotypes.
Compiled according to O.S. Lomova, 1979 [160, p. 54–107]

Oxides and modules	Ia	Ib	II	III	1	16	17
	Clay		Carbonate clays	Pelagic clays	Pelagic clay	Carbonate clays	
	Super-siallite	Pseudo-siallite	(pseudosilit)	(pseudosiallite)		Alkaline pseudosiallite	Carbona-tolite
n	2	5	2	6			
SiO_2	51.95	55.79	49.11	52.49	51.98	53.63	12.05
TIO_2	0.85	0.44	0.50	0.63	0.08	0.62	0.09
Al_2O_3	18.42	11.01	11.15	11.56	13.26	15.30	1.73
Fe_2O_3	6.35	6.13	2.92	6.43	7.65	4.99	2.58
FeO	0.05	0.14	0.20	0.25	0.20	0.34	0.05
MnO	0.03	0.11	0.01	0.04	0.08	0.01	0.02
MgO	2.70	5.47	10.77	6.35	4.76	4.57	2.42
CaO	1.72	1.24	3.16	1.24	2.08	1.09	43.96
Na_2O	0.28	0.27	0.14	1.81	1.17	0.25	0.30
K_2O	0.35	1.29	1.92	1.99	1.69	4.82	0.46
H_2O^+	7.09	7.56	9.10	8.82	9.86	6.72	2.99
H_2O^-	10.04	10.25	6.70	6.35	6.79	7.33	1.47
CO_2	0.00	0.00	3.60	0.17	0.17	0.00	32.25
P_2O_5	0.08	0.10	0.18	0.71	0.51	0.01	0.07
LOI	0.14	0.17	0.15	0.52	0.05	0.20	0.14
Total	100.01	99.96	100.44	101.90	100.32	100.47	100.58
HM	0.49	0.32	0.30	0.36	0.41	0.40	0.37
FM	0.18	0.21	0.28	0.25	0.24	0.18	0.42
AM	0.35	0.20	0.23	0.22	0.26	0.29	0.14
TM	0.046	0.040	0.044	0.055	0.006	0.041	0.052
FerM	0.33	0.56	0.27	0.55	0.59	0.34	1.46
NKM	0.03	0.14	0.18	0.33	0.21	0.33	0.44
AlkM	0.80	0.20	0.10	0.90	0.70	0.10	0.70

Note: Cluster II: F = 0.86; cluster III: Cl = 1.19, SO_3 = 1.35, F = 0.59.

case, the compositions of "continental" clays form a band of negative correlation of parameters (with the ejection of anomalous Carboniferous *samples 16* and *17* from it), while oceanic clays are outside this strip. This difference makes it possible to doubt that the tertiary clays, according to O.S. Lomova, belong to the same genetic type ("camouflaged volcanogenic-sedimentary"). Thus, lithochemical analysis prompts one to think: what is the reason for the differences in clays of the same (?) genotype? Why is the seemingly uniform lithotype of Miocene clays so heterogeneous?

An even more complex picture of the relationship "lithotypes-chemotypes" is observed when processing data on silica rocks of the Cretaceous-Paleogene flysch of the Carpathians. Although the lithologist distinguishes here four lithotypes of silicites [10], all clusters defined on the TM–FerM module diagram turn out to be mixed (combining different lithotypes), and only by chance there are four of them too (Fig. 36, Table 39). This means that the lithological information is not detailed enough here and requires clarification.

Cluster I is formed by clay silicites, silica, radiolarites, opoka-like silicites. These are hypotitanic and normal rocks. *Cluster II* includes phtanites, clay phtanites, and silica. These rocks are more ferruginous and hypertitanium. *Cluster III* is formed by phtanites and silicas with maximum titanium and iron content. *Cluster IV* includes phtanites, silica, radiolarites.

If one is guided by the siallite standard, then two geochemical features of the Carpathian silicites can be noted: a) increased iron content (many

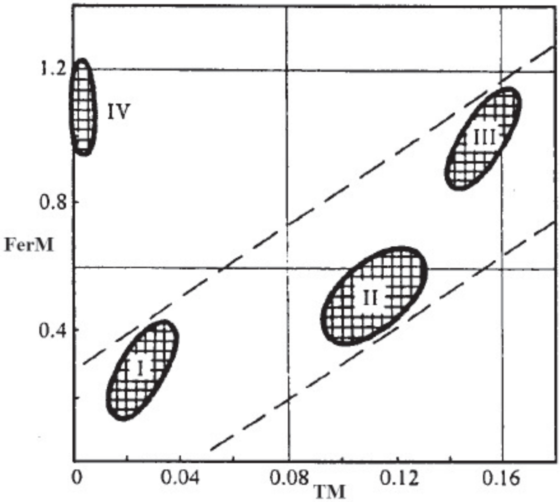

Fig. 36. Module diagram for silica rocks of the Paleogene flysch of the northern slope of the Ukrainian Carpathians.
Compiled according to I.M. Afanasyeva, 1983 [10, p. 144–146]

compositions of super- and hyperferrous, and in eight analyzes out of 20 the FerM value is > 1); b) increased titanium value (half of the compositions are super- and hypertitanium, and in 3 analyzes out of 20 the TM value is > 0.100. At the same time, the titanium and iron values can be very poor; for example, phtanites contain only 0.01–0.08% TiO_2. Both features associated with the presence of pyrogenic impurities.

In fig. 37, 38, the values of lithochemical modules are compared with an important lithological characteristic of silica rocks – the content of free

Table 39

Average chemical silica rocks composition of the Paleogene flysch of the northern slope of the Ukrainian Carpathians.
Compiled according to I.M. Afanasyeva, 1983 [10, p. 144–146]

Oxides and modules	I	II	III	IV
	Normosilite	Hypersilite		
SiO_2	79.93	89.06	93.41	93.33
TIO_2	0.18	0.32	0.18	0.00
Al_2O_3	6.30	2.84	1.18	0.98
Fe_2O_3	1.52	0.84	0.55	0.56
FeO	0.76	0.81	0.72	0.51
MnO	0.03	0.06	0.04	0.04
MgO	1.56	0.75	0.49	0.48
CaO	3.10	1.12	0.47	0.69
Na_2O	0.37	0.27	0.20	0.20
K_2O	0.97	0.52	0.37	0.12
H_2O	5.11	1.47	1.18	1.84
P_2O_5	0.00	0.09	0.03	0.02
CO_2	0.62	1.03	0.60	1.15
S	0.13	0.17	0.11	0.25
SO_3	0.04	0.01	0.11	0.05
C_{org}	0.12	0.45	0.48	0.49
Total	100.74	99.81	100.07	100.69
SiO_{2free}	70.48	84.79	91.64	91.85
HM	0.11	0.05	0.03	0.02
FM	0.05	0.03	0.02	0.02
AM	0.08	0.03	0.01	0.01
TM	0.028	0.113	0.149	0.000
FerM	0.36	0.54	0.96	1.12
NKM	0.21	0.28	0.48	0.32
AlkM	0.40	0.50	0.50	1.70

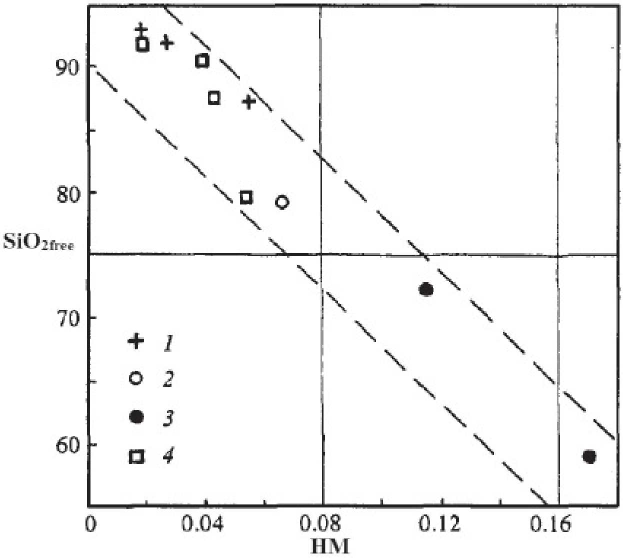

Fig. 37. SiO_{2free} content and HM ratio in silica rocks of the southern slope of the Ukrainian Carpathians. *Compiled according to I. M. Afanasyeva, 1983 [10, p. 144–146].* 1 – phtanites, 2 – clay phtanites and radiolarites, 3 – highly clay phtanites, 4 – sandstones

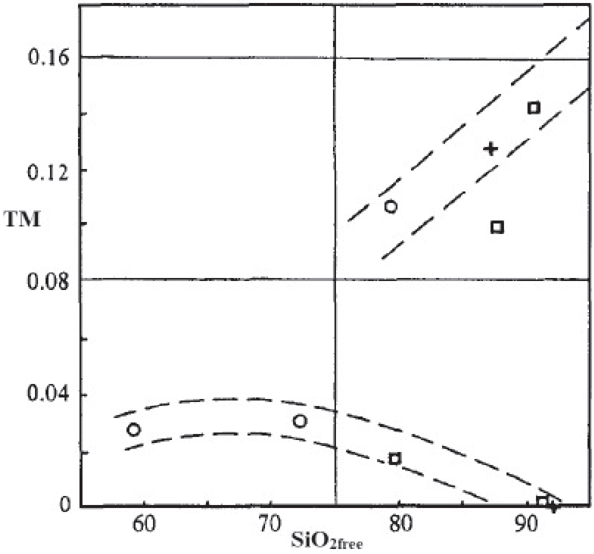

Fig. 38. SiO_{2free} content and TM ratio in silica rocks of the southern slope of the Ukrainian Carpathians. See the legend in Fig. 37

silicic acid (SiO_{2free}). This value is used in the lithological silica rocks systematics as an additional classification parameter. If SiO_{2free} values correlate very closely with the modules' values, then there is obviously no need to use the latter (in the presence of phase analysis). As can be seen from Fig. 37, only for the graph with HM there is a clear negative correlation, because the HM value in silicites is determined mainly by the denominator (SiO_2). However, this graph also shows that different lithotypes (for example, "clay phtanites" and "silicas") can have very similar SiO_{2free} contents. As for the NKM, FerM, and TM modules (Fig. 38), they do not correlate at all with SiO_{2free} value. This means that this indicator cannot replace modules.

The difference between silicites with different titanium content is very curious. In normatitanium silicites, the TM value is almost unrelated to SiO_{2free}, and in hypertitanium silicites ($TM > 0.100$), as SiO_{2free} grows, the titanium content increases. This group is represented by phtanites and clay phtanites.

Interestingly, the study of another statistical sample, along the southern slope of the Ukrainian Carpathians, including Cretaceous silicites [11], revealed a clear nonlinearity of the HM dependence on the SiO_{2free} value. It turns out that for three lithotypes (phtanites, clay phtanites, and highly clay phtanites), the slope of the HM regression line on SiO_{2free} is different. This means that the statistical combination of these rocks seemingly forming a single genetic series, would be questionable.

An even more complex picture is given by typical "geosynclinal" silicites (jasper and jasperoids), in which a pyrogenic (usually exhalative) admixture is very noticeable.

In the Northern Mugodzhary, the Devonian silica-dolerite Kurkuduk sedimentary-volcanogenic complex 300–500 m thick is developed, which is interpreted as paleooceanic. The share of sedimentary rocks – red-colored silicites – here accounts for 30–35 % of the complex volume [108]. To characterize the silica rocks of the set and compare them with the silica sediments of the Pacific Ocean, E.V. Zaikova plotted points of *average compositions* (*n* from 2 to 13) on the diagram in the coordinates "(Fe + Mn)/Ti – Σ Fe, %". Despite the chaotic arrangement of points on the graph, she defined rocks of three material-genetic types: sedimentary (I), hydrothermal-sedimentary (II) and intermediate, *"with a significant admixture of hydrothermal material"* (III).

The (Fe + Mn)/Ti module is a well-known FerMT module proposed by N.M. Strakhov to distinguish between substantially terrigenous (FerMT usually < 20) from substantially hydrothermal (FerMT usually > 25) sediments. This module has two obvious disadvantages. First, there is no aluminum in it – a component no less terrigenous than titanium. Secondly, titanium is not such a clear indicator of "terrigenousness", because high-Ti basaltic pyroclastics are often present in oceanic sediments. These reasons greatly narrow the scope of the use of FerMT for diagnostic purposes. However, E.V. Zaikova rightly noted that "*hydrothermal-sedimentary rocks differ from sedimentary ones also by a low content of aluminum oxide and, accordingly, a high value of the* SiO_2/Al_2O_3 *ratio... which indicates an insignificant admixture of silicate material in them*" [108, p. 1208].

To consider both diagnostic parameters (iron content and alumina content), we plotted E.V. Zaikova's data on the FerM–AM graph. On such a graph, one can expect that in the series of sediments from substantially terrigenous (aluminosilicate) to substantially hydrothermal (manganese-ferruginous), a negative correlation of parameters should be observed. As a result of data processing (note that 11 out of 12 analyzes are the *average* of 3–13), the picture is shown in Fig. 39 and tab. 40.

Clusters I and *II* and compositions *3, 4, 7–9* represent Devonian silicites of the Northern Mugodzhary, while *cluster III* and compositions *12, 13* are sediments of the Pacific Ocean. Devonian silicites are sharply differentiated in terms of FerM: "ferruginous-silica rocks" of *cluster II* have an FerM about 36, while "jasper and silicites" of *cluster I* have only about three. Part of the Pacific sediments (more clay) entered cluster III, while the Neogene silica sediments of the near-Californian part of the Pacific Ocean (*an. 12, 13*) differ from them not only in poor alumina contents, but

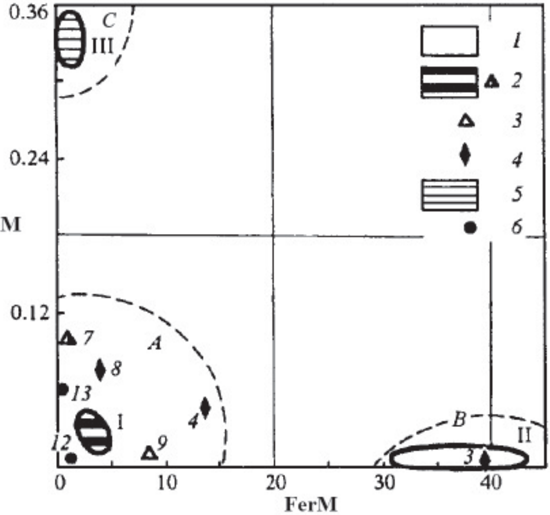

Fig. 39. Module diagram for silica rocks of the Kurkuduk set, the Northern Mugodzhary and Pacific sediments.

Compiled according to the E.V. Zaikova's data, 1985 [108, p. 1207].

1–3 – Kurkuduk complex, rocks: ferruginous-silica (1), jasper and silicites (2), clay-silica (3), silica-ferruginous (4); 5 – sediments of the Pacific Ocean: clay-silica (5) and silica (6)

Table 40

Chemical composition of various silica rocks' types, Kurkuduk set, Mugodzhary.
Compiled according to the E.V. Zaikova's data, 1985 [108, p. 1207]

Oxides and modules	Ia	Ib	II	3	4	7	8	9	12	13
	Ferruginous-siliceous rocks	Jaspers and silicites	Clay-silica sediments of the Pacific Ocean (Mn hypohydrolysate)	Silica-iron rocks		Silicites, argillites, siltstones (myosilite)	Iron-silica rocks (siferlite)	Jasper with hydrothermal material (normosilite)	Silica rocks of the Pacific Ocean (hypersilite)	Layered silicites of the Pacific Ocean (normosilite)
	Normosilite			Myosilite	Hypohydrolisate					
m	16	10	4	13	9	6	7	5	4	6
n	2	2	2							
SiO_2	88.38	84.05	46.97	79.41	50.63	71.15	62.58	85.83	91.77	79.81
TIO_2	0.01	0.12	0.86	0.01	0.16	0.44	0.31	0.09	0.16	0.29
Al_2O_3	0.25	2.38	15.87	0.43	2.62	7.46	4.97	0.89	1.07	5.30
Fe_2O_3	6.39	4.66	12.43	13.72	36.10	6.30	20.35	5.56	1.60	2.56
FeO	2.76	2.97	0.36	3.53	2.10	2.47	1.53	2.77	0.27	0.64
MnO	0.06	0.12	1.83	0.09	0.20	0.28	0.16	0.09	0.01	0.19
MgO	0.12	1.29	2.82	0.16	0.70	2.88	1.16	0.56	0.43	1.37
CaO	0.91	1.54	2.47	1.32	3.47	1.37	3.02	1.30	1.03	0.98
Na_2O	0.07	0.28	1.17	0.17	0.11	1.12	0.45	0.19	0.39	1.40
K_2O	0.07	0.12	2.54	0.07	0.17	0.38	0.39	0.13	0.24	1.15
P_2O_5	0.06	0.15	0.17	0.07	0.31	0.40	0.44	0.26	0.07	0.19
LOI	0.82	2.12	12.73	1.01	3.25	5.47	4.48	2.00	2.98	6.16
Total	99.86	99.76	100.19	99.99	99.82	99.72	99.84	99.67	100.02	100.04
HM	0.11	0.12	0.67	0.22	0.81	0.24	0.44	0.11	0.03	0.11
FM	0.10	0.11	0.33	0.22	0.77	0.16	0.37	0.10	0.03	0.06
AM	0.00	0.03	0.34	0.01	0.05	0.10	0.08	0.01	0.01	0.07
TM	0.026	0.051	0.054	0.023	0.061	0.059	0.062	0.101	0.0150	0.055
FerM	35.87	3.10	0.87	39.41	13.81	1.15	4.17	8.59	1.52	0.61
NKM	0.52	0.16	0.23	0.56	0.11	0.20	0.17	0.36	0.59	0.48
AlkM	1.00	2.40	0.50	2.40	0.60	2.90	1.20	1.50	1.60	1.20

Note. Here and below, *m* is the number of preliminary averaged analyzes.

also in higher alkalinity (NKM 0.48–0.59 versus 0.23) and sodium content (AlkM 1.2–1.6 versus 0.46), which is typical for hydrothermal essentially silica formations.

As one can see, the expected linear negative correlation is not observed. The real picture is more complicated, which allows to select three fields on the FerM–AM graph.

Field A: rocks with relatively low iron (FerM < 15) and low alumina (AM < 0.12). Although the number of chemotypes in field A is not less than that of lithotypes (hypersilites, normosilites, myosilites, syferlites, hypohydrolysates), they correlate poorly with lithotypes.

This includes compositions of Devonian “ferruginous-silica” (*cluster I* and *an. 3*), “silica-ferruginous” (*an. 4, 8*) and “clay-silica” (*an. 3*) rocks, “silicilites, argillites, siltstones" (*an. 7*), as well as the Neogene "layered silicitolites" of the Pacific Ocean. Despite such a variety of lithotypes, one should recognize that the figurative points within the rather extensive field A are located chaotically.

Field B: rocks with high iron and low alumina. It is represented only by Devonian “jaspers and silicites” (*cluster II*) and “silica-ferruginous rocks” (*an. 3*), containing about 17% Fe_2O_3 + FeO.

Field C: rocks with low iron content and relatively aluminous. It is represented (*cluster III*) only by deep sea sediments of the western part of the Pacific Ocean – clay and clay-silica. In contrast to silica-normosilites, these sediments are classified as manganese hypohydrolysates. They are distinguished by a high HM value (due to the summation of both alumina and iron noticeable contents) and an increased MnO content – on average 1.83 %.

Thus, the processing of E.V. Zaikova’s data using the FerM–AM module diagram showed that part of the Ural Devonian silicites and part of the deep-sea sediments of the Pacific Ocean are clearly individualized in chemical composition (fields *B* and *C*), while part of the Ural and Pacific silicites turns out to be within the same field *A* (mixture of lithotypes), which may indicate the genetic unity of these rocks.

5.3. Incomplete coincidence of chemotypes with lithotypes

In the above examples, the lithotypes either basically coincided with the independently isolated chemotypes, or the coincidence was incomplete, with certain complications. Almost all such cases allow obtaining non-trivial information about lithotypes, which we will consider.

Even in situations where chemotypes turn out to be a *mixture of lithotypes*, it is sometimes possible to obtain a genetic interpretation. A very typical example is the Miocene–Early Pliocene continental red-colored rocks, the belt of which stretches for thousands kilometers in Asia from the foothills of the Himalayas to the Urals and then goes to southern Europe up to Greece. These are mainly proluvial deposits, less often alluvial-lacustrine. The presence of a significant carbonate amount in terrigenous rocks is characteristic – in the form of calcite phytomorphoses (loess dolls), calcite and dolomite microconcretions. Silica particles of aleuropelite dimension are surrounded by films of iron oxides. The clay substance is mainly montmorillonite-hydromica; the admixtures of kaolinite and chlorite are usually allotygenic. This "*red-colored carbonate association",* as V. S. Erofeev and Yu. G. Tsekhovsky write, is "*an example of a lithogenetic process, colossal in terms of the extent of its territory coverage, formed according to a certain type*" [104, p. 8].

Table 41 processed 20 analyzes of red-coloured rocks. Due to the presence of montmorillonite and dolomite, almost half of the compositions are classified as magnesian (pseudosiallites) and carbonate (CaO 6–16 %)[2]. The picture on the module diagram (Fig. 40) reveals a very characteristic feature – weak chemical differentiation of lithotypes. First, the compositions of sandy (*cluster I*) and clay rocks (*IIb*) are closely located (and even overlap). Secondly, 13 out of 20 compositions form mixed clusters: sandstones + argillites (*cluster IIa*), siltstones + crushed stones (*III*). The randomness of

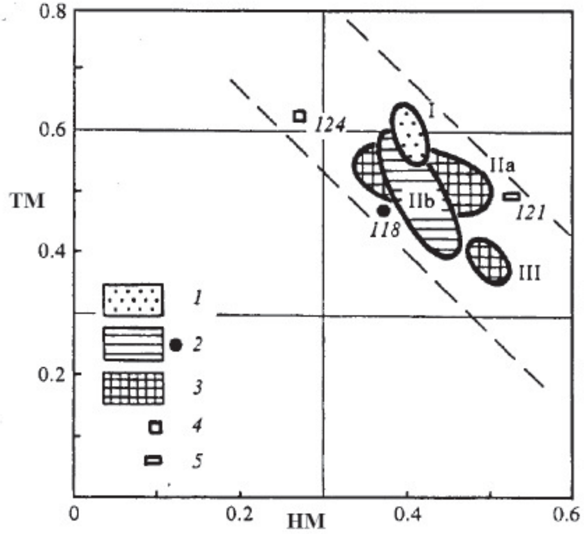

Fig. 40. Module diagram for the "red-colored carbonatic association".
Compiled according to the data of V. S. Erofeev, Yu. G. Tsekhovsky, 1983 [104, p. 187, 188].
1 – sands and sandstones, 2 – clays and argillites, 3 – a mixture of lithotypes, 4 – silts and siltstones, 5 – marls

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[2] In the CO_2 absence in the analyzes, such certification has to be given for CaO, which, in the case of gypsum presence, may turn out to be erroneous.

Table 41

Chemical composition of the "red-colored carbonatic association".

Compiled according to the V S. Erofeev, and Yu. G. Tsekhovsky's data, 1983 [104, p. 187, 188]

Oxides and modules	I	IIa	IIb	III	118	121	124
	Sands and sandstones (carbonate pseudosiallite)	Clays and sandstones (normosiallite)	Clays and argillites (pseudosiallite)	Siltstones and crushed stone (supersiallite)	Clays and argillites (carbonate normosiallite)	Clay marl (pseudosiallite)	Aleurolites and siltstones (myosilite)
n	2	7	6	2			
SiO_2	45.91	57.57	49.98	54.12	43.91	37.10	68.31
TIO_2	0.73	0.86	0.72	0.69	0.52	0.60	0.77
Al_2O_3	12.42	16.49	14.31	17.55	10.92	12.05	12.35
Fe_2O_3	4.74	6.42	5.41	8.18	4.19	6.74	4.34
FeO	0.63	0.89	0.73	1.29	0.65	-	0.91
MnO	0.10	0.12	0.10	0.09	0.08	0.08	0.07
MgO	3.46	2.52	3.23	1.61	2.87	3.02	1.72
CaO	10.58	1.88	7.08	3.46	11.47	16.25	1.61
Na_2O	1.46	1.68	1.44	1.80	1.45	0.11	1.72
K_2O	2.17	2.46	2.84	1.40	2.42	2.12	2.02
P_2O_5	0.13	0.12	0.17	0.11	0.14	0.20	0.15
LOI	16.90	8.75	13.72	9.94	21.08	22.20	6.37
Total	99.20	99.76	99.73	100.22	99.70	100.47	100.34
HM	0.41	0.43	0.43	0.51	0.37	0.52	0.27
FM	0.19	0.17	0.19	0.20	0.18	0.26	0.10
AM	0.27	0.29	0.29	0.32	0.25	0.32	0.18
TM	0.058	0.052	0.050	0.039	0.048	0.050	0.062
FerM	0.42	0.43	0.42	0.52	0.43	0.54	0.41
NKM	0.29	0.25	0.30	0.18	0.35	0.19	0.30
AlkM	0.70	0.70	0.50	1.30	0.60	0.10	0.90

the graph is intensified by the presence of carbonate compositions (*samples 121, 118*), which are not subject to averaging. And only one siltstone (*sample 124*, Zaisan trough) exhibits an increased TM – a probable sign of dynamic sorting of the material (alluvium?).

So, the weak "resolution" of lithotypes on the module diagrams is explained by the weak differentiation of clastic material in arid lithogenesis. Consequently, this feature can be used for diagnostic purposes when there is a lack of full lithological information (for example, in the lithochemistry of metamorphites).

A similar picture of poor resolution of lithotypes on module diagrams is characteristic of flysch and flyschoid strata of folded areas. Table 42 and Fig. 41 processed fourteen analyzes corresponding to four lithotypes of the Upper Paleozoic – Lower Mesozoic terrigenous strata of Sakhalin – argillites, siltstones, sandstones, and silicified sandstones [193]. It turns out that lithotypes are poorly discriminated against. Only *cluster III* is “clean”, corresponding to silicified sandstones, but the other three are mixed. One can’t achieve a complete separation of lithotypes with the help of other module diagrams – everywhere the points of argillites are near the points of siltstones

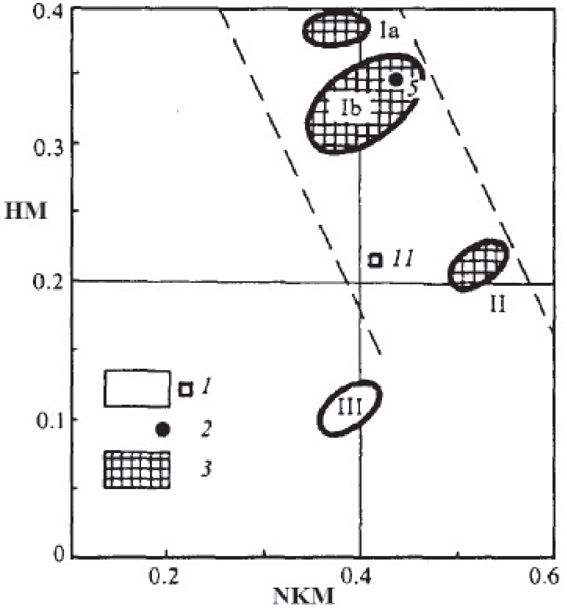

Fig. 41. Module diagram for Sakhalin terrigenous rocks.
Compiled according to N.G. Brodskaya et al., 1979 [193, p. 111–113].
1 – silicified sandstones, 2 – argillites, 3 – mixture of lithotypes

Table 42

Chemical composition of lithotypes from geosynclinal deposits of Sakhalin. *Compiled according to N.G. Brodskaya et al., 1979 [193, p. 111–113]*

Oxides and modules	Ia	Ib	II	III	5	11
	Argillite and siltstone	Argillites	Sandstones (alkaline myosilite)	Silicified sandstones (normosilite)	Argillite (alkaline normosiallite)	Silicified sandstones (myosilite)
	Alkaline normosiallite					
n	2	6	2	2		
SiO_2	61.21	64.74	73.45	83.79	62.43	66.26
TIO_2	0.82	0.73	0.44	0.34	0.81	0.48
Al_2O_3	17.39	14.94	13.12	6.51	17.82	10.13
Fe_2O_3	1.89	2.67	1.91	1.04	2.20	1.11
FeO	3.73	3.40	0.74	1.50	1.20	2.83
MnO	0.07	0.16	0.04	0.08	0.04	0.09
MgO	2.07	1.86	0.49	0.49	1.49	1.09
CaO	1.41	1.75	1.16	1.54	0.99	6.98
Na_2O	3.25	3.14	4.42	1.07	2.30	2.57
K_2O	3.25	2.76	2.42	1.46	5.53	1.65
P_2O_5	0.17	0.10	0.06	0.09	0.19	0.05
CO_2	0.03	0.08	0.00	0.84	0.00	4.70
C_{org}	0.25	0.25	0.05	0.00	0.63	0.08
H_2O	3.73	3.30	2.06	1.39	4.31	2.25
Total	99.22	99.88	100.34	100.11	99.94	100.27
HM	0.39	0.34	0.22	0.11	0.35	0.22
FM	0.13	0.12	0.04	0.04	0.08	0.08
AM	0.28	0.23	0.18	0.08	0.29	0.15
TM	0.047	0.049	0.034	0.052	0.045	0.0147
FerM	0.31	0.40	0.20	0.38	0.18	0.38
NKM	0.37	0.39	0.52	0.39	0.44	0.42
AlkM	1.00	1.10	1.80	0.70	0.40	1.60

and sandstones. Such a picture can be considered typical for shale-greywacke geosynclinal strata – with their inherent low maturity of clastic material, its poor granulometric sorting and an admixture of volcanic clastic – both terrigenous (erosion of nearby volcanic edifices) and pyrogenic.

Sometimes the picture of a lithotypes mixture is additionally complicated by a wide scatter of points on the module diagrams, which always contains information about some unaccounted dispersion factors; if such factors can be defined, then the very fact of scatter acquires heuristic (genetic) significance.

Table 43 and Fig. 42 processed 19 analyzes of rocks " carbonaceous-siderite-pyrite association" developed in the Paleogene of NW Asia. Of these, 16 belong to the Zaisan trough and 3 – to the Chuya depression of Gorny Altai [104, p. 181–182]. According to the lithological description, the deposits are represented by three lithotypes: clay, silty and sandy. However, in the HM–TM module diagram, only one *cluster Ib* exactly corresponds to the lithotype – in this case, silt. The remaining four clusters are mixed: sandstones + siltstones (la), siltstones + argillites (*III, IV*) and even sandstones + + clays (*II*).

Thus, the lithochemical information appears to be depleted in comparison with the lithological information; however, this impression is misleading. In fact, lithochemical data provide the lithologist with non-trivial information.

First, important differences are found among the similarly-named lithotypes – these are composition points outside the clusters. Thus, among the siltstones, we see varieties with obvious siderite (FeO – sample 60), with calcite (CaO – sample 65), and with anomalously low TM (sample 66), and among the clays we find a hypertitanium-hydrolytic composition (sample 52), apparently enriched in kaolinite. Second, cluster IV with anomalously low TM (TM of only 0.002) and with a geochemical

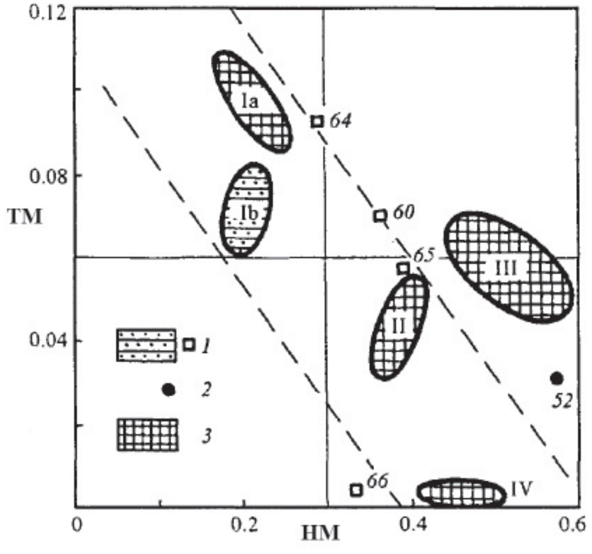

Fig. 42. Module diagram for the Paleogene carbonaceous-siderite-pyrite association in NW Asia. *Compiled according to V.S. Erofeev, Yu. G. Tsekhovsky, 1983 [104, pp. 181–182].*

1 – silts and siltstones, 2 – argillites, 3 – mixture of lithotypes

Table 43

Rocks chemical composition of the Paleogene carbonaceous-siderite-pyrite association in NW Asia.

Compiled according to V.S. Erofeev and Yu. G. Tsekhovsky, 1983 [104, p. 181–182]

Oxides and modules	Ia	Ib	II	III	IV	52	60	64	65	66
	Siltstones and sandstones	Siltstones and aleurites	Clays and sandstones (normosiallite)	Clays and siltstones		Clays and argillites (hypohydrolisate)	Aleurites and siltstones			
	Myosilite			Supersiallite	Normosiallite		Normosiallite	Myosilite	Normosiallite	
n	2	3	2	6	2					
SiO_2	75.44	73.71	63.88	54.07	56.42	50.96	64.58	68.84	57.16	66.08
TIO_2	1.05	1.03	0.85	1.09	0.04	0.85	1.02	1.32	0.90	0.07
Al_2O_3	10.83	12.91	19.27	19.47	18.94	26.72	14.50	14.25	15.85	20.02
Fe_2O_3	1.95	2.01	3.07	4.32	4.85	0.62	1.64	2.43	4.30	0.36
FeO	2.43	1.36	1.27	3.22	1.72	1.14	6.59	2.15	1.24	1.72
MnO	0.25	0.02	0.02	0.18	0.11	0.01	0.03	0.04	0.25	0.00
MgO	0.45	0.43	0.24	1.00	1.53	0.49	0.16	0.89	0.00	0.40
CaO	1.14	1.25	1.06	1.37	2.44	1.23	0.78	0.65	7.53	1.38
Na_2O	0.78	0.34	0.00	0.29	0.51	0.00	0.56	0.16	0.00	0.00
K_2O	1.71	1.81	1.02	2.08	1.26	0.85	2.21	1.77	2.01	2.11
P_2O_5	0.04	0.04	0.06	0.07	0.60	0.04	0.05	0.03	0.05	0.08
LOI	3.93	5.13	9.31	12.55	11.57	16.30	7.32	7.20	11.32	7.38
Total	99.97	100.03	100.03	99.70	99.97	99.21	99.44	99.73	100.61	99.60
HM	0.22	0.23	0.38	0.52	0.45	0.58	0.37	0.29	0.39	0.34
FM	0.06	0.05	0.07	0.16	0.14	0.04	0.13	0.08	0.10	0.04
AM	0.14	0.18	0.30	0.36	0.34	0.52	0.22	0.21	0.28	0.30
TM	0.097	0.080	0.044	0.056	0.002	0.032	0.070	0.093	0.057	0.003
FerM	0.39	0.24	0.22	0.38	0.35	0.06	0.53	0.30	0.35	0.10
NKM	0.23	0.17	0.05	0.12	0.09	0.03	0.19	0.04	0.13	0.11
AlkM	0.50	0.20	0.00	0.10	0.40	0.00	0.30	0.10	0.00	0.00

anomaly in phosphorus (P_2O_5 0.60 %) clearly falls out of the broad band of negative correlation of the HM–TM parameters. It turns out that these analyzes characterize the deposits of the Chuya depression. This means that the petrofund of these rocks was somewhat different from the petrofund of the Zaisan depression. Finally, the extremely low TM of one of the Zaisan siltstones (sample 66) and the increased hydrolysability of the other (sample 64), although not directly explained, at least raise questions for the lithologist that require resolution.

A complex relationship between lithotypes and chemotypes is often noted in silica rocks. Above, we have already mentioned cases of their non-coincidence for flysch silicites of the Carpathians and for "geosynclinal" paleo-oceanic silicites; even less correspondence between litho- and chemotypes is observed in platform opal-cristobalite rocks – *opalites*. The discrepancy here is due to two factors: a) the presence in the opalites of a variable in the amount and composition of terrigenous admixture; b) diagenetic silica redistribution, increasing (SiO_2 removal) or decreasing (SiO_2 input – silicification) hydrolysate module HM. An example is the Eocene opalites of Western Siberia [69], among which there are proper opokas and their varieties (clay-silty, sandy and “silicified”), trepel and diatomites (variety – clay). As one can see from the table 44 and fig. 43, the average compositions of these rocks form three clusters. Cluster I is represented only by opokas – sandy and “silicified”. These most silica rocks are classified as supersilites, differing in slightly increased titanium value (TM 0.060–0.067) and relatively high alkalinity (NKM 0.24–0.36). *Cluster II* is the most numerous (242 analyzes) and

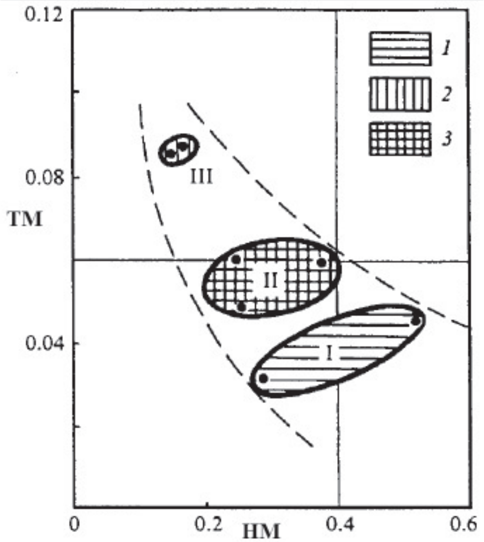

Fig. 43. Module diagram for the Eocene opal-cristobalite rocks of Western Siberia. Each point represents the average of 3–158 analyzes.

Compiled according to P.P. Generalov and N.B. Drozhashikh, 1987 [69, p. 180]

1 – opokas, 2 – clay opokas and diatomites, 3 – a mixture of lithotypes (opokas, trepels, diatomites)

Table 44

Average chemical composition of the Eocene opal-cristobalite rocks of Western Siberia.

Compiled according to P.P. Generalov and N.B. Drozhashikh, 1987 [69, p. 180]

Oxides and modules	I	II	III
	Opokas (supersilite)	Opokas, tripoli, diatomites (normosilite)	Clay opokas, diatomites (myosilite)
m	4	242	64
n	2	3	2
SiO_2	85.95	78.91	73.16
TIO_2	0.38	0.42	0.57
Al_2O_3	5.91	7.98	11.44
Fe_2O_3	1.92	2.62	3.67
FeO	0.36	0.27	0.38
MnO	0.01	0.03	0.04
MgO	0.75	1.19	1.44
CaO	0.39	0.38	0.42
Na_2O	0.62	0.66	0.54
K_2O	1.21	1.32	1.51
SO_3	0.10	0.40	0.36
LOI	2.36	5.76	6.71
Total	99.93	99.94	100.22
HM	0.10	0.14	0.22
FM	0.04	0.05	0.08
AM	0.07	0.10	0.16
TM	0.063	0.052	0.050
FerM	0.36	0.35	0.34
NKM	0.30	0.25	0.18
AlkM	0.50	0.50	0.40

includes all three types of opalites: opokas, tripoli, and diatomites. These are normotitanium normosilitees (HM 0.14, TM 0.052). *Cluster III* includes opalites with a high content of silicate admixtures: clay-silty opokas and clay diatomites. These are already myosilites, also normotitanic, with a relative minimum of alkalinity (NKM 0.18). Thus, minus the opokas with a sandy admixture (*cluster I*), the lithotypes of opalites do not have a clear chemical identity, at least with regard to the bulk composition[3].

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[3] it cannot be ruled out that the differences in lithotypes in the phase composition (opal SiO_{2free} content) will be more significant.

One of the most significant works in lithology in the 1980s was the monograph by Yu. G. Volokhin (student of Prof. V. T. Frolov) on the Triassic-Jurassic silica sediments of the Sikhote-Alin [56]. The author has developed a special classification of silicites and related silica-argillaceous rocks on two grounds: the content of SiO_{2free} (in %) and the presence of authigenic impurities. As a result, 15 lithotypes were defined, and if we restrict ourselves to only the first three groups (silicites + clay silicites) – then 9 lithotypes (Table 45).

Table 45

Classification of silicites and silica argillites.
According to Yu. G. Volokhin, 1985 [56, p. 32]

SiO_{2free}	Impurity of authigenic components		
	Oxides and hydroxides	Sulfides and carbonates	Carbonaceous matter
> 80	Jasper	Flints	Phtanites
50–80	Clay jasper	Clay flints	Clay phtanites
30–50	Jasper argillites	Silica argillites	Carbonaceous silica argillites

Lithochemical treatment of 199 analyzes from Yu. G. Volokhin's book allows to distinguish 12 clusters and 11 individual compositions (Table 46); the latter mainly fall into the contours of clusters on the alkali–HM module diagram (Fig. 44).

Clustering, as usual, was performed in two steps: first, large clusters were defined on the base diagram "alkali–HM", then they are more fractionally divided considering TM, AlkM and some other indicators.

It turned out that within the first three *clusters I–III*, the most titanium varieties (denoted by the subscript "b") with a TM 0.172–0.287 correspond to the most silica rocks with the lowest HM values and, at the same time, with a relatively increased sodium content (AlkM 0.52–0.69 versus 0.11–0.49).

Individual (not subject to averaging) compositions are abnormal in the content of P_2O_5 (*samples 61, 152*), carbonate (*sample 167*), C_{org}, differing in extreme TM and NKM values of (*samples 72, 153, 173*) or especially sodium (*sample 194*).

Comparison of chemotypes in clusters with lithotypes gives the results shown in table 47.

Only one chemotype (alkaline myosilite), represented by the minimal *VIb cluster*, fully corresponds to the lithotype. All other chemotypes correspond to a mixture of lithotypes.

Some of them are with a sharp predominance of one lithotype (*Ia, c* – essentially silica, *VIa* – significantly represented by jasper argillites), while others in comparable proportions are represented by a mixture of two (*IIb, Ib, V*), but more often

Table 46

Chemical composition of Triassic-Jurassic silicites and silica argillites of the Sikhote-Alin geosynclinal region.
Compiled according to Yu. G. Volokhin, 1985 [56, p. 165–172]

Oxides and modules	Ia	Ib	Ic	IIa	IIb	IIc	IIIa	IIIb	IV	V	Via	VIb
	Flints				Jaspers	Clay phtanites		Clay jaspers	Clay flints	Clay phnanites	Silica argillites	
	Hypersilite		Supersilite				Normosilite	Supersilite	Normosilite	Myosilite		Alkaline myosilite
n	57	18	18	15	6	7	26	6	16	7	10	2
SiO_2	94.95	95.10	91.74	90.81	91.40	84.29	82.86	85.98	78.54	74.64	72.29	70.40
TIO_2	0.10	0.18	0.16	0.20	0.34	0.30	0.35	0.57	0.42	0.55	0.53	0.35
Al_2O_3	1.34	0.63	2.46	3.44	1.52	5.22	6.70	3.29	9.87	11.33	12.95	13.82
Fe_2O_3	0.54	0.55	0.72	0.89	2.13	1.60	1.08	2.83	1.62	3.18	1.86	1.91
FeO	1.20	1.28	1.77	1.63	1.77	1.63	1.08	1.11	1.23	0.63	2.68	0.79
MnO	0.04	0.05	0.06	0.05	0.07	0.04	0.04	0.09	0.08	0.05	0.09	0.15
MgO	0.30	0.26	0.46	0.57	0.12	0.89	0.89	0.90	1.03	0.89	1.48	0.73
CaO	0.25	0.40	0.32	0.51	1.05	1.51	0.22	1.50	0.46	0.17	0.46	1.89
Na_2O	0.12	0.15	0.32	0.19	0.13	0.15	0.19	0.73	0.97	0.36	1.61	4.80
K_2O	0.36	0.24	0.65	0.44	0.25	0.36	1.78	1.06	2.35	2.59	2.92	2.48
P_2O_5	0.10	0.09	0.15	0.22	0.24	0.32	0.14	0.11	0.20	0.39	0.14	0.15
LOI	0.59	0.85	1.11	0.99	0.80	3.49	4.75	1.77	3.08	5.16	2.86	2.27
Total	99.89	99.79	99.91	99.93	99.82	99.80	100.06	99.92	99.85	99.92	99.87	99.72
C_{org}	0.16	0.06	0.48	0.33	0.06	0.93	1.68	0.05	0.14	1.31	0.10	0.04
HM	0.03	0.03	0.06	0.07	0.06	0.10	0.11	0.09	0.17	0.21	0.25	0.24
FM	0.02	0.02	0.03	0.03	0.04	0.05	0.04	0.06	0.05	0.06	0.08	0.05
AM	0.01	0.01	0.03	0.04	0.02	0.06	0.08	0.04	0.13	0.15	0.18	0.20
TM	0.071	0.287	0.063	0.057	0.222	0.058	0.052	0.172	0.043	0.048	0.041	0.025
FerM	1.24	2.30	0.97	0.70	2.13	0.59	0.31	1.04	0.28	0.32	0.34	0.20
NKM	0.35	0.62	0.40	0.18	0.25	0.10	0.29	0.54	0.34	0.26	0.35	0.53
AlkM	0.30	0.6	0.50	0.40	0.50	0.40	0.10	0.70	0.40	0.10	0.60	1.90

Table 46 (continuation)

Oxides and modules	61	63	72	152	153	155	167	173	176	185	194
	Clay phtanite		Flint (hypersilite)	Clay flint (normosilite)	Flint		Jasper			Clay flint (normosilite)	Clay jasper (myosilite)
	Normosilite	Carbonaceous supersilite			Hypersilite				Supersilite		
SiO_2	81.80	83.15	94.40	85.00	95.80	91.20	77.00	96.20	91.00	77.47	74.37
TIO_2	0.34	0.28	0.06	0.13	0.05	0.36	0.24	0.08	0.28	1.14	1.57
Al_2O_3	7.32	3.25	0.07	8.50	0.01	1.62	1.06	0.07	1.48	6.01	8.15
Fe_2O_3	0.06	1.03	0.56	0.01	0.05	0.96	0.51	0.56	1.88	1.52	7.22
FeO	1.03	0.49	1.70	2.83	2.50	1.86	1.75	0.78	1.31	4.12	0.97
MnO	0.01	0.08	0.06	0.24	0.01	0.08	0.18	0.05	0.10	0.04	0.15
MgO	0.89	0.32	0.60	1.77	0.01	0.01	0.45	0.01	0.27	2.52	1.50
CaO	0.01	0.01	0.15	0.34	0.68	2.00	10.04	0.28	0.43	2.90	1.55
Na_2O	0.07	0.07	0.20	0.46	0.30	0.20	0.22	0.13	0.47	1.33	2.58
K_2O	3.67	1.10	0.26	0.39	0.19	0.64	0.28	0.42	0.83	0.58	0.19
P_2O_5	0.78	0.13	0.39	0.41	0.24	0.20	0.28	0.06	0.05	0.19	0.18
LOI	3.93	9.50	2.15	0.01	0.06	0.89	8.25	1.10	1.40	1.80	1.60
Total	99.91	99.41	100.60	100.09	99.90	100.02	100.26	99.74	99.50	99.62	100.03
C_{org}	1.70	6.35	0.07	0.08	0.15	0.07	0.02	0.04	0.04	0.07	0.05
HM	0.11	0.06	0.03	0.14	0.03	0.05	0.05	0.02	0.06	0.17	0.24
FM	0.02	0.02	0.03	0.05	0.03	0.03	0.04	0.01	0.04	0.11	0.13
AM	0.09	0.04	0.00	0.10	0.00	0.02	0.01	0.00	0.02	0.08	0.11
TM	0.046	0.086	0.857	0.015	5.000	0.222	0.226	1.143	0.189	0.190	0.193
FerM	0.14	0.45	17.85	0.36	42.67	1.46	1.88	9.27	1.87	0.79	0.86
NKM	0.51	0.36	6.57	0.10	49.00	0.52	0.47	7.86	0.88	0.32	0.34
AlkM	0.00	0.10	0.80	1.20	1.60	0.30	0.80	0.30	0.60	2.30	13.60

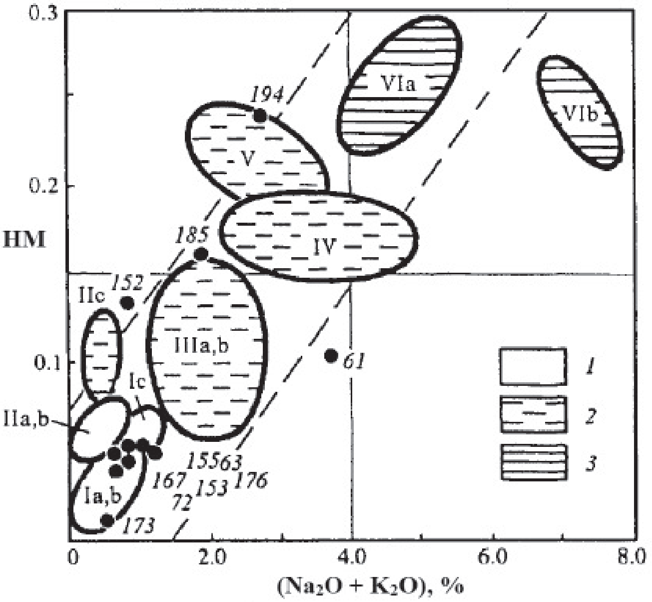

Fig. 44. Module diagram for Triassic-Jurassic silicites and silica argillites of the Sikhote-Alin geosynclinal area.
Compiled according to Yu. G. Volokhin, 1985 [56, p. 165–172].
1 – flint and jaspers, 2 – clay silicites (phtanites, jaspers and flint), 3 – silica argillites

Table 47

Percentage of lithotypes in clusters

Lithotype	Ia	Ib	Ic	IIa	IIb	IIc	IIIa	IIIb	IV	V	Via	VIb
Jaspers	12	22	11	67	67	14		33				
Flints	83	78	83	33	33							
Phtanites	5		6									
Clay jaspers							4	33	19		10	
Clay flints						43	34	33	75	43	10	
Clay phtanites						43	46		6	57		
Jasper argillites											80	
Silica argillites												100

three lithotypes. For example, the cluster *IIb* (supersilites) is represented in equal proportions by proper jaspers, clay jaspers, and clay silica. It is very interesting that phtanites in this clustering are nowhere distinguished as an independent (or at least predominant) lithotype.

As can be seen from Fig. 44, the *IIc* and *V clusters* clearly fall out of the band of parameters positive correlation, and the alkaline myosilites of the *VIb cluster* undoubtedly represent a different set, being distinguished not only by the total alkalinity, but also by the supersodium content (AlkM = 1.93). These rocks most likely contain an admixture of feldspar pyroclastics.

So, a comparison of the silica rocks lithotypes with chemotypes allows us to draw a number of conclusions.

1. Among silicites, the most chemically individualized lithotypes are "silica" and, to a lesser extent, "jasper". Phtanites are not distinguished in the chemotype rank; this means that the C_{org} content does not correlate with either the silica value or the total alkalinity of silicites.
2. Among clay silicites, only a part of "clay silica" is chemically relatively individualized (*cluster IV*).
3. There is a sharp differentiation within the same lithotypes (and corresponding chemotypes) by TM; the most titanium and at the same time relatively more sodium are the most silicious varieties of silicites.
4. The studied silica strata form at least two aggregates – proper sedimentary and sedimentary with an admixture of pyroclastics, which has not been defined lithologically, but manifests itself as anomalies in total alkalinity and sodium content.

These data, along with the identification of anomalous individual compositions that are not subject to clustering, provide the lithologist with either direct geochemical information about the rocks, or, at least, information for thought. In particular, it would be very important to establish what is the reason for the appearance of extratitanium compositions (TM > 1, i.e., three orders of magnitude higher than the "clarke" values of the siallite standard) along with hyperalkaline compositions (NKM > 1, which exceeds the norm for common alkaline minerals).

It is clear that even if such complex relationships of litho- and chemotypes are possible for unmetamorphosed sedimentary rocks, they are all the more likely for *parametamorphites*. We will give an anecdotal example – when, instead of one lithotype, it is necessary to distinguish ... about 20 chemotypes. We are talking about the so-called clay rocks of the South African Silverton Formation, which occur in the upper part of the Transvaal superseries (system). P. Ericsson et al. in their work [331] give 31 analyzes of "clay rocks" of these thick strata (named by the authors as Archean, but apparently belonging to the upper Karelian) and 3 average compositions. Weighted average calculated for the whole strata is compared by the authors with various other averages for ancient clay rocks.

Our processing of analytical data is shown in table 48 and in the module diagram (fig. 45). It is possible to identify at least seven clusters, which

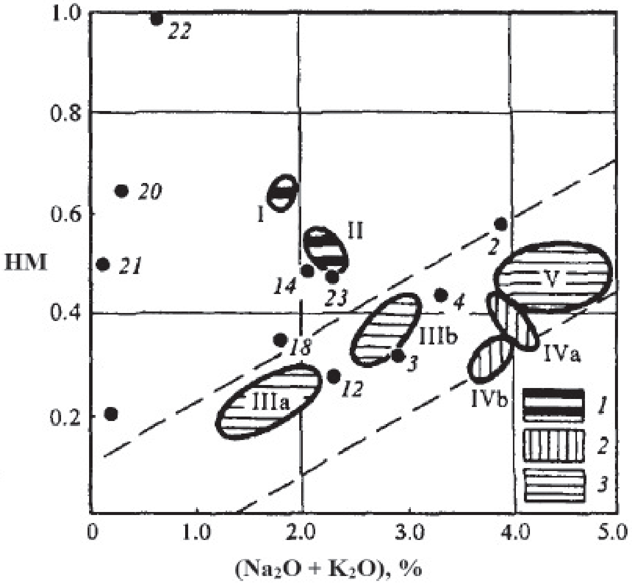

Fig. 45. Module diagram for "clay rocks" of the Silverton Formation, Transvaal superseries, South Africa.

Compiled according to P. Ericsson et al., 1990 [331, p. 454–462].

1 – metahydrolysates, 2 – metagreywackes and/or metatuffoids, 3 – metasandstones, metaaleurolites and metapelites

shows the extreme doubtfulness of any *average* estimates for the strata as a whole.

Cluster I is represented by shale-hypohydrolysates. The high HM value and negligible alkali content show that we are dealing with formations of the weathering crust, and the poor TM value indicates a WCr acidic substrate: granites or rhyolites.

Cluster II responds to supersiallites; the substrate of these rocks, apparently, was also acidic or average. One can think that the rocks of *clusters I* and *II* are related formations, which is emphasized by their falling out of the band of positive correlation "alkali–HM", where the rest of the rocks fall.

Clusters IIIa, b, and *V* are represented by myosilites and siallites somewhat more titanium than rocks in *clusters I–II.* They appear to be members of a continuous series sandstone ⇒ siltstone ⇒ argillite. In this series, HM and alkali content grow.

Cluster IVa is represented by magnesian and calcium rocks with relatively increased titanium and iron values, moreover, by sodium rocks (AlkM 15). Obviously, these are some kind of metagreywackes with basic clastics, but by no means normal shales. The close location of *cluster IVb* to it suggests that these rocks (also relatively

Table 48

The chemical composition of the "clay rocks" of the Silverton Formation, Transvaal superset, South Africa.

Compiled according to P. Ericsson et al., 1990 [331, p. 454–462]

Oxides and modules	I	II	IIIa	IIIb	IVa	IVb	V	2	3
	Hypohydrolisate	Supersiallite	Myosilite	Normosiallite	Pseudosiallite	Hyposiallite	Normosiallite	Pseudo-hydralisate	Pseudosiallite
n	2	3	4	3	2	2	3		
SiO_2	54.27	59.51	70.20	63.35	59.78	64.72	61.53	51.81	62.91
TIO_2	0.66	0.93	0.44	0.71	0.94	0.77	0.77	1.64	0.59
Al_2O_3	24.10	24.83	12.54	15.37	12.72	15.39	19.43	12.36	13.26
Fe_2O_3	9.98	5.45	3.10	6.83	9.13	4.30	8.50	15.79	6.16
MnO	0.12	0.04	0.08	0.05	0.13	0.06	0.07	0.25	0.07
MgO	2.74	0.85	1.80	2.23	6.02	2.17	1.20	5.44	4.40
CaO	0.44	0.27	0.28	0.32	5.39	2.04	0.00	8.29	0.53
Na_2O	0.53	0.48	0.39	0.79	3.74	3.36	0.80	3.64	2.45
K_2O	1.31	1.77	1.30	2.03	0.30	0.45	3.54	0.27	0.47
P_2O_5	0.05	0.02	0.03	0.06	0.03	0.04	0.04	0.13	0.00
Total	94.18	94.16	90.14	91.73	98.15	93.29	95.88	99.62	90.84
HM	0.64	0.53	0.23	0.36	0.38	0.32	0.47	0.58	0.32
FM	0.23	0.11	0.07	0.14	0.25	0.10	0.16	0.41	0.17
AM	0.44	0.42	0.18	0.24	0.21	0.24	0.32	0.24	0.21
TM	0.028	0.038	0.034	0.047	0.074	0.050	0.040	0.133	0.044
FerM	0.42	0.22	0.25	0.43	0.68	0.27	0.43	1.15	0.45
NKM	0.08	0.09	0.13	0.18	0.32	0.25	0.23	0.32	0.22
AlkM	0.40	0.30	0.30	0.50	15.30	7.50	0.20	13.50	5.20

Table 48 (continuation)

Oxides and modules	4	12	14	15	18	20	21	22	23
	Pseudosiallite	Pseudosilite	Pseudosiallite	Myosilite	Pseudosiallite	Hypo-hydrolisate	Supersiallite	Normo-hydralisate	Normosiallite
SiO_2	55.38	62.15	54.75	75.66	51.01	52.24	61.79	44.11	50.08
TIO_2	0.60	0.57	0.58	0.57	0.51	0.39	0.39	0.65	0.49
Al_2O_3	13.21	13.18	15.11	11.96	13.23	27.00	27.00	34.90	19.83
Fe_2O_3	10.28	3.45	10.66	3.23	4.35	6.55	3.45	7.80	3.35
MnO	0.15	0.01	0.16	0.11	0.04	0.07	0.06	0.18	0.02
MgO	8.70	4.73	8.24	1.60	3.78	0.01	0.16	2.06	1.72
CaO	6.97	0.05	9.63	7.28	0.47	0.01	0.01	0.53	0.41
Na_2O	2.87	0.11	1.92	0.23	0.83	0.01	0.01	0.06	1.06
K_2O	0.45	2.20	0.16	0.00	0.99	0.32	0.15	0.62	1.25
P_2O_5	0.07	0.00	0.02	0.10	0.06	0.08	0.07	0.10	0.11
Total	98.68	86.45	101.23	100.74	75.27	86.68	93.09	91.01	78.32
HM	0.44	0.28	0.48	0.21	0.36	0.65	0.50	0.99	0.47
FM	0.34	0.13	0.35	0.06	0.16	0.13	0.06	0.22	0.10
AM	0.24	0.21	0.28	0.16	0.26	0.52	0.44	0.79	0.40
TM	0.045	0.043	0.038	0.048	0.039	0.014	0.014	0.019	0.025
FerM	0.76	0.25	0.69	0.27	0.32	0.24	0.13	0.22	0.17
NKM	0.25	0.18	0.14	0.02	0.14	0.01	0.01	0.02	0.12
AlkM	6.40	0.10	12.00	-	0.80	-	0.10	0.10	0.80

more magnesian, calcium, titanium, and sodium) are either more acidic metagreywackes or basic (andesitic?) metatuffoids.

Among the *individual compositions*, we find obvious basites or their tuffs, recognizable by magnesiality, which can be combined with calcium content, sodium content, and occasionally with titanium value (*samples 2, 3, 4, 12, 14, 18*), and clearly hydrolysate formations, which could be quartz-kaolinite or essentially kaolinite sediments (*samples 15, 20, 21, 22*).

Thus, it turns out that under the name "clay rocks of the Silverton formation", in fact, very different rocks are combined: a) hydrolysate formations – metamorphized WCr for acidic and average (?) substrate; b) a small amount of normal shales, but more silty shales, metasiltstones and, apparently, metasandstones-greywackes with an abundant clay matrix (?); c) basic tuffoids or greywackes with basic lithoclasts.

A complete triumph of lithochemistry!

5.4. The problem of taxa boundaries: from destination to search

The above materials clearly show that complete coincidence of the boundaries of chemotypes and lithotypes of oxide and silicate rocks is out of the question. Nevertheless, one gets the impression that it is possible to achieve their greater correspondence "unilaterally" – by changing ("fitting") the selected boundaries of chemotypes in the HM modulus.

For example, it would be highly desirable that the "silite/siallite" boundary would correspond to the boundary between pelitolites and psammitolites. Most likely, this is impossible due to the wide dispersion of the psammitolite composition. Nevertheless, the cases considered above, when the boundary between "argillites" and "sandstones" passed along HM = 0.25 (i.e., within the "silite" chemotype), may suggest an idea: is it possible to lower the boundary of siallites to a HM value = 0.25? And although practice will quickly show the harmfulness of such a decrease, the question itself is quite legitimate. Exactly the same situation, as already mentioned, arose when defining the boundaries of magnesian "pseudo-sedimentary" rocks (3 or 5 % MgO?). Such situations arise because, unlike the boundaries of other taxa (which are assigned according to a firm rule – 50 % of the normative component), the boundaries of the silite/siallite and siallite-hydrolysate taxa, namely, the HM values equal to 0.30 and 0.55, are assigned purely intuitively – according to the experience of the authors of the chemical classification. And if this experience has flaws, then classification will suffer the same flaws.

In this sense, an example of the designation of the boundaries of such a broad and not very definite concept as "metapelites", which is understood as metamorphosed analogs of pelitic sedimentary rocks, is indicative. From substantive considerations, it is more or less obvious that metamorphic analogs of argillites and siltstones, preferably not too carbonatic, should be referred to as "metapelites". In this regard, the considerations of K.B. Kepezhinskas, who specially studied the petrochemistry and mineral paragenesis of metapelites, deserve attention: “Since <...> the term “pelitic rocks” (“metapelites”) are largely collective and conditional, after conversion to dry matter, only those analyzes were selected in which (in wt %) the SiO_2 content was within the range 57–67 with a CaO content less than 3 <...> These boundaries are to some extent also conditional, but at the same time they are quite specific (which is especially important here). Their choice was made for the following reasons. The SiO_2 content is less than 67 wt. % is chosen with the expectation to avoid the ingress of rocks of granite composition and transitional differences to quartzites; from the side of the values of SiO_2 is less than 57 and CaO is more than 3 wt. % – to limit the samples from the occurrence of medium igneous and volcanic-sedimentary rocks and carbonate-containing "semi-pelitic" <...> rocks. It is important to note here that the SiO_2 content, equal to 57 wt. %, practically coincides with one of the frequency minima in the total distribution, which includes all existing classes of terrigenous and chemogenic rocks. The same can be said about the boundary of CaO less than 3 wt. %” [131, p. 147].

In our opinion, the contents of SiO_2 and CaO are an overly crude diagnostic proxy. Our two modules are more informative: HM and AlkM. We would classify as metapelites, firstly, low-calcium rocks with a HM of 0.20 and higher (i.e., from myosilites to hydrolysates) and, secondly, which is very important, mainly potassium rocks with an AlkM value < 1. If AlkM > 1, then either we are dealing with volcanogenic-sedimentary metapelites (for example, with bentonites), which usually give themselves out with increased magnesiality, or we have a case of an allochemical superimposed process – paragonitization or albitization.

Thus, it is fundamentally impossible to avoid getting into the "metapelites" of rocks of volcanogenic-sedimentary – otherwise the very meaning of the term will be perverted. After all, "pelit" is nothing more than the dimension of debris particles, regardless of their genesis. However, these criticisms are not important for our topic. ***The most valuable here is the methodological technique used by K.B. Kepezhinskas – drawing the chemotype boundary not by intuition, but objectively – at a minimum on the frequency distribution curve. Ideally, this would be how all classification boundaries should be set***. Therefore, a statistical study of the frequency distributions of modules on sufficiently large samples is one of the urgent problems of global lithochemistry. In particular, it is only in this way that one can hope to improve the siallite standard.

We performed this work in relation to our databank counting about 1,760 samples and over 32,300 separate analyzes, distributed as follows:

Chemotypes	Number of samples	*n*
Silites	630	11735
Siallites (pseudosiallites)	401 (181)	3962 (1175)
Siferlites	32	108
Hydrolysates (pseudo-hydrolysates)	127 (79)	383 (312)
Alkalites	36	103
Carbonatolites	225	14421
Phosphatolites	48	147

A detailed statistical study of this set of analyzes is a matter of the future. Here we will restrict ourselves to just a few examples.

Fig. 46 shows the frequency distribution of the HM value in the set of silites.

The “nonmodality” of this distribution turns out to be unexpected: the difference in the frequencies of individual histogram classes is not too large. At the same time, it turns out that, contrary to the previously designated "strong-willed" division of the silites according to HM (<0.05, 0.06–0.10, 0.11–0.20, 0.21–0.30), in reality, the "natural" boundary divides the aggregate of silites into only two parts according to the HM value = 0.20.

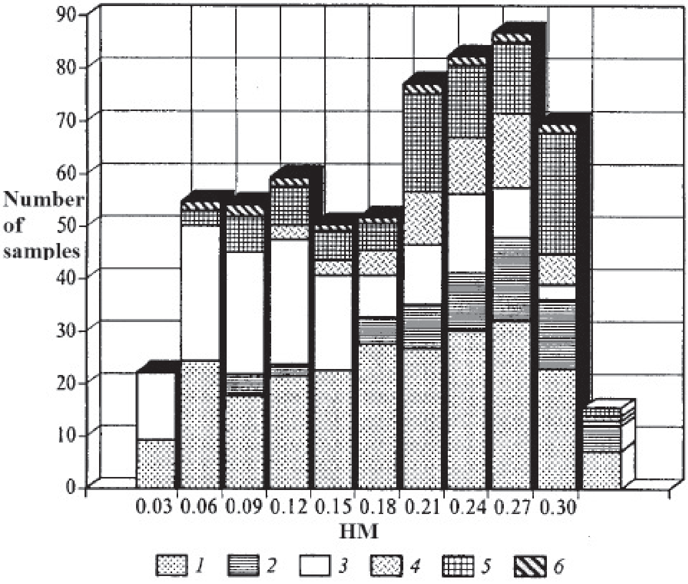

Fig. 46. Frequency distribution of the HM value in silites (630 statistical samples, 11735 analyzes).

Rocks: 1 – sandy, 2 – silty-clay, 3 – silica, 4 – tuffoids, 5 – metamorphic rocks, 6 – others

Fig. 47 shows the distribution of the HM value in the set of siallites.

Here, the boundaries corresponding to the values of ~ 0.38 and ~ 0.46 are clearly visible. If we compare them with the class boundaries assigned earlier [301] (0.35, 0.45 and 0.50), it turns out that the first two were assigned quite successfully (the discrepancy is small). However, the previously proposed boundary of hypersiallites (HM 0.50) does not manifest itself in the frequency graph in any way; we must admit that there are no grounds for distinguishing such siallites gradation.

Figure 48 shows the distribution of FerM values in the set of siallites.

The ferrous module is distributed normally with a clear mode in the range of 0.35–0.45. However, the frequencies of hyperiron siallitis, with FerM in the 0.65–0.75 range, are very low. This means that the previously [301, 302] assigned boundary between siallites and siferlites in terms of FerM = 0.75 is indeed outsized. As expected, it should actually be lowered – most likely, to FerM = 0.70.

Fig. 49 shows the distribution of the alkalis sum.

The alkalis distribution is close to normal, but with a noticeable left-handed asymmetry due to two dozen samples of low alkaline rocks with $Na_2O + K_2O < 3\%$. At the same time, it was unexpected that the modal value of the sum of alkalis lies in the range of 4.5–6.0 %. Meanwhile, we previously classified siallites with $Na_2O + K_2O > 5\%$ as "alkaline" [301, 302]. It is

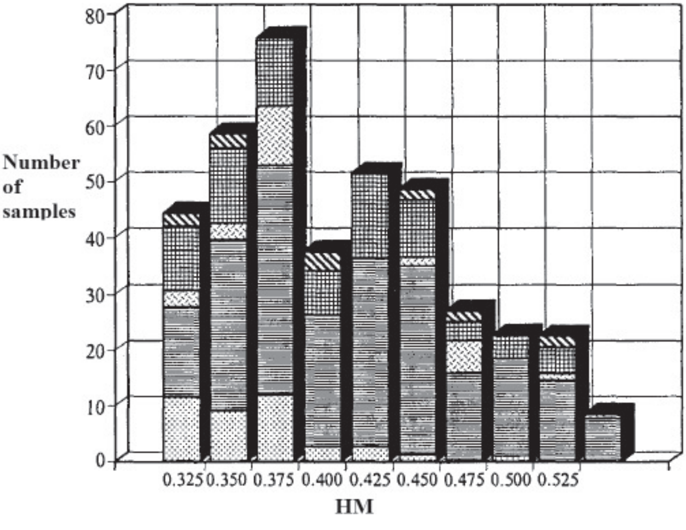

Fig. 47. Frequency distribution of HM value in siallites (401 statistical samples, 3962 analyzes). See the legend in Fig. 46

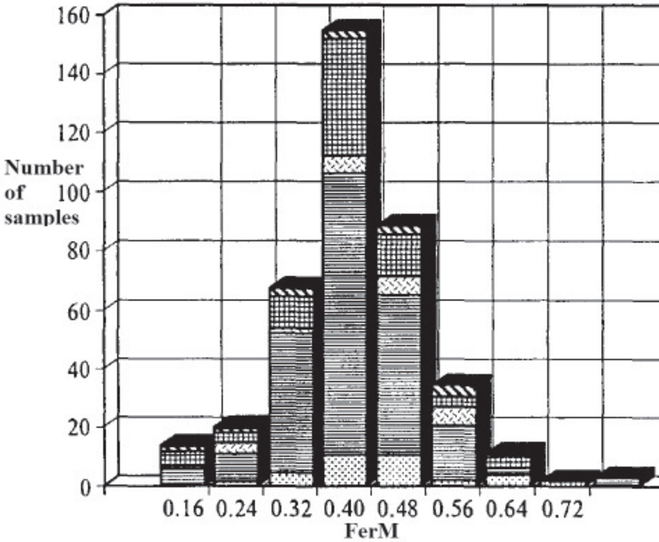

Fig. 48. Frequency distribution of FerM value in siallites (401 statistical samples, 3962 analyzes). See the legend in Fig. 46

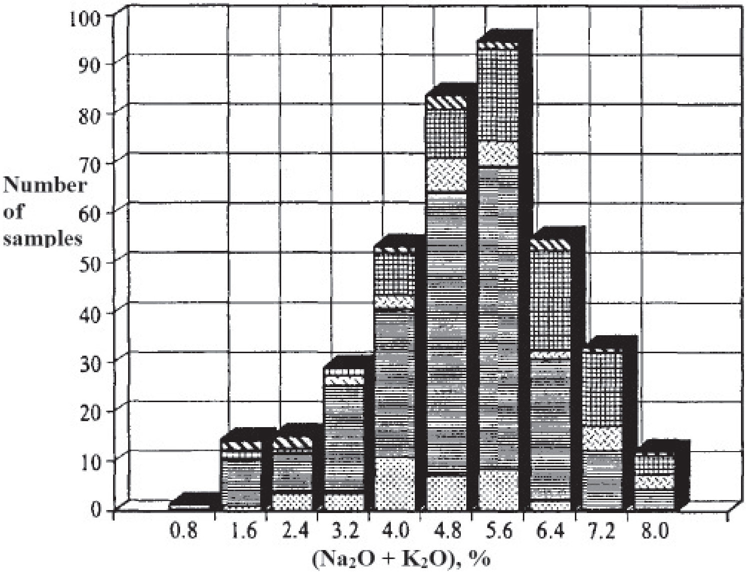

Fig. 49. Frequency distribution of $Na_2O + K_2O$ in siallites (401 statistical samples, 3962 analyzes). See the legend in Fig. 46

now clear that this boundary has been greatly underestimated; siallites with $Na_2O + K_2O > 6.5$ % should be classified as "alkaline".

We have already given some other examples of statistical data use in Ch. 3 – when characterizing the frequency distribution of several modules.

5.5. Lithochemical mirages: composition of sedimentary formations

There is a section of the sedimentary rocks geochemistry that can be called *small-scale regional geochemistry* — the study of the average composition of large sedimentary shell units [295]. In Russian lithology, this direction was intensively developed by A.B. Ronov, A.A. Migdisov, A.A. Yaroshevsky, A. A. Beus [18, 224, 228, 229]. Within this direction, not only the compositions of same-named various aged and facies-associated lithotypes, but also of dissimilar lithotypes are averaged using weight coefficients that consider their prevalence in the section. The resulting averages are intended to characterize either the average composition of certain lithotypes of different ages and/or different facies, or the composition of complex rock associations – formations, sedimentary formations, or the entire sedimentary cover of huge territories, for example, the Russian Plate or even entire continents [224, 228, 229].

Obviously, with such a strong averaging, several factors can simultaneously influence the obtained averages. One knows, in particular, that the material composition of sedimentary formations is determined by the powerful influence of three factors: petrofund, climate and tectonic regime [102]. It is quite possible that the complex interaction of these factors will mask the lithochemical patterns obtained in the study of specific lithotypes of a certain age and/or facies. For example, table 49 and Fig. 50 processed 12 analyzes of clay rocks belonging to the three Eocene flyschoid subformations of Armenia [205]. However, on the module diagrams it is possible to distinguish only two pure "formation" clusters (*IIIa and b*), while the other two are mixed. The weakest individualized clays are “carbonate-terrigenous flysch subformation”, which is indistinguishable from “pyroclastic-sedimentary”.

Note that a good correlation in the coordinates FM–TM and TM–FerM indicates that these rocks are petrogenic. We also note that the composition of clays of the "pyroclastic-sedimentary flyschoid subformation" is characterized by a relatively low titanium value, which may indicate acidic pyroclastics. Although these clay rocks are polymineral, they are still dominated by montmorillonite, hence their noticeable sodium content (AlkM up to 0.96), whereas, for example, the average AlkM for Phanerozoic clay deposits is 0.36 [228, pp. 142–144].

This example shows that even if specific lithotypes are often poorly individualized in their chemical composition, then such highly generalized

Table 49

Chemical composition of the Eocene clay formations in Armenia.
Compiled according to I. Kh. Petrosov, 1983. [205, p. 174–184]

Oxides and modules	I	II	IIIa	IIIb	11
	Siltstones and sandstones	Siltstones and aleurites	Clays and sandstones (normosiallite)	Claysand-siltstones	
n	5	2	2	2	
SiO_2	62.30	52.17	54.68	59.33	61.12
TIO_2	0.74	0.69	0.74	0.90	1.27
Al_2O_3	16.12	17.00	14.18	12.69	17.06
Fe_2O_3	3.36	6.60	7.19	6.24	1.36
FeO	2.31	1.64	2.14	2.03	1.54
MnO	0.02	0.03	0.01	0.03	0.00
MgO	1.77	2.92	2.60	4.29	1.39
CaO	2.16	2.17	2.54	1.35	2.94
Na_2O	2.08	1.49	1.08	1.95	2.00
K_2O	2.88	2.74	2.55	2.30	2.50
S	0.14	-	-	-	0.25
H_2O	2.11	6.43	6.28	3.24	4.68
LOI	4.70	6.36	5.62	6.27	4.60
Total	100.69	100.20	99.60	100.61	100.71
HM	0.36	0.50	0.44	0.37	0.35
FM	0.12	0.21	0.22	0.21	0.07
AM	0.26	0.33	0.26	0.21	0.28
TM	0.046	0.040	0.052	0.071	0.074
FerM	0.34	0.47	0.63	0.61	0.16
NKM	0.31	0.25	0.26	0.34	0.26
AlkM	0.70	0.50	0.40	0.80	0.80

units as *formational lithotypes* can lose features of chemical individuality even more.

Table 50 and Fig. 51 show the *average* compositions of terrigenous and carbonate rocks of two regions (Chu-Ili ore belt and NE of Central Kazakhstan), representing different stages of their development – geosynclinal, orogenic and platform (subplatform) – in a huge age range – from Riphean to Carboniferous [78]. These compositions are the result of a very strong averaging, since they are represented by the average of 2–5 analyzes of collective samples, each of many hundreds and thousands of individual samples. Despite this, the resulting clusters are still very loose, which clearly shows that such broad averaging is invalid for the purposes of lithochemistry.

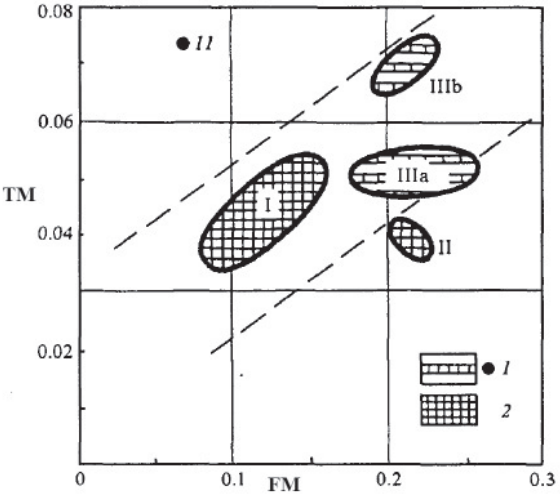

Fig. 50. Module diagram for clay rocks of the Eocene flyschoid subformations of Armenia.
Compiled according to I. Kh. Petrosov, 1983 [205, p. 174–184].
Clusters: 1 – "clean", 2 – mixed

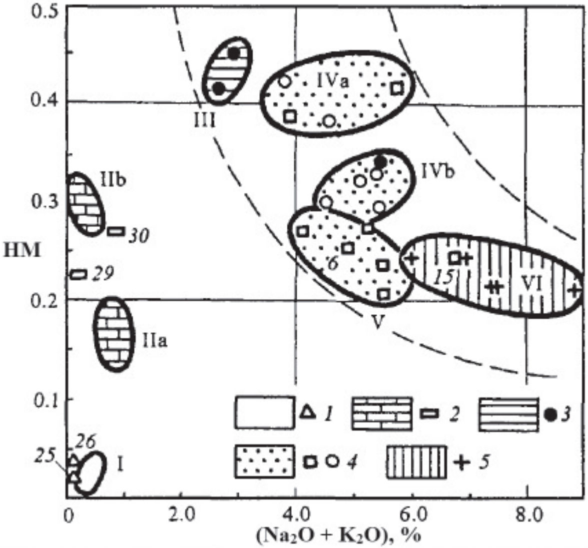

Fig. 51. Module diagram for the *average compositions* of the main rock types of the Chu-Ili ore belt and NE of Central Kazakhstan.
Compiled according to the data of I.V. Glukhan et al., 1983 [78, p. 118–121].
Each point corresponds to the composite sample analysis made up of hundreds and thousands of individual samples. 1 – silica rocks, 2 – carbonate rocks, 3 – argillites, 4 – sandstones and siltstones, 5 – acidic effusive rocks

Table 50

Chemical composition of the main types of rocks of the Chu-Ili ore belt and north-eastern Central Kazakhstan.

Compiled according to I.V. Glukhan et al., 1983 [78, p. 118–121]

Oxides and modules	I	IIa	IIb	III	IVa	IVb	V
	Silica rocks	Carbonate rocks		Argillites	Sandstones, siltstones	Siltstones	Sandstones
	Hypersilite	Carbonatolite		Normosiallite		Alkaline hyposiallite	Alkaline myosilite
m	3186	1755	1139	290	3680	2995	3567
n	2	2	2	2	4	5	4
SiO_2	96.11	23.05	5.72	56.80	58.88	64.06	69.48
TiO_2	0.08	0.14	0.06	0.89	0.82	0.69	0.58
Al_2O_3	1.15	2.38	0.63	17.83	16.72	14.61	12.74
Fe_2O_3	0.35	0.80	0.64	3.89	2.51	3.52	1.88
FeO	1.31	0.42	0.25	2.22	3.75	1.78	2.20
MnO	0.02	0.11	0.09	0.05	0.09	0.11	0.07
MgO	0.11	3.36	4.47	1.63	2.08	2.51	1.32
CaO	0.18	36.17	46.13	1.79	3.14	2.99	2.73
Na_2O	0.08	0.36	0.24	0.82	2.44	2.98	3.01
K_2O	0.24	0.48	0.13	2.00	2.05	2.18	2.04
P_2O_5	0.05	0.06	0.06	0.16	0.24	0.19	0.16
LOI	0.38	32.09	41.12	11.24	6.88	4.13	3.88
Total	100.03	99.38	99.52	99.29	99.59	99.75	100.08
HM	0.03	0.17	0.29	0.44	0.41	0.32	0.25
FM	0.02	0.20	0.94	0.14	0.14	0.122	0.08
AM	0.01	0.10	0.11	0.31	0.28	0.23	0.18
TM	0.066	0.059	0.096	0.050	0.049	0.047	0.046
FerM	1.38	0.52	1.43	0.33	0.36	0.35	0.31
NKM	0.27	0.35	0.58	0.16	0.27	0.35	0.40
AlkM	0.30	0.70	1.80	0.40	1.20	1.40	1.50

Silica geosynclinal rocks (*cluster I* and *an. 25, 26*) are classified as hypersilites. Their difference is that in *cluster I* they are hypotitanium and normo-iron, and in *an. 25* and *26* – hypertitanium and hyper-iron. Therefore, it can be assumed that the latter contain an admixture of basic pyroclastics. At the same time, there is no clear difference between the rocks of the two regions.

Clay rocks of the subplatform and platform stages form *cluster III* and are classified as normosiallites normal in all parameters. However, one composition of "argillites" turned out to be alkaline hyposiallite and, as a result, fell into the contour of siltstone *cluster IVb*; it is obvious that these are actually siltstones, not argillites.

Table 50 (continuation)

Oxides and modules	VI	6	15	25	26	29	30
	Acidic effusives (alkaline myosilite)	Sandstones (myosilite)	Siltstones (alkaline myosilite)	Silica rocks (hypersilite)		Carbonate rocks (carbonatolite)	
m	6467	976	208	22	52	118	250
n	5						
SiO_2	73.14	69.15	69.33	96.00	95.00	4.37	23.87
TiO_2	0.26	0.80	0.55	0.10	0.10	0.03	0.19
Al_2O_3	13.71	11.91	12.76	0.73	0.49	0.15	3.95
Fe_2O_3	1.42	1.78	2.30	0.10	0.10	0.41	1.77
FeO	1.55	3.47	1.72	1.70	3.07	0.29	0.39
MnO	0.06	0.07	0.05	0.03	0.04	0.12	0.23
MgO	0.44	2.49	1.38	0.16	0.22	13.76	1.33
CaO	0.95	2.35	2.30	0.24	0.15	36.47	38.30
Na_2O	3.97	3.06	3.61	0.11	0.06	0.12	0.62
K_2O	3.37	1.77	3.20	0.09	0.04	0.08	0.26
P_2O_5	0.08	0.19	0.12	0.01	0.01	0.09	0.10
LOI	1.04	3.24	2.55	0.05	0.15	43.49	28.72
Total	99.98	100.28	99.87	99.32	99.43	99.38	99.73
HM	0.23	0.26	0.25	0.03	0.04	0.23	0.27
FM	0.05	0.11	0.08	0.02	0.04	3.31	0.15
AM	0.19	0.17	0.18	0.01	0.01	0.03	0.17
TM	0.019	0.067	0.043	0.137	0.204	0.200	0.048
FerM	0.22	0.42	0.31	2.20	5.44	4.56	0.58
NKM	0.54	0.41	0.53	0.27	0.20	1.33	0.22
AlkM	1.20	1.70	1.10	1.20	1.50	1.50	2.40

Clastic rocks form *clusters IVa, IVb*, V and separate compositions *6* and *15.* Orogenic + subplatform sandstones of *cluster V* are classified as alkaline myosilites; geosynclinal + orogenic + subplatform siltstones of *cluster IVb* – as alkaline hyposiallites; geosynclinal + subplatform + platform sandstones and siltstones of *cluster IVa* – as normosiallites.

As one can see, there is no "tectonic" filling in these clusters: each of them contains rocks of different stages. At the same time, the fall of two "sandstones" analyzes (geosynclinal and subplatform) into clearly siltstone *cluster IVa* shows the true value of all this tectonic typification. So, the first turned out to be a magnesian rock – an alkaline pseudosiallite, i.e., most likely, some tuffoid. As for the "sandstone" *an. 15* composition, its entry into the *cluster VI* contour (acidic effusive) shows that it is either acidic tuffoid or simply effusive. In any case, in terms of total and normative alkalinity, it is no different from them.

And only for carbonate rocks can we talk about some kind of "tectonic" specialization. With the same composition of carbonate matter (weakly dolomitic limestones), the subplatform less pure carbonates of the *IIa cluster* are, oddly enough, relatively less hydrolysate (HM 0.17) and ferruginous (FerM 0.52) than pure (reefogenic?) geosynclinal carbonates of the *cluster IIb* (HM 0.29, FerM 1.43). The latter are also distinguished by a higher titanium value (TM 0.096 versus 0.059). However, in relation to pure carbonate rocks, the use of HM can be questionable due to the possible influence of carbonate iron (FeO_{carb}).

Many sedimentary formations are distinguished not by the litho-tectono-stratigraphic basis, but by the mineral presence in them. These are, in particular, phosphate-bearing formations with non-phosphate deposits of very different composition. Table 51 and Fig. 52 show the average compositions of the three main phosphate-bearing formations: glauconite (Upper Cretaceous, Ordovician), terrigenous-carbonate (Upper Cretaceous of the Near East) and silica-dolomite (Cambrian, Karatau). As can be seen, the lithochemical clusters on the NKM–FM module diagram do not completely coincide with the formation groups. Only *cluster III* is entirely formed by the Cambrian phos-

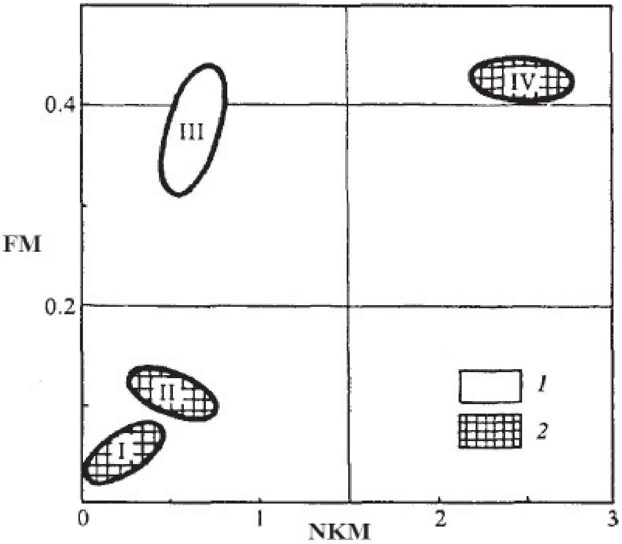

Fig. 52. Module diagram for phosphorites of the main phosphate-bearing formations – silica-dolomite (1) and various (2).
Compiled according to A.I. Smirnov, 1972 [241, pp. 94–97]

Table 51

Average phosphorites chemical composition of the main phosphate-bearing formations.
Compiled according to A.I. Smirnova, 1972 [242, p. 94–97]

Oxides and modules	I	II	III	IV
	Glauconite (phosphatic supersilite)	Various (phosphatic normosilite)	Silica-dolomitic	Various
			Phosphatolite	
n	2	2	2	2
SiO_2	72.21	37.80	9.11	6.02
Al_2O_3	1.46	2.10	1.08	0.23
Fe_2O_3	2.44	2.22	1.90	1.81
FeO	0.48	0.28	0.46	1.16
MnO	0.06	-	0.01	-
MgO	0.32	0.48	2.35	1.78
CaO	10.49	28.89	43.37	46.13
Na_2O	0.21	0.26	0.64	0.58
K_2O	0.29	0.72	-	0.04
P_2O_5	7.24	15.75	27.37	29.03
CO_2	1.20	6.65	6.53	7.01
C_{org}	2.48	0.28	-	-
SO_3	1.30	0.80	1.40	1.50
FeS_2	-	0.01	0.18	0.90
F	0.62	1.50	2.48	2.83
LOI	3.23	2.57	2.71	1.79
Total	104.02	100.29	99.56	100.87
HM	0.06	0.12	0.38	0.53
FM	0.04	0.08	0.52	0.79
AM	0.02	0.06	0.12	0.04
FerM	2.04	1.19	2.20	13.18
NKM	0.34	0.47	0.60	2.76
AlkM	0.70	0.40	-	14.50

phorites of Karatau, while *clusters I, II, IV* are mixed: Ordovician + Cretaceous (*cluster I*), Cretaceous + Cambrian (*clusters II and IV*).

As a result, it should be recognized that for the purposes of formational, supra-regional, and global comparisons, requiring a large and very large averaging of analytical material, rather thin lithochemical tools are in most cases, apparently, simply unnecessary due to the very weak correlation of structural-formational features with lithochemical ones.

Brief conclusion

1. The consistent application of the chemical classification in some cases leads to a collision with the lithological tradition, when a discrepancy between the lithological and chemical boundaries is revealed. In such a situation, two ways are possible, in terms of the "iterative procedure M (meron) $\Rightarrow$ T (taxon)": a) adaptation ("fitting") of the lithochemical taxon T_1 to the existing lithological taxon T_0 by changing the initially specified meron M_1 according to the scheme: T_0: $(M_1 \Rightarrow T_1) \Rightarrow (M_2 \Rightarrow T_0)$; b) changing the boundaries of the lithological taxon according to the scheme: $T_0 \Rightarrow (M_1 \Rightarrow T_1)$.

The second way gives priority to the chemical taxon over the lithological one and is more important.

2. Practice shows that the problem of the lithological (lithotypes) and chemical (chemotypes) taxa ratio is relevant only for silicate and oxide rocks, the chemical classification of which uses the hydrolysate module HM. For such rocks a partial mismatch of lithotypes with chemotypes is most often observed. An analysis of such examples shows that the "lithochemical reality", as a rule, is much richer than the "lithological reality", i.e., in most cases, the number of chemotype clusters identified on the module diagrams turns out to be greater than the number of described lithotypes. This is of great heuristic significance, because it gives the geologist "information for thought", prompting a more thorough study of seemingly homogeneous lithotypes.

3. Nevertheless, it should be borne in mind that the module chemotypes boundaries we use, and in particular the siallite standard, are boundaries *assigned* on the basis of practical experience and intuition. They should be refined in the future in an objective statistical way – by studying frequency plots for petrochemical modules.

4. The average compositions of formations, sedimentary formations, or entire sedimentary shell segments, which are often used in *small-scale geochemistry of the sedimentary shell*, are an ungrateful object for lithochemical research. The enormous averaging of the material, in fact, integrating the complex interaction of tectonic, climate, and petrofund factors, devalues the fine proxys of lithochemical analysis. Therefore, for the purposes of formation analysis and other methods involving a strong averaging of chemical analyzes, lithochemistry techniques, as a rule, turn out to be ineffective. Thus, we do not recommend their use.

CHAPTER 6

BRIEF DESCRIPTION OF THE BASIC TAXONS

6.1. Silites

As indicated in Ch. 2, the “silites” taxon embraces aluminosilicate rocks with a HM < 0.30. It includes silica (aquatic), quartz-feldspar (petrogenic) and essentially quartz (lithogenic) clastic rocks, as well as some pyrogenic – acid tuffoids. Petrogenic and pyrogenic rocks are often classified as alkaline silites ($Na_2O + K_2O > 5\%$).

Hyper- and supersilites. The classes of *hypersilites* (HM < 0.05) and *supersilites* (HM 0.06–0.10) cover highly pure silica and quartz rocks, and the SiO_2 content in hypersilites is usually at least 80 %. In particular, judging by the analyzes given by V.N. Shvanov [276, p. 151–152], the hypersilites include *quartz sandstones* (HM 0.004–0.015) and partly *oligomictic sandstones* (HM 0.02–0.08). Hyper- and supersilites are, for example, the Upper Vendian quartz sandstones of the Berezhkov formation of Trans-Dniester (HM 0.02), Vorontsov and Lontov formations of the Baltic region (HM 0.05 and 0.10) [72, p. 76–77]. Many Paleozoic phtanites and flints [98, 297] are hypersilites[1]; part of trepels, spongoliths and flint-like variety of the Cretaceous–Paleogene opokas of the Russian Platform [182] are also certified as hypersilites.

In the absence of sufficient lithological data (especially when working with quartzites, in which the original structures have been destroyed by recrystallization and blastesis), the problem of identifying aquagenic (flint rocks) and lithogenic silites of the second cycle rock type (monoquartz sandstones) is very urgent. Our experience shows that such a diagnosis can be quite successful when four to five silites signs are considered.

1. *The nature of the rock association*. The association of silites with hydrolysates (for example, with kaolinite clays) is strong evidence in favor of

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[1] It was the need to somehow isolate especially silica silicites (with SiO_2 often even > 90 %) in the black shale strata of the Pai-Khoi that forced us in 1977—1981 within the class "eusilites" (HM < 0.10) additionally introduce the subdivision "ultra-evsilites" with HM < 0.05 [302, p. 18].

their lithogenic nature, while the association with manganese carbonates, alkaline siallites, and alkalites is characteristic of aquagenic (flint) silites.

2. *Titanium value.* For lithogenic silites of the second cycle type, due to the Migdisov's law, super- and hypertitanium value is very characteristic, while for aquatic silites, increased TM is observed mainly in jasper and much less often in phtanites (and is usually due to the influence of basic pyroclastic or ferruginous exhalations, which is issued by a positive correlation TM–FerM).

3. *Alkalinity.* Substantially quartz psammitolites contain very little clay (or micaceous) impurities and therefore have a minimum total alkalinity. On the contrary, aquagenic silites (flints) are closely associated with tuffoids and, therefore, are often more alkaline. The NKM value is also different: in "mature" lithogenic silites there is usually an extremely low "feldspar/mica" ratio, therefore the NKM value is small, and in aquatic ones, on the contrary, an admixture of feldspar pyroclastics often causes high NKM values.

4. *Manganese and iron content.* Jaspers and phtanites are often associated with hydrogenic accumulations of iron and manganese, which is unusual for lithogenic quartz sandstones (with the very characteristic exception of glauconite ones).

5. C_{org} *content.* Many flint rocks (phtanites) are classified as "black shales" as they are characterized by an increased (> 1 %) content of C_{org}, sometimes reaching the cahytolites level [300]. On the contrary, OM accumulations are completely uncharacteristic for lithogenic silites. Therefore, in particular, "graphite quartzites" are, with a high probability, metasilicites, and not metapsammites[2].

Let us note the cases of the Nature's special "cunning", when aquagenic (biogenic) silica material is mixed in different proportions to the terrigenous quartz material, forming, for example, silica cement of quartz sandstones. Such rocks – silicified quartz sandstones and siltstones – are observed in the Paga formation D_2 of the Lemva structural-facies zone of the Northern Urals. During the sediments accumulation of this formation, detrital quartz from the weathering crusts on the Russian Plate was discharged by turbid flows onto the continental slope of the Ural Paleocean, where the "background" sediments were silica [98].

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[2] The most voluminous materials (hundreds of analyzes and dozens of statistical samples processed in the lithochemical standard of the South Caucasus) characterizing the black shale silica strata of the Paleozoic bathyal type [218] are concentrated in our monographs on the Pai-Khoi and Lemva zone of the North Urals, to which the interested reader refers [98, 297]. Many average compositions of carbonaceous silites of different ages throughout the world (from the Archean to the Cenozoic, inclusive) are given in the book "Geochemistry of Black Shales" [300].

An equally "cunning" case is the association of Eocene platform silicite–opalites (opokas, trepels, and diatomites) with quartz sands and sandstones in Western Siberia. Here, the diagnosis can be complicated by diagenetic migrations of silica, which leads to secondary silicification of both the sands and the silicites themselves [69]. One of the signs of such (metasomatic) silicification can be the extremely high TM and FerM values with poor titanium and iron contents. The fact is that silicification is accompanied by the removal of alumina, which leads to a sharp increase in TM and FerM values. Such a case, apparently, is represented by "quartzites" among the Paleozoic–Mesozoic "geosynclinal silicites" of Sakhalin, described by N. G. Brodskaya [193]. Both flint and terrigenous rocks could serve as the primary substrate for these apparently secondary formations.

Normosilites. The normosilites class (HM 0.11–0.20) embraces most sandstones, many felsic tuffoids, and, perhaps, also most flint rocks (although the share of the first two classes is quite noticeable among them). This includes arkoses, a feldspar-quartz and mica sandstones, felsic greywackes, as well as many quartz siltstones, in which a clay or mica admixture is already significant. Among the Paleozoic silica rocks, normosilites are usually “clay-silica shales” [98, 297], and among the younger ones, for example, most of the Eocene opokas, trepels, and diatomites of the West Siberian Plate [69] and part of the Cretaceous–Paleogene diatomites of the Russian Platform [182].

Judging by the average data for sandy rocks given in the books of V. N. Shvanov, F. Pettijon, and others, the normosilites are “average sandstone” [207] with TM, FerM, and NKM values of 0.056, 0.44, 0.35, respectively, almost all arkoses (HM 0.15–0.20), including albitophyric (0.16–0.18), and among greywackes – polymictic quartz (0.13), calcareous lithoclastic quartz (0.12), calcareous quartz (0.18) [276, p. 151–152, 173, 188].

Myosilites. The myosilites class (HM 0.21–0.30) forms a natural transition from silites to siallites. On the one hand, these are greywacke psammitolites, and on the other, they are simply more silty, in particular, many siltstones. Both features are associated with an increased proportion of feldspar and/or clay–mica material. This is clearly seen in the example of the Riphean greywackes and siltstones of the Armorican massif, NW France [329], where greywacke sandstones are on average alkaline myosilites, while siltstones are alkaline hyposiallites. At the same time, siltstones are slightly more ferruginous (FerM 0.32 versus 0.29) and much less sodium (AlkM 0.83 versus 1.6). These characteristics have an obvious explanation: there is more quartz and plagioclases in sandstones (therefore, lower HM, higher NKM and AlkM), and in siltstones, on the contrary, there is less quartz and more clay matter (therefore, higher HM and lower NKM).

Judging by the analyzes of the Lower Paleozoic "greywackes" of southeastern Australia [361], of which the Ordovician ones are especially rich in feldspars, the HM value in them can reach the level of hyposiallites.

According to the average data for sandy rocks, myosilites include acidic petroclastic greywackes (HM 0.21), greywackes proper (0.29) and lithoid arenites (0.21) by F. Pettijon et al. [208], evgeosynclinal sandstones by G. Middleton [343] (0.28), lithoclastogenic greywackes by V.D. Shutov [281] (0.21). For example, as can be judged from the I. P. Druzhinin's analyzes [100, p. 88], the Middle Carboniferous "quartz–feldspar greywackes" of Dzhezkazgan contain up to 15 % carbonate and are certified as normo- and myosilites (deposits of spits and barrows) and even as alkaline normosiallites (deltaic deposits). The alkaline variety of myosilite is characterized by the minimum iron content and judging by the NKM value (0.44), is the richest in feldspars. There is a tendency towards a positive correlation TM–FerM, which is typical for petrogenic material that has not undergone significant weathering. Petrogenic sodium arkoses of the Achimov formation K_1 in Western Siberia also belong to alkaline myosilites (materials by B.A. Lebedev, 1997).

Among Paleozoic silica rocks, myosilites are, as a rule, "silica-clay shales" [98, 297], and among younger ones, for example, Eocene "clay-silty opokas" and "clay diatomites" of the West Siberian plate [69] and part of the Cretaceous–Paleogene diatomites of the Russian Plate [182].

Note also that myosilites (and related hyposiallites) include such a formation as atmospheric dust, which is mainly a mixture of petrolitogenic and pyrogenic material. For example, judging by the three analyzes given by E.V. Sobotovich et al. [243, p. 94–95], the dust collected on the Near-Elbrus glacier Garabashi belongs to the hyposiallites class and a close class of myosilites. The sodium dust is characteristic (AlkM > 1), which is typical of both psammoids and tuffoids.

Formally, granites and liparites also belong to myosilites [18, p. 279], which have HM 0.23 and 0.22, respectively. Naturally, these compositions are close to their derivatives composition – arkoses. Yet arkoses, as a rule, are more silica rocks (more often normo- than myosilites) and often with a lower TM. Both are a consequence of the feldspar loss during weathering. However, mechanical differentiation of clastic can, on the contrary, significantly increase the arkoses' TM in comparison with the original granites. As for especially low-titanic rhyolites, then any arkose's TM is apparently always higher than that of any rhyolite.

In the absence of sufficient lithological information for recognizing aquagenic (silica) and petrolitogenic (terrigenous) myosilites, the value of total alkalinity is the most informative. Alkaline hyperpotassium myosilites

(AlkM < 0.30) with $Na_2O + K_2O > 5$ % are of particular interest. These are very specific formations – red-colored high-potassium arkoses, characteristic only of the Precambrian, when, due to the increased content of CO_2 in the atmosphere, the weathering was quite intense even in an arid climate. Such weathering gave rise to thick terrigenous strata represented by high potassium rocks – arkoses (alkaline silites) and clays (alkaline siallites and even hydrolysates) [298]. Thus, the association "silites (alkaline silites) – alkaline siallites ± alkaline hydrolysates" characterizes the products of ancient arid weathering[3].

6.2. Siallites

This taxon includes most of the petrolithogenic clay and silty-clay rocks, some sandy rocks, and alkaline varieties of siallites can be either pyrogenic rocks – tuffoids, or, in the case of their association with alkaline hydrolysates, – derivatives of the weathering crust.

For example, siallites include the *petroclastic basic greywackes* described by V.N. Shvanov [276, p. 188], associated with the destruction of tholeiitic basalts (HM 0.39) and porphyrites (HM 0.43). The first of them, despite its belonging to normosiallites, has a hypertitanium and superiron composition (TM 0.101, FerM 0.56). The second, in these parameters, is similar to a clay rock, but differs in the AlkM value = 1.9, which is impossible for any clays, whereas even for the most sodium-rich Catarhean metapelites, the AlkM does not exceed 0.7, and for the Phanerozoic ones it is half as much [228, p. 142–144].

We noted above that *hyposiallites* (HM 0.31–0.35) are closely related to myosilites, and this relationship reflects the intermediate position of the aleurite rocks composition between sandy and clay rocks. At the same time, one can notice a certain pattern: ***the aleurite rocks of humid formations during clustering are usually associated with clay rocks, while in arid strata they are more often combined in single clusters with sandy rocks.***

On the other hand, *supersiallites* (HM 0.49–0.55) are a natural bridge to hydrolysates – weathering crust formations. For example, "clay with halloysite" in the Paleogene deposits composition of the East European platform [214, p. 157] is certified as superalumina supersiallite (HM 0.50, AM 0.38).

The role of siallites in the sedimentary shell. As already indicated, siallites are the most common rocks of the sedimentary shell. For example, on four ancient platforms, the volume fraction of clay rocks in the sedimentary cover is 43.1 % [226], and all of them are certified as siallites – the embodiment of the siallite standard. Indeed, the average clay rocks composition of the

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[3] We consider the question of arid weathering in more detail in Ch. 8.

sedimentary cover of ancient platforms corresponds to such normosiallites, which refer to the "norm" in almost all parameters: normotitanium (TM 0.052), normoalkaline (NKM 0.29), hyposodium (AlkM 0.26), normoferrous (FerM 0.33), and normofemic (FM 0.14). In addition to sedimentary siallites, very widespread magmatic and metamorphic rocks of medium-sized composition, as well as whole lithospheric shells, such as "granite" and "basaltic", are also certified as siallites. In particular, the average compositions calculated by A.A. Beus [18, pp. 280–281] correspond to: *granodiorites* – hyposiallite, normal by TM, FerM, hypofemic and superalkaline; *charnockites* – hyposiallite, normal in TM, FM, FerM, superalkaline; *andesites* – normosiallite, normal in all parameters. Thus, andesite turns out to be, as it were, a standard of average siallite. Nevertheless, andesite has two fundamental differences from clay: 1) sodium content, AlkM > 1, and in most clays AlkM <1; 2) high silicate CaO content (6.1 %), which cannot be found in clays.

The certification of the average metamorphites' compositions calculated by A. A. Beus is also indicative: *paragneisses* are hyposiallites, and *crystalline shales* are normosiallites; both are normal in all respects.

Even from these highly averaged data on the granite-metamorphic shell composition of the continental crust, it is clear that "paragneisses" originated mainly from psammoids, and "crystalline shales", respectively, from pelitoids. At the same time, overall, the granite-metamorphic shell is closest to the paragneisses' composition.

As for the *model composition of the continental sedimentary shell* (which is traditionally presented as a 2:1 mixture of granulite-basite and granite-metamorphic shells), it has long been established that its composition is close to andesite. The difference is increased titanium value (TM 0.065 versus 0.049) and iron content (FerM 0.45 versus 0.38), which is explained by the contribution of basalts – rocks rich in iron and titanium.

Paragenesis of siallites. The siallites studied by us form hundreds of samples processed in the lithochemical standard YuK; here we will restrict ourselves to a few examples showing the paragenetic relationships of these rocks with silites and hydrolysates.

Table 52 and Fig. 53 shows the compositions of terrigenous rocks of the Middle Riphean Shatak formation in the Southern Urals, including sandstones (quartz and subarkoses), siltstones and argillites [202]. There are seven clusters and one separate composition.

Cluster I combines *quartz and subarkose sandstones*; they are certified as normoalkaline supersilites. Their falling into one cluster shows the conventionality of the lithological definition, in this case the lithochemical boundary is more valid. Inclusion into cluster I of the neighboring sample 7 is formally possible, but doubtful due to the

Table 52

Chemical composition of terrigenous rocks of the Middle Riphean Shatak formation of the Southern Urals.

Compiled according to the data of V. P. Parnachev et al., 1986 [202, p. 51]

Oxides and modules	I	IIa	IIb	III	IVa	IVb	V	7
	Quartz sandstones	Subarkoses sandstones		Siltstones			Argillites	Quartz sandstone (hypersilite)
	Supersilite		Normosilite	Alkaline myosilite		Hyposiallite	Alkaline normosiallite	
n	2	2	2	2	3	3	5	
SiO_2	90.73	87.59	81.13	71.51	70.93	67.40	64.20	95.30
TiO_2	0.16	0.23	0.47	0.51	0.82	0.68	0.74	0.24
Al_2O_3	3.53	7.05	11.39	16.97	17.29	15.81	19.52	1.41
Fe_2O_3	2.21	0.80	1.13	1.19	2.41	3.85	4.19	0.76
FeO	0.88	0.49	0.58	0.37	0.99	2.17	1.73	1.50
MnO	0.02	0.01	0.01	0.02	0.01	0.02	0.02	0.03
MgO	0.75	0.85	1.38	2.11	1.37	1.61	2.15	0.09
CaO	0.64	0.50	0.47	0.34	0.61	1.25	0.61	0.11
Na_2O	0.06	0.07	0.24	0.15	0.15	0.14	0.14	0.20
K_2O	0.97	2.42	3.13	6.39	5.27	4.75	6.64	0.25
P_2O_5	0.07	0.0!	0.03	0.01	0.15	0.42	0.07	0.11
Total	100.00	100.00	99.95	99.55	100.00	98.09	100.00	100.00
HM	0.07	0.10	0.17	0.27	0.30	0.33	0.41	0.04
FM	0.04	0.02	0.04	0.05	0.07	0.11	0.13	0.02
AM	0.04	0.08	0.14	0.24	0.24	0.23	0.30	0.0!
TM	0.045	0.033	0.041	0.030	0.047	0.043	0.038	0.170
FerM	0.84	0.18	0.14	0.09	0.19	0.37	0.29	1.39
NKM	0.29	0.35	0.30	0.39	0.31	0.31	0.35	0.32
AlkM	0.10	<0.10	0.10	<0.10	<0.10	<0.10	<0.10	0.80

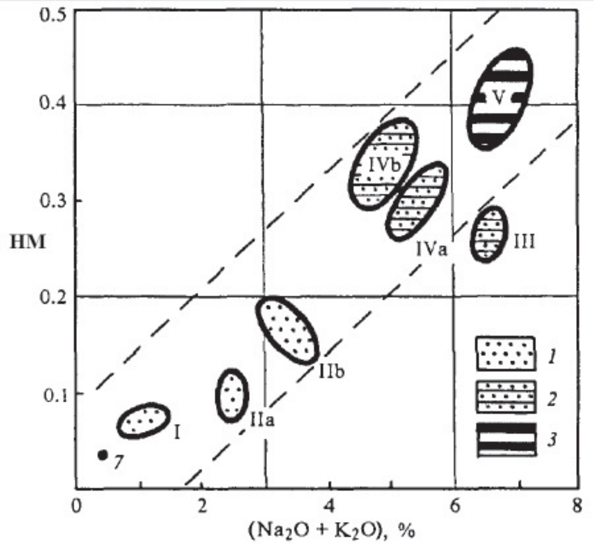


Fig. 53. Module diagram for terrigenous rocks of the Middle Riphean Shatak formation of the Southern Urals. *Compiled according to V.P. Parnachev et al., 1986 [202, p. 51].* 1 – sandstones, 2 – siltstones, 3 – argillites

anomalous values of TM and FerM in this sandstone. Apparently, it is enriched in the heavy fraction (washing?).

Cluster II is formed by *subarcose sandstones*: these are normalkaline hypotitanic normosilites.

Clusters III and IV are represented by *siltstones*. Obviously, the myosilites of cluster III are less rocks, while the hyposiallites of cluster IV are more clay. Note that cluster IV also includes one argillite sample; again, the lithochemical boundary turns out to be more reliable than the lithological one.

Cluster V is represented by *argillites*–normosiallites.

Consideration of the average compositions of the Upper Vendian argillites in the Russian Platform, studied by A.V. Sochava et al. [72], shows that against the background of dominant siallites with HM 0.37–0.50, there is an argillites' hydrolysate composition of Mogilev and close to it Yaryshev formations of Transdniester and Pletenev formation of Moscow syneclises (HM 0.55–0.65), which suggests the presence of weathering crust redeposition products in these strata. These formations are located at the very base of the Upper Vendian strata (lower reaches of the Redkin horizon). As noted by A.V. Sochava et al., these and some other composition features *"are associated, in particular, with an increased content of kaolinite and are determined by the participation in their formation ... the weathering crust on the crystalline basement of the platform <...>"* [72, p. 72].

The above examples show that the identification of siallites' classes (hypo-, normo-, supersiallites) is by no means a purely formal procedure: ***siallites of different classes often carry quite a definite genetic load.*** In particular, a long-standing tradition of Siberian lithology (originating from V.P. Kazarinov and Yu.P. Kazansky) is the differentiation of platform terrigenous strata according to the degree of "maturity," that is, in terms of lithochemistry, according to the siallites classes. This differentiation allows making facies reconstructions, which, in turn, can be used to predict the ore content of sedimentary strata.

Table 53 and Fig. 54 given by S.V. Saraev [235] the *average* compositions of sedimentary rocks of the Lower Riphean (?) Sukhopit Group of the Yenisei Ridge, in the formations composition (from bottom to top) Kordin, Gorbilok, Uderei (gold-bearing and partly black-shale), Pogoryui and Sosnov. The clear separation of clay rocks of the Pogoryui and Sosnov formations (cluster I) from the phyllites of the Uderei and Gorbilok formations (cluster II) is striking. Obviously, the former is aleuritic (certified as hyposiallites), while the latter are more clay and certified as supersiallites.

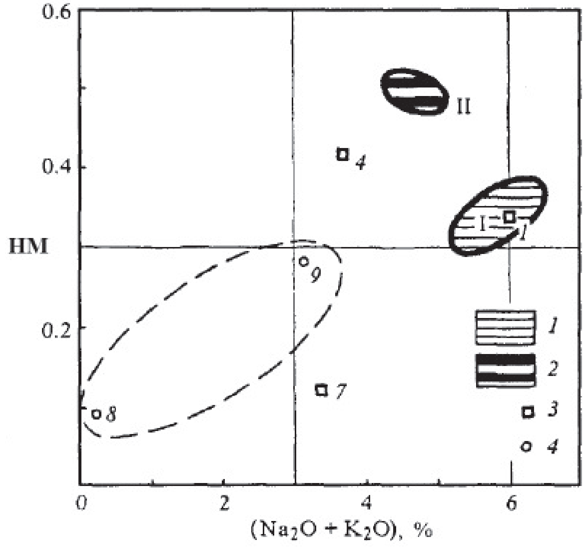


Fig. 54. Module diagram for the average compositions of the Sukhopit Group of the Yenisei Ridge. Each point corresponds to the average of 5–19 analyzes. *Compiled according to the data of S. V. Saraev, 1983 [235, pp. 128–129].*

1 – clay and silty shales (Pogoryui and Sosnov formations), 2 – clay shales and phyllites (Uderei and Gorbilok formations), 3 – metaaleurolites and metanesides (Kordin, Uderei, Sosnov formations), 4 – limestones and calcareous shales of the Sosnov formation

Table 53

Chemical sediments composition of the Sukhopit Group of the Yenisei Ridge.

Compiled according to the data of S. V. Saraev, 1983 [235, p. 128–129]

Oxides and modules	I	II	1	4	7	8	9
	Shale (alkaline hyposiallite)	Slates and fnlites (supersiallite)	Metaterrigenous rocks (alkaline normosiallite)	Metaaleurolites (normosiallite)	Sandstone (normosilite)	Limestone (carbonatolite)	Calcareous shale (carbonate Mn myosilite)
m	31	35	6	14	5	3	9
n	3	2					
SiO_2	65.78	59.31	64.19	63.09	78.72	4.52	47.95
TiO_2	0.89	1.16	0.76	1.34	0.22	0.03	0.44
Al_2O_3	16.02	19.25	14.59	15.80	7.09	0.01	7.48
Fe_2O_3	1.49	2.48	2.00	2.21	0.47	0.09	3.35
FeO	3.57	6.18	4.49	7.03	1.77	0.30	1.16
MnO	0.03	0.13	0.07	0.07	0.08	0.02	1.29
MgO	1.69	1.68	2.62	1.99	0.73	0.70	2.16
CaO	0.66	0.56	2.07	0.63	3.71	51.10	16.80
Na_2O	2.13	1.45	1.95	0.94	1.96	0.12	1.43
K_2O	3.62	3.26	4.05	2.73	1.40	0.07	1.70
P_2O_5	0.09	0.13	0.12	0.17	-	0.06	0.14
LOI	3.73	4.05	2.56	3.81	3.95	41.40	15.76
Total	99.70	99.63	99.47	99.81	100.10	98.42	99.66
CO_2	0.89	-	-	-	2.83	40.90	14.87
HM	0.33	0.49	0.34	0.42	0.12	0.10	0.29
FM	0.10	0.17	0.14	0.18	0.04	0.24	0.14
AM	0.24	0.32	0.23	0.25	0.09	0.00	0.16
TM	0.056	0.060	0.052	0.085	0.031	3.000	0.059
FerM	0.30	0.43	0.43	0.54	0.32	10.25	0.73
NKM	0.36	0.24	0.41	0.23	0.47	19.00	0.42
AlkM	0.60	0.40	0.50	0.30	1.40	1.70	0.80

Accordingly, the former has lower HM (0.33 versus 0.49) and AM (0.24 versus 0.32) and noticeably higher sodium levels (AlkM 0.56 versus 0.44). According to S.V. Saraev, "*the stratigraphic levels with increased gold content (Uderei formation) corresponded to the most mature sediments, the material of which came from tectonically stable areas*" [235, p. 136].

Without denying this conclusion, we note, however, that the cluster I composition also includes the Gorbilok phyllites, which practically do not differ in composition from the Uderei phyllites. As for carbonate, carbonate-bearing, and meta-terrigenous rocks, they all belong to the Sosnov formation and show significant diversity (an. 7, 8, 9). The Uderei siltstones (an. 4) tend to "their" phyllites of cluster II, while the Korda meta-siltstones differ little from the Pogoryui and Sosnov clay rocks (an. 1 in the contour of cluster I).

Sodium siallites. Most siallite-pelitoids are characterized by low and moderate values of the alkaline module AlkM, which allow them to be certified as hyposodium (AlkM < 0.30) and normosodium (AlkM < 0.31–1.0). However, in some cases, the pelitoids turn out to be significantly sodium (AlkM > 1). Such exceptions to the general rule carry certain genetic information.

Table 54 and Fig. 55 processed 8 analyzes of Carboniferous argillites in the Lvov-Volyn basin [22]. These analyzes have two features. First, argillites are clearly hydrolyzatic: four supersiallites (cluster I and sample 3) and

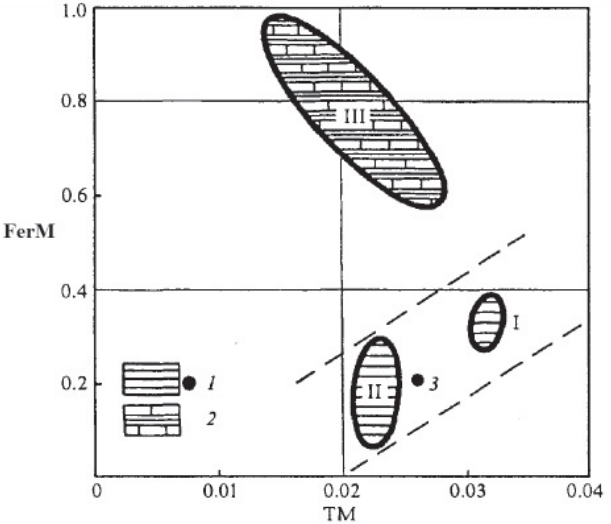


Fig. 55. Module diagram for Carboniferous argillites of the Lvov-Volyn basin.
Compiled according to D.P. Bobrovnik, 1977 [22, p. 83].
Argillites: 1 – low iron, 2 – ferruginous

Table 54

Chemical Carboniferous argillites composition of the Lvov-Volyn basin.
Compiled according to D.P. Bobrovnik, 1977 [22, p. 83]

Oxides and modules	I	II	III	3
	Supersiallite	Hypohydrolisate		Alkaline supersiallite
п	3	2	2	
SiO_2	56.49	45.24	46.14	56.04
TiO_2	0.68	0.59	0.43	0.58
Al_2O_3	21.53	26.09	19.27	22.14
Fe_2O_3	1.78	1.40	1.79	1.84
FeO	5.74	3.42	12.88	2.99
MnO	-	-	0.10	-
MgO	1.45	1.12	0.43	0.89
CaO	0.36	6.19	2.15	0.75
Na_2O	3.16	2.66	0.29	4.53
K_2O	1.76	1.21	3.86	2.53
LOI	7.80	16.18	12.32	6.88
Total	100.76	104.10	99.65	99.17
HM	0.53	0.70	0.75	0.49
FM	0.16	0.13	0.33	0.10
AM	0.38	0.58	0.42	0.40
TM	0.032	0.023	0.022	0.026
FerM	0.34	0.18	0.75	0.21
NKM	0.23	0.15	0.22	0.32
AlkM	1.80	2.20	0.10	1.80

four hydrolysates (clusters II and III). Second, although these are undoubted pelitoids, in five analyzes, AlkM > 1: from 1.4 to 2.2. This is explained by the unusual composition of clay matter – the dominance of *hydroparagonite* in it. Two samples (cluster III) contain diagenetic siderite cement, which preserved the primary hydromica – illite; that is the reason that these rocks remained hyposodium, which is normal for pelitoids. According to D.P. Bobrovnik, the formation of hydroparagonite is due to the reaction of clays with sodium chloride waters, i.e., to an allochemical process (or *superimposed epigenesis* in the B.A. Lebedev's understanding [153]). Consequently, the sodium content of the siallite pelitoids may be an indication of an allochemical process.

6.3. Siferlites

Siferlites differ from siallites in higher iron content. Despite the seemingly purely arbitrary designation of the siferlite boundary in value of FerM = 0.75, the rich lithochemical practice has shown the justification for distinguishing this taxon. As a rule, siferlites turn out to be "non-simple" rocks; they are closely associated either with magnesian pyro- and petrogenic (pseudosiallites, etc.), or with hydrolysate formations.

Among terrigenous clastic rocks, siferlites often turn out to be greywackes. For example, the analysis of the basic greywacke of the Alai ridge given by V. N. Shvanov [276, p. 128] corresponds to siferlite: HM = 0.49, FerM = 0.97. This clearly petroclastic rock is rich not only in iron (Fe_2O_3 + + FeO = 14.60 %), but also in titanium (TiO_2 = 2.25 %), which gives a strongly increased TM = 0.171.

While ferruginous pelitic rocks in most cases are certified as hydrolysates rather than siallites (HM > 0.55), ferruginous psammitic (and even psephitic) rocks often turn out to be precisely siferlites (and not silites). Such formations are found, for example, in the composition of laterite covers, where they form glandular shells – cuirasses. However, unlike the in-situ cuirass, such cuirasses are found on the slopes, slope trains and even on the plains. As V.M. Sinitsyn notes, they arise when the sediments are replenished with groundwater carrying reduced iron, which is oxidized at the water outlets. *"In these types of cuirasses, in contrast to the cuirass of boval cementation, not fragments of cracked eluvial ferruginous rock are exposed, but overburden deposits participating in gravitational movement (deluvium, proluvium, and even alluvium)"* [236, p. 47–48].

An example of ferruginous psammites and psephites are hematite conglomerates and sandstones of the *Alkesvozh strata* in the Subpolar Urals, which were enriched in iron due to erosion of the ancient (Cambrian) weathering crust over Vendian basalts [111, 304, 308].

Sometimes both genetic lines of siferlites (associated with iron-magnesian basites and with ferruginous weathering crusts) can be combined, and then magnesian ferruginous rocks – *pseudosiferlites* – are formed. Such are, for example, Triassic sandy-siltstone rocks in the lower reaches of the river Lena, described by A.V. Ivanovskaya [113]. Their composition has three features: a) high values of HM (> 0.45, and one composition even at the border of hydrolysates: HM = 0.55); 6) hypertitanium value of three Ladin (T_2) samples: TM = 0.092–0.245; c) magnesium content. The latter forces us to use a graph with FM for composition averaging, on which two clusters can be distinguished, uniting the Upper and Middle Triassic rocks (Table 55). The carriers of Fe and Mg in these rocks are terrigenous ilmenite, magnetite, hematite, and authigenic ones – Fe-Mg chlorite and goethite–hydrogoethite, which form grains or oolitic bobbins. *"Apparently, iron-bearing minerals are closer to coastal areas or are concentrated in the underwater parts of deltas <...> The source area of iron-rich minerals was the basic effusive rocks, the pebbles of which were recorded among the Ladin sandstones. The named rocks were*

Table 55

The average chemical composition of ferruginous sandy-siltstone Triassic rocks in the river Lena lower reaches.

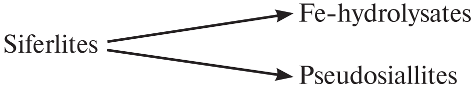
Compiled according to the data of A.V. Ivanovskaya, 1967 [113, p. 42–43]

Oxides and modules	I	II
	Siferlite	
n	2	3
SiO_2	60.02	56.18
TiO_2	0.96	1.76
Al_2O_3	13.12	10.14
Fe_2O_3	4.12	8.15
FeO	8.04	8.49
MnO	0.07	0.08
MgO	3.04	5.78
CaO	0.57	1.13
Na_2O	2.36	0.01
K_2O	0.90	0.88
H_2O	0.73	1.42
S	0.04	0.16
LOI	5.63	5.75
Total	99.58	99.92
HM	0.44	0.51
FM	0.25	0.40
AM	0.22	0.18
TM	0.073	0.173
FerM	0.87	1.40
NKM	0.25	0.09
AlkM	2.60	< 0.10

probably exposed to chemical weathering. Additional concentrations of minerals with a high specific gravity were created by natural dressing in the littoral zone" [113, p. 101–103].

Obviously, the conclusion about the participation of WCr in the formation of these pseudosiferlites can be made more confidently and not presumably. Indeed, A.V. Ivanovskaya points out that among the clay minerals, "mobile" chlorite and kaolinite are dominant – quite definite signs of humid weathering. And the localization of pseudosiferlites in the shallowest facies (in particular, they are present among sandstones with lingulas, but absent among siltstones with ammonoids) clearly indicates that these sediments were formed in the very immediate vicinity of the eroded weathering crusts along the mafic rock substrate.

Thus, it can be assumed that, in contrast to pseudosiallites (and some, and perhaps most of pseudohydrolysates), pseudosiferlites indicate not only the relationship of rocks with basites, but also the development of weathering crusts along basites. Thus, we can talk about two lines of paragenesis of siferlites:



6.4. Hydrolysates

Most of the hydrolysates are exogenous and are formed in weathering crusts on various substrates. However, there are also other hydrolysates – products of endogenous hydrothermal-metasomatic processes. These are many *argillisites* and rocks of the *secondary quartzite* formation. Diagnostics of convergent hydrolysates (especially metahydrolysates) is one of the lithochemistry global problems and we discuss it in detail in Ch. 9.

The hydrolysates classes are easily distinguished by the leading hydrolysed component — iron, aluminum, manganese, and, in rare cases, titanium. Specific types of hydrolysates are alum and dawsonite ones.

Al-hydrolysates. These include all industrial bauxite and clay rocks of bauxite-bearing weathering crusts. For example, in the Paleogene bauxite strata of Central Kazakhstan (Arkalyk deposit), it is possible based on analyzes given by V.S. Erofeev and Yu.G. Tsekhovsky [104, p. 178], to distinguish subtypes of titanium Al-hydrolysates (Table 56, Fig. 56): *normohydrolysates*, represented by kaolinite clays of cluster I and sample 19; *superhydrolysates*, represented by dried bauxite of clusters IIa and IIb, and *hyperhydrolysates*, represented by stony bauxite of clusters IIIa and IIIb.

Fe-hydrolysates. Fe-hydrolysates include *industrial iron ores*, the composition of which, in particular, is given in the summary by H. James [337]. They differ in age and mineral composition (Table 57, Fig. 57).

Oolitic hematite iron ores are certified as super- and normohydrolysates with huge values of FerM – up to 170. There is a tendency for the inverse correlation of HM with alkalinity and titanium value. The graph NKM–FerM shows that, regardless of the iron content, these ores fall into two groups: hypoalkaline (NKM <0.10) and alkaline (NKM 0.20–0.40). In particular, the first group includes the Lias ores of North Göttingen, Silurian ores in states of New York and Pennsylvania, Lower Ordovician in New Foundland.

Precambrian hematite and magnetite ores are mainly certified as normohydrolysates, the FerM in them reaches 129 with a moderate TM value.

Table 56

Chemical composition of variegated bauxite ore deposits in Central Kazakhstan. *Compiled according to V.S. Erofeev and Yu.G. Tsekhovsky, 1983 [104, p. 178]*

Oxides and modules	I	IIa	IIb	IIIa	IIIb	19
	Clays (Ti normohydrolysate)	Rusky bauxites (Ti superhydrolysate)		Stony bauxites (Ti hyperhydrolysate)		Clays (hypohydrolysate)
n	2	2	2	2	3	
SiO_2	36.95	19.69	11.17	4.89	2.33	47.27
TiO_2	2.52	4.41	2.42	2.60	2.89	0.60
Al_2O_3	37.50	45.22	49.39	58.54	45.72	35.23
Fe_2O_3	6.33	6.25	9.78	1.15	22.39	1.31
FeO	0.04	0.04	0.07	0.00	0.16	0.00
MnO	0.01	0.49	0.01	0.00	0.05	0.00
MgO	0.45	0.33	0.07	0.29	0.12	0.58
CaO	0.09	0.17	0.83	0.18	0.57	0.00
Na_2O	0.14	0.13	0.18	0.12	0.07	0.18
K_2O	0.14	0.12	0.08	0.11	0.08	0.18
P_2O_5	15.42	22.62	25.71	31.66	25.20	14.18
LOI	0.09	0.16	0.05	0.16	0.12	0.14
Total	99.65	100.01	99.72	99.68	100.15	99.67
HM	1.26	2.87	5.52	12.74	30.62	0.79
FM	0.18	0.34	0.89	0.29	9.75	0.04
AM	1.02	2.30	4.42	11.97	19.66	0.75
TM	0.067	0.097	0.049	0.044	0.063	0.017
FerM	0.16	0.14	0.19	0.02	0.46	0.04
NKM	0.01	0.01	0.01	0.00	0.00	0.00
AlkM	1.00	1.00	2.20	1.10	0.90	1.00

Note: CO_2 = 0–0.29, C= 0–0.21%.

There is a clear negative correlation between HM–NKM. The highest alkalinity (HKM 0.60) is the specularite (= hematite–magnetite ore) from Atlantic City, Wyoming (however, the total alkalinity remains very low, only 0.27 %).

Ferrous chlorites of the 7Å-septechlorite family are an important component of many Fe-hydrolysates. In contrast to the comparatively high temperature 14 Å-diseptechlorites, they can also form in sedimentogenesis: *"7 Å-chlorites are low temperature formations that form during sedimentation and diagenesis in weathering crusts, more often in shallow water areas, apparently in desalinated basins in weak basins. During catagenesis, as well as dur-*

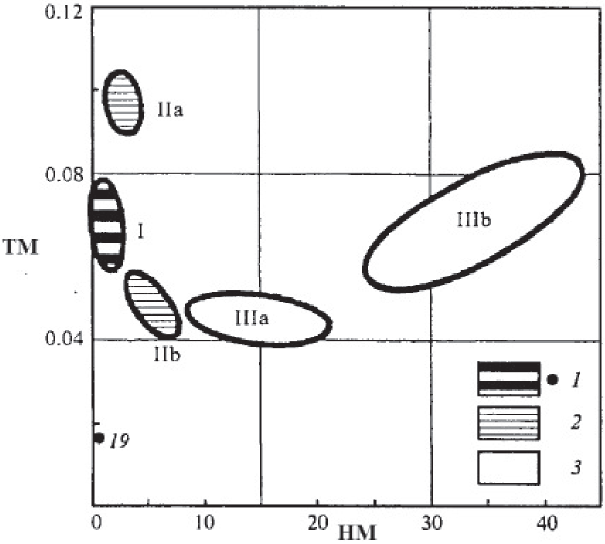


Fig. 56. Module diagram for rocks of the Paleogene bauxite strata of Central Kazakhstan.
Compiled according to V.S. Erofeev and Yu. G. Tsekhovsky, 1983 [104, p. 178].
1 – clays, 2, 3 – dry bauxite (2) and stony (3)

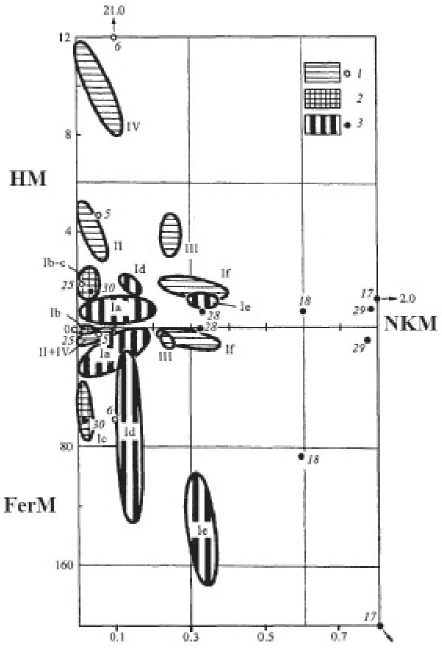


Fig. 57. Module diagrams for industrial iron ores.
Compiled according to H. James, 1966 [337, p. W18–W23].
Ores: 1 – Phanerozoic oolitic, 2 – uneven-aged, 3 – Precambrian

Chemical composition of industrial iron ores.
Compiled according to H. James, 1966 [337, pp. WI8–W23]

Oxides and modules	Ia	Ib	lc	ld	Ie	If	11	III	IV
	Normohydrolisate	Carbonate normohydrolysate	Normohydrolysate				Carbonate superhydrolysate	Superhydrolisate	Carbonate superhydrolysate
n	5	3	2	3	3	3	4	2	2
SiO_2	45.97	23.35	36.70	34.81	46.13	33.83	12.78	16.34	5.41
TiO_2	0.25	0.66	0.03	0.02	0.04	0.30	0.25	0.21	0.22
Al_2O_3	3.28	10.67	1.19	1.19	0.37	6.21	7.02	4.81	4.83
Fe_2O_3	13.28	4.44	44.49	35.20	50.26	45.67	36.64	55.52	31.24
FeO	22.15	20.71	15.22	20.03	2.05	1.32	10.46	0.21	15.31
MnO	0.28	0.16	0.08	0.33	0.01	0.32	0.24	0.15	0.18
MgO	2.81	2.93	0.97	1.49	0.15	1.29	2.53	1.77	1.33
CaO	1.83	14.89	0.26	0.59	0.41	3.42	12.80	8.70	21.05
Na_2O	0.12	0.15	0.01	0.01	0.08	0.07	0.14	0.07	0.13
K_2O	0.22	0.11	0.02	0.10	0.04	1.72	0.23	1.14	0.14
H_2O	3.17	7.28	0.47	3.93	0.25	4.02	4.07	2.62	3.34
P_2O_5	0.20	1.37	0.09	0.03	0.12	0.78	1.35	1.61	1.11
CO_2	6.35	11.64	0.59	2.59	0.06	1.93	10.49	6.69	15.97
$S+SO_3$	0.57	0.90	0.10	0.03	0.20	0.08	1.19	0.03	0.00
C	0.60	0.57	-	0.04	0.09	-	0.36	-	-
Total	101.06	99.83	100.18	100.43	100.26	100.97	100.53	99.84	100.22
HM	0.85	1.57	1.66	1.63	1.14	1.59	4.27	3.73	9.58
FM	0.83	1.20	1.65	1.63	1.14	1.43	3.88	3.52	8.86
AM	0.07	0.46	0.03	0.03	0.01	0.18	0.55	0.29	0.89
TM	0.076	0.062	0.021	0.017	0.117	0.048	0.035	0.044	0.045
FerM	10.13	2.23	49.40	46.04	126.58	7.27	6.51	11.13	9.27
NKM	0.10	0.02	0.02	0.14	0.33	0.29	0.05	0.25	0.06
AlkM	0.50	1.30	0.70	0.70	2.10	< 0.10	0.60	0.10	0.90

Table 57 *(continuation)*

Oxides and modules	6	17	18	25	28	29	30
	Carbonate hyperhydrolysate	Normohydrolysate	Hypohydralisate	Carbonatolite	Mn hypohydralisate		Carbonatic Mn pseudohydrolisate
SiO_2	2.59	46.94	56.23	15.60	51.18	48.11	29.35
TiO_2	0.10	0.01	0.02	0.18	0.51	0.52	0.01
Al_2O_3	0.75	0.01	0.45	6.96	11.95	3.27	0.70
Fe_2O_3	52.56	51.00	34.96	2.24	8.09	13.62	4.41
FeO	0.88	1.41	5.67	18.25	12.15	16.69	39.51
MnO	0.11	0.02	0.07	0.56	2.71	3.27	1.02
MgO	0.21	0.00	1.13	8.83	2.42	2.91	3.81
CaO	22.40	0.01	0.81	17.64	1.12	0.80	2.10
Na_2O	0.05	0.01	0.15	0.01	2.12	0.24	0.01
K_2O	0.03	0.01	0.12	0.02	1.86	2.32	0.01
H_2O	1.33	0.68	0.52	3.52	1.26	2.18	2.85
P_2O_5	0.08	0.39	0.05	0.80	0.54	0.44	0.14
CO_2	18.50	-	0.06	24.99	3.70	5.62	16.37
$S+SO_3$	0.32	-	-	-	-	-	0.06
C	0.08	-	-	-	-	-	0.08
Total	99.99	100.49	100.24	99.60	99.61	99.99	100.43
HM	21.00	1.12	0.73	1.81	0.69	0.78	1.56
FM	20.71	1.12	0.74	1.88	0.44	0.69	1.63
AM	0.29	0.00	0.01	0.45	0.23	0.07	0.02
TM	0.133	1.000	0.044	0.026	0.043	0.159	0.014
FerM	63.00	2621.50	86.60	2.95	1.84	8.86	63.30
NKM	0.11	2.00	0.60	0.00	0.33	0.78	0.03
AlkM	1.70	1.00	1.30	0.50	1.10	0.10	1.00

Note. Cluster Ia, sample 28–30 — silicate ferruginous rocks; cluster lb, sample 25 - chamosite rocks; clusters Ic, d, e, sample 17–18 — hematite rocks with magnetite; clusters lf, II, III, sample 6 — oolitic hematite iron ores; cluster IV is composed of different breeds.

ing experiments under conditions of increasing pressure and temperature, they transform into 14 Å-chlorites" [276, p. 72]. Chamosite is the basic component of Paleozoic and Mesozoic oolitic iron ores, and grinalite is an essential component of Precambrian ferruginous quartzites.

Judging by the H. James' summary, *chamosite ores* are normohydrolysates, among which there are carbonate varieties. Their iron content is much lower than in oxide ores (FerM is usually in the range of 2–4), and titanium value is generally higher – up to 0.093 in Lias calcite–chamosite ore from Gцttingen. Obviously, this is a manifestation of the Migdisov's law – dynamic sorting of sedimentary material.

Ferruginous quartzites of the Saksan formation of the Karelian age in the Krivoy Rog basin can serve as a typical representative of ancient Fe-hydrolysates [148]. Their average composition allows the rocks to be certified as hyperferrous, normotitanium normohydrolysates – HM 0.97, FerM 7.89, TM 0.039 (Table 58).

Table 58

Chemical ferruginous quartzites composition of the Saksagan Formation.
Compiled according to D. A. Kulik and V. V. Pokalyuk, 1990 [148, p. 40–41]

Oxides	Content, %	Oxides	Content, %
SiO_2	46.60	MgO	1.67
TiO_2	0.19	CaO	0.90
Al_2O_3	4.87	Na_2O	0.34
Fe_2O_3	28.02	K_2O	1.59
FeO	11.81	CO_2	3.19
MnO	0.08	Total	99.26

Although in the given example the TM is low, many Precambrian Fe-hydrolysates are characterized by an increased TM value, which may be genetically related to their formation over the titanium basite substrate. For example, the Vendian iron ores on the southern slope of the Dzhetym-Too ridge in the Naryn region of Kyrgyzstan (the Dangi iron ore site) have an increased TM (0.076–0.095) [53]. Here magnetite, hematite and martite[4] ores are distinguished from the oxidation zone, and the martitization of magnetite leads to an increase in TM. Since the FerM also increases, then, obviously, this process is accompanied by some loss of alumina.

A typical example of *Fe-hyperhydrolysates* can be industrial KMA ores, which are ancient lateritic WCr based on ferruginous quartzites of the Karelian age [34]. For example, at the Lebyazhin deposit, these ores consist of martite, hydrohematite, and hydrogoethite. As you can see from the

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[4] Martite is a pseudomorphosis of trigonal hematite over cubic magnetite, very typical for the oxidation zone of iron ore deposits with magnetite.

table 59, they have a huge HM and FerM, respectively – about 58 and 63, with normal TM value (0.052). The hydrolysate nature of these formations is also indicated by a high AM value (0.86).

More TM value (0.391) are the goethite iron ores known in the Paleogene deposits of the East European Platform; they are certified as *manganese Fe-hyperhydrolysates*: MnO 1.17%, $Fe_2O_3 = 77.92\%$, HM = 24.62, FerM = 36.45.

Table 59

Chemical composition of KMA (Kursk magnetic anomaly) industrial iron ores.
Compiled according to A.P. Bulgakova, 1967 [34, p. 55]

Oxides and modules	I	II	III	3	7
	Hyperhydrolisate		Ferruginous carbonatolite	Carbonate hyperhydrolysate	
n	2	3	3		
SiO_2	3.67	1.61	1.39	0.95	2.27
TiO_2	0.49	0.07	0.10	0.05	0.36
Al_2O_3	4.47	1.38	1.37	0.82	4.51
Fe_2O_3	71.96	86.12	29.85	64.39	54.62
FeO	8.20	5.02	35.68	18.27	19.85
MnO	0.05	0.04	0.07	О.Об	0.09
MgO	0.25	0.20	1.36	0.54	0.72
CaO	0.41	0.33	2.33	1.04	1.52
Na_2O	0.07	0.08	0.09	0.08	0.13
K_2O	0.05	0.04	0.05	0.04	0.05
P_2O_5	0.39	0.10	0.13	0.09	0.31
S	0.20	0.07	0.35	0.12	0.29
H_2O^+	5.74	2.69	1.61	1.05	4.35
C_{org}	0.28	0.09	0.28	0.14	0.51
CO_2	4.39	2.20	25.08	12.23	13.41
Total	100.59	100.03	99.73	99.87	99.97
HM	23.20	57.65	48.37	87.99	33.67
FM	21.91	56.85	48.24	87.58	33.12
AM	1.22	0.86	0.99	0.86	0.67
TM	0.109	0.052	0.069	0.061	0.235
FerM	16.20	62.66	44.68	95.08	39.98
NKM	0.03	0.08	0.10	0.15	0.12
AlkM	1.60	2.00	1.90	2.00	2.60

Note. Ores: 1 – weakly siderite hydrogoethite-martite; II – non-siderite martite; III – highly siderite martite; 3 – siderite martite; 7 – hydrogoethite-martite siderite

The alumosilicon module of these formations is also increased (AM 0.47) [214, p. 157].

Fe-hydrolysates, which are formed in weathering crusts over hyperbasites, are often “doped” with significant amounts of manganese, chromium, cobalt and nickel. Such are, for example, the formations of the Triassic–Jurassic gibbsite-bearing nickel-bearing WCr over the ultrabasic rocks of the Kola massif in the Northern Urals [147]. On the serpentinite substrate, rocks are formed containing 69 % Fe_2O_3, 1.08 % MnO, and 2.91 % NiO + + CoO + Cr_2O_3. They are certified as Mn–Fe *hyperhydrolysates* (HM 20.7). Along chloritized serpentinite less ferruginous and more aluminous rocks are formed, which are certified as super- and hyperhydrolysates (HM 9.3–39.4). They contain 17–35 % Al_2O_3, 22–48 % Fe_2O_3 and 1.62–2.68 % NiO + + CoO + Cr_2O_3.

An even more exotic type of Fe-hydrolysates are *natural schlichs* – accumulations of heavy minerals in alluvium. The composition of the *heavy fractions* gives an idea of these rare rock types. For example, B.M. Osovetsky [196], based on 185 analyzes, calculated 7 average heavy fraction compositions of the modern alluvium of the Kama region rivers. The processing of these figures makes it possible to group the alluvium into two "lithological" clusters. Cluster I corresponds to sandy and pebble alluvium. If this fraction was a real rock, it would be certified as *Cr–Ti–Fe–normohydrolysate* (Table 60).

Cluster II corresponds to clay and silty alluvium. The heavy fractions in them are much more titanium (TiO_2 8.50 % versus 2.25 %) and ferrous (Fe_2O_3 + FeO 24.23 + 6.63 % versus 14.26 + 5.03 %) and are certified as *Cr–Ti–Zr–Al–superhydrolysates* (ZrO_2 1.64 % versus 0.23 %).

Table 60

Average chemical composition of the heavy fraction of sandy and pebble alluvium (n = 4).
According to B.M. Osovetsky, 1986 [196, p. 165]

Oxides	Content, %	Oxides	Content, %
SiO_2	32.81	CaO	15.25
TiO_2	2.25	Na_2O	0.05
Al_2O_3	24.83	K_2O	0.02
Fe_2O_3	14.26	Cr_2O_3	0.87
FeO	5.03	H_2O	1.98
MnO	0.51	B_2O_3	0.17
MgO	1.35	ZrO_2	0.23
		Total	99.61

Ti-hydrolysates. Like the rock-forming aluminum and iron, titanium is also a hydrolysate element. However, due to the much lower clarke, strong titanium accumulations in hydrolysate products are much less common than the aluminum and iron concentrations. As a rule, the condition for such accumulations is the favorable titanium mineral form in the substrate (ilmenite) and the primary enrichment of the substrate with it – gabbroids, tuffs, or kimberlites. For example, A.D. Savko and A.D. Dodatko described the Devonian WCr based on the tuffs of the Antontaran formation of the Donbass, underlying the Frasnian deposits. This WCr is characterized by strong titanium accumulations in the form of anatase, reaching 13.38 % TiO_2 in the hematite–hydromica formations of the II (intermediate) zone of the WCr [233]. In the work by Yu.G. Tsekhovsky et al. [269, p. 42] provides data on the increased titanium value of the Jurassic bauxites of Syria (TiO_2 up to 4.5 %, TM up to 0.078) and genetically related iron ores (TM up to 0.120); the substrate of these rocks are basalts and their tuffs.

In the zone of interformational contact between the Riphean–Vendian Pre-Uralid complex and the Caledonian–Hercynian Uralid complex in the Subpolar Urals, the metamorphosed Cambrian weathering crust has been preserved in places. If it developed along the Vendian basaltoids – rocks markedly enriched in titanium (2–3 % TiO_2) and iron (13–15 % FeO + + Fe_2O_3), then these components accumulated strongly in WCr: up to 7–9 % TiO_2 in the form of leucoxene and about 25 % Fe_2O_3 in the form of hematite [111].

An interesting variety is represented by high-titanium weathering crusts by *alkaline ultrabasic rocks*. Table 61 and Fig. 58, ten analyzes of rocks from weathering crusts were processed for picrite porphyrites from one of the regions of Siberia [240].

Oddly enough, the original rocks are not at all rich in titanium[5] (1.7 % TiO_2), although a very high TM value (0.206) should be noted. Moreover, during the initial leaching and carbonatization (sample 2), the TiO_2 content even decreases (1.5 %), and TM also decreases (0.164). However, with the onset of hydrolysis in the zone of nontronitization (sample 4), hydromica (sample 3), and kaoliniteization (cluster I and sample 6), the TiO_2 content sharply increases (6.5–9.7 %), and the TM value also rises strongly (1.0–1.9). This tendency reaches its maximum in the oxides and hydroxides zone (cluster II and sample 8), where the TiO_2 content reaches 20 %, and TM – a fantastic value – 5.503. Due to the high titanium value, most weathering crust formations are certified as "titanium" hydrolysates

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[5] The accumulation of a small component in the weathering crust, judging by the B.L. Shcherbov's data [283], is a quite common phenomenon, and he connects this phenomenon with the elements' lateral redistribution in the WCr.

Table 61

Chemical composition of picrite porphyrite and products of its weathering, Siberian platform.

Compiled according to A.D. Slukin, 1967 [240, p. 157]

Oxides and modules	1	11	1	2	3	4	6	8
	Ti normohydralysate	Ti superhydralysate	Pseudohydrolisate	Mn carbonate pseudohydrolysate	Ti carbonate pseudohydrolysate	Ti pseudohydrolysate	Ti superhydralysate	Ti hyperhydralysate
n	2	2						
SiO_2	34.28	13.55	33.01	13.45	24.81	35.03	16.18	5.72
TiO_2	6.61	15.22	1.74	1.55	4.64	8.56	18.35	20.14
Al_2O_3	24.81	15.28	8.44	9.45	4.16	9.21	9.66	3.66
Fe_2O_3	17.98	41.61	6.97	13.07	14.32	25.76	41.35	56.35
FeO	0.00	0.00	7.19	27.27	1.87	1.46	0.29	0.00
MnO	0.39	0.35	0.18	1.24	0.36	0.01	0.23	0.01
MgO	0.57	0.36	22.35	6.14	9.83	3.75	0.56	0.82
CaO	0.61	0.76	9.86	1.80	18.97	0.79	1.09	0.28
Na_2O	0.47	0.12	0.43	0.31	0.28	0.08	0.12	0.24
K_2O	0.07	0.06	1.50	2.56	0.86	1.30	0.40	0.09
H_2O	12.57	11.53	4.61	3.71	7.30	12.32	9.72	10.35
CO_2	0.50	0.00	1.74	17.86	11.40	0.34	0.49	-
NiO	0.01	-	0.09	0.07	0.12	0.05	0.10	-
Cr_2O_3	0.02	0.11	0.17	0.23	-	0.10	0.10	-
P_2O_5	0.92	1.21	1.14	0.01	0.68	0.36	2.15	2.05
Total	99.79	100.14	99.54	99.72	99.69	99.34	100.79	99.71
HM	1.45	5.35	0.74	3.91	1.02	1.28	4.32	14.01
FM	0.54	3.10	1.11	3.46	1.05	0.88	2.61	9.99
AM	0.72	1.13	0.26	0.70	0.17	0.26	0.60	0.64
TM	0.266	0.996	0.206	0.164	!.! 15	0.929	1.900	5.503
FerM	0.58	1.38	1.41	3.78	1.88	1.53	1.49	2.37
NKM	0.02	0.01	0.23	0.30	0.27	0.15	0.05	0.09
AlkM	6.70	2.00	0.30	0.10	0.30	0.10	0.30	2.70

Note. I – kaolinized rock; II – zone of oxides and hydroxides; 1 – picrite porphyrite with phlogopite; 2 – disintegrated porphyrite; 3 – hydromica rock with calcite; 4 – nontronitized rock; 6 – kaolinized order; 8 – zone of oxides and hydroxides. SO_3 content = 0–0.22 %

or pseudohydrolysates (the latter are formations from the nontronite and hydromica zones, still retaining a significant amount of magnesium).

It is interesting how clearly on the “Alkali–HM” module diagram the processes of hydrolysis with the accumulation of alkalis (sample 1, sample 2) and leaching with the alkali loss (series from sample 1 to sample 8) are distinguished.

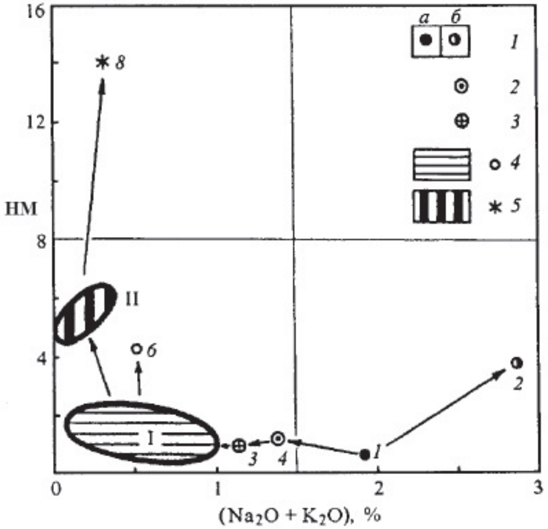

Fig. 58. Module diagram for WCr for picrite porphyrites.
Compiled according to the data of A.D. Slukin, 1967 [240, p. 157].
1 – initial (a) and disintegrated (b) picrite porphyrites. WCr zones: 2 – nontronite, 3 – hydromica, 4 – goethite–kaolinite, 5 – oxides and hydroxides

Hydrolysates associated with the alum process. It is known that the basic agent of terrestrial laterite weathering, starting at least from the Devonian, was soil humic acids. The products of the *alum process*, low temperature sulfuric acid weathering, which can develop during the oxidation of rocks with abundant sulfides, are much less common. Mineralogy of the alum process is very specific and was described in detail by E.A. Ankinovich in Kazakhstan [290] and Acad. N.P. Yushkin on Pai Khoi, where pyrite-rich black shales of the Carboniferous were weathered [297, p. 218–220]. The mineral indicators of the alum process include, firstly, various sulfates, sulfate phosphates and aluminosulfates, and secondly, halloysite and alunite.

The superposition of the alum process on the usual "humus" weathering can greatly complicate the final picture of weathering products. Early Paleogene karst formations (Khoper horizon) on the substrate of the Upper Cretaceous limestones of the Voronezh anteclise illustrate this situation.

Table 62 and Fig. 59 processed 14 analyzes of rocks of the Khoper horizon, which have a very variegated composition (from myosilites to alkalites). Due to the predominance of montmorillonite, halloysite, or metahalloysite with an admixture of allophane, boehmite, and kaolinite (in one of the samples and residual hydromica) among clay minerals Na-Ca montmorillonite, halloysite, or metahalloysite (in one of the samples and residual

Table 62

Chemical composition of clay formations of the Khoper horizon of the Voronezh anteclise.

Compiled according to B.V. Askochensky and V.P.Semenov, 1973 [9, p. 120–125]

Oxides and modules	I	IIa	IIb	III	1	2	3	6	8	12
	Hyposiallite	Carbonate hypersiallite	Normohydrolisate		Sulfate alkalite	Alkaline super-hydrolysate	Pseudo-siallite	Normo-hydrolisate	Alkaline hypo-hydrolysate	Normo-hydrolisate
п	2	2	2	2						
SiO_2	57.39	49.59	43.42	43.63	1.00	17.56	53.62	40.14	44.63	28.68
TiO_2	0.71	0.39	0.79	0.06	0.00	0.00	0.42	0.46	0.13	0.04
Al_2O_3	15.35	19.19	32.51	36.53	37.81	36.24	18.56	15.92	22.23	44.39
Fe_2O_3	1.72	7.56	5.42	1.46	0.00	0.00	6.20	26.44	7.16	3.51
MnO	0.10	0.05	-	-	-	-	0.05	0.05	0.03	-
MgO	2.34	0.92	1.31	0.19	0.18	0.07	3.10	0.56	1.26	0.81
CaO	3.09	10.38	1.72	0.26	0.11	0.70	1.03	6.67	4.18	4.56
Na_2O	0.61	1.16	1.03	3.84	1.94	1.51	1.16	0.92	5.23	0.69
K_2O	1.55	1.36	0.43	0.14	7.13	4.61	2.02	1.11	0.79	0.31
H_2O	5.24	-	-	-	0.38	3.26	4.14	8.32	-	-
P_2O_5	0.07	1.10	0.59	-	0.01	0.01	0.44	-	-	0.84
SO_3	0.55	-	0.03	-	7.81	0.94	0.05	-	-	-
LOI	11.82	9.28	13.84	13.73	44.29	35.59	9.01	-	9.81	15.93
Total	100.51	100.98	101.07	99.82	100.66	100.49	99.80	100.59	95.45	99.76
HM	0.31	0.55	0.89	0.87	37.81	2.06	0.47	1.07	0.66	1.67
FM	0.07	0.17	0.16	0.04	0.18	0.00	0.17	0.67	0.19	0.15
AM	0.27	0.39	0.75	0.84	37.81	2.06	0.35	0.40	0.50	1.55
TM	0.046	0.020	0.024	0.002	0.000	0.000	0.023	0.029	0.006	0.001
FerM	0.11	0.39	0.16	0.04	0.00	0.00	0.33	1.62	0.32	0.08
NKM	0.14	0.13	0.04	0.11	0.24	0.17	0.17	0.13	0.27	0.02
AlkM	0.40	0.90	2.40	28.40	0.30	0.30	0.60	0.80	6.60	2.20

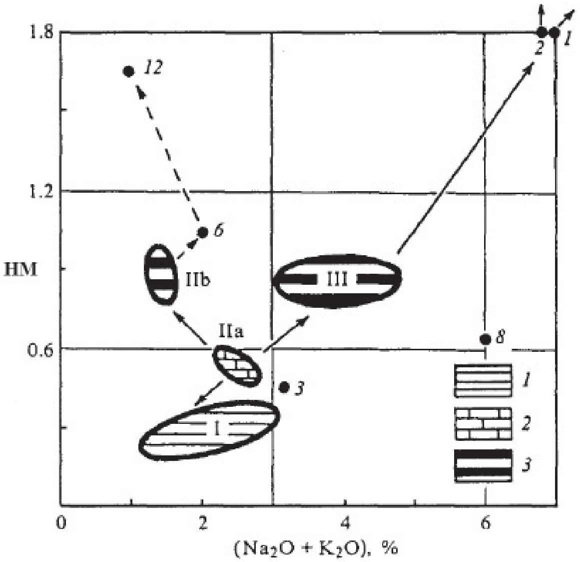

Fig. 59. Module diagram for clay formations of the Khoper horizon (Lower Paleogene). *Compiled according to B.V. Askochensky and V.P. Semenov, 1973 [9, p. 120–122, 124–125].* Clays: 1 – simple, 2 – carbonate, 3 – hydrolyzed. The arrows show the direction of the WCr formation processes

hydromica), the alkali content is unusual for pelitoids: either very low or with Na_2O dominance[6]. According to B.V. Askochensky and V.P. Semenov [9], the initial clay matter of the Khoper horizon was hydromica, which underwent both early weathering, coupled with the karst formation, and later, superimposed on karst eluvium. Such a late process was sulfuric weathering, which occurred due to the oxidation of pyrite from glauconite sands at the base of the Upper Paleocene (top of the Khoper horizon), as well as marcasite from clay eluvium on limestones of the Lower Santonian (bottom of the Khoper horizon). Thus, epigenetic transformations of two types are added to the "eluvial" weathering line of *hydromica ⇒ montmorillonite ⇒ kaolinite* [9, p. 135]: *kaolinite ⇒ halloysite ⇒ allophane ⇒ diaspore ⇒ (gibbsite); allophane ⇒ boehmite ⇒ alunite.*

Mn- and Fe–Mn–hydrolysates. If at low MnO contents, which constitute 0.1–0.3 % in most sedimentary rocks, the inclusion or non-inclusion of MnO in the hydrolysate module does not significantly change anything, then for Fe-Mn oxide ores, the calculation of HM without MnO would be a gross error.

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[6] For some reason, halloysite rocks with an admixture of allophane have such a composition.

In contrast to Al- and Fe-hydrolysates, the overwhelming majority of which is associated with the eluvial process – terrestrial (and less often underwater) weathering of the basic or ultrabasic substrate, Mn or (more often) Fe-Mn hydrolysates are usually volcanogenic sedimentary formations. Therefore, they are associated with silica deposits and tuffoids, which can be silites, alkaline siallites, and even alkalites.

As you can see from the table 63, Paleogene Fe-Mn ores of SE Armenia [6] are certified as hyperferrous (HM 16–53) superhydrolysates (HM 3.5–7.1), and among them there are carbonate varieties (CO_2 13.3–14.7 %), in which the MnO: MnO_2 ratio is higher than in non-carbonate ones.

These ores (cluster III) are in the most characteristic association with jaspers (cluster I) and tuffoids (cluster II), which also contain geochemical anomalies of manganese, often quite strong. For example, "diorite porphyrite tuff" contains 4.95 % MnO_2 and is certified as an alkaline hypohydrolysate. Another important feature of the paragenesis of rocks accompanying Fe-Mn ores is the presence of alkaline varieties both among jasper and tuffoids. Here we find even one alkalite – diorite porphyrite tuff.

In this situation, the genetic relationship between jasper and tuffoids is beyond doubt; in particular, one analysis of the most titanium jasper rock and three analyzes of tuffoids fall into the IIa cluster contour. Note the increase in titanium value in the series: jaspers (cluster I) ⇒ tuffoids + jasper (IIa cluster) ⇒ hydrolysate and alkaline tuffoids (cluster IIb). However, in the cluster of oxide ores (cluster III), the TM value is no longer higher than in cluster IIb.

Modern nontronite clays with abundant Fe and Mn hydroxides, which form hydrothermal hills at the bottom of the Pacific Ocean, can serve as a *prototype* of Meso-Cenozoic manganese hydrolysates [151]. As you can see from the table 64, they are characterized by hyperalkalinity (NKM from 1.1 to 25.4), which is 10 or more times higher than the norm for feldspars (which are also present in them). This phenomenon is explained by the sediments' composition: the replacement of the Al structural positions by the Fe^{3+} ion. This also explains the presence of a positive correlation FerM – NKM. However, the total alkalinity of these sediments is also high: in five samples out of 13, it is more than 5 %.

Such characteristics are completely uncharacteristic of residual Fe-hydrolysates from continental weathering crusts, where the accumulation of Fe^{3+} is preceded by the removal of alkalis. The fact is that in the modern ocean three processes are superimposed on each other: a) galmyrolysis of the basalt substrate with the Fe-smectites formation; b) Na^+ and K^+ absorption by them from sea water; c) an addition to the sediment of the coagulation products of Fe-Mn sols formed during the discharge of hydrothermal fluids into the bottom waters. Note that manganese sediments are well separated from ferruginous ones (samples 1–2, 9) on the FerM – NKM graph.

Table 63

Chemical composition of Cretaceous–Paleogene manganese-bearing rocks of southeastern Armenia.

Compiled according to P.F. Andrushchenko and A.T. Suslov, 1978 [6, p. 190]

Oxides and modules	I	IIa	IIb	IIIa	IIIb	7
	Jasper (supersilite)	Tuffs (alkaline normosiallite)	Tuffites (carbonatenormosiallite)	Manganese ore		Tuff (alkaline hypohydrolysate)
				(Mn superhydrolysate)	(carbonate Mn superhydrolysate)	
n	3	2	2	2	2	
SiO_2	91.93	59.34	37.45	13.84	11.83	52.34
TiO_2	0.00	0.88	0.39	O.O!	0.13	0.83
Al_2O_3	0.65	15.62	9.32	1.41	2.32	13.15
Fe_2O_3	5.43	4.65	3.50	6.62	7.87	12.12
FeO	0.00	0.70	0.54	0.00	0.00	0.00
MnO	0.59	0.29	0.61	61.10	35.87	4.06
MgO	0.08	1.56	1.19	0.53	1.27	0.98
CaO	0.31	5.05	22.94	3.24	16.79	3.74
Na_2O	0.07	4.34	1.10	0.13	0.04	2.60
K_2O	0.14	2.63	2.55	0.30	0.40	3.34
H_2O	0.64	1.74	2.49	3.70	4.49	3.81
P_2O_5	0.00	0.55	0.16	0.00	0.00	0.20
CO_2	0.04	2.28	17.16	1.83	14.04	0.65
Total	99.88	99.90	99.36	93.04	95.17	97.92
HM	0.07	0.37	0.38	5.00	3.90	0.58
FM	0.06	0.12	0.14	0.52	0.77	0.25
AM	0.0!	0.26	0.25	0.10	0.20	0.25
TM	0.005	0.056	0.041	0.004	0.054	0.063
FerM	9.20	0.34	0.48	48.02	17.92	1.16
NKM	0.33	0.45	0.39	0.31	0.19	0.45
AlkM	0.50	1.60	0.40	0.40	0.10	0.80

Note. MnO_2 is converted to MnO, therefore the analytical sums are underestimated. In sample 7, CoO = 0.65 % is determined. BaO content = 0–0.37 %

6.5. Magnesian "pseudo-sedimentary" rocks

In Ch. 2, we presented considerations in favor of distinguishing the magnesian rocks subtypes: pseudosilites, pseudosiallites (as well as pseudosiferlites), and pseudohydrolysates. The practice of lithochemistry fully justified the idea of isolating these taxa. Less confidently, one can speak of the correctness of the assignment of a such rocks' specific lower boundary in terms of the MgO content (3 %). This is where considerations of logic and practical convenience come into conflict.

At first, when developing a chemical classification, the lower limit was drawn differently: for pseudosilites and pseudohydrolysates, 3 % each, and

Table 64

Chemical composition of hydroxide–nontronite sediments
of the Galapagos hydrothermal hills.
Compiled according to V.B. Kurnosov, 1982 [151, p. 52–53]

Oxides and module	1	11	1	2	3	8	9
	Fe pseudohydrolisate	Fe hypohydrolisate	Mn alkaline pseudohydrolisate	Mn-Fe pseudohydrolisate	Fe alkaline pseudosiferlite	Carbonatolite	Mn pseudohydrolisate
n	6	2					
SiO_2	40.07	42.51	17.76	26.57	46.17	7.58	2.19
TiO_2	0.04	0.02	0.18	0.01	0.02	0.08	0.04
Al_2O_3	0.56	0.36	4.78	0.27	0.20	2.06	0.36
Fe_2O_3	21.56	22.47	2.40	16.23	24.02	1.30	0.55
FeO	0.79	0.69	0.37	0.37	1.27	0.60	0.30
MnO	0.69	0.07	34.97	23.81	0.09	0.19	58.36
MgO	3.41	3.04	3.34	1.61	3.19	1.13	3.43
CaO	3.06	0.86	0.46	0.93	0.39	43.18	0.62
Na_2O	2.34	2.68	4.50	2.67	1.78	2.32	2.83
K_2O	2.42	2.29	0.94	1.46	3.30	0.38	0.94
P_2O_5	0.25	0.31	0.22	0.24	0.28	0.13	0.26
LOI	24.95	24.85	30.19	25.55	19.49	41.15	30.21
Total	100.12	100.12	100.11	99.72	100.20	100.10	100.09
HM	0.59	0.56	2.40	1.53	0.55	0.56	27.22
FM	0.64	0.62	0.34	0.69	0.62	0.40	1.95
AM	0.01	0.01	0.27	0.01	0.00	0.27	0.16
TM	0.066	0.056	0.038	0.037	0.100	0.039	0.111
FerM	38.71	61.92	7.61	144.32	115.36	0.98	148.03
NKM	8.52	13.99	1.14	15.30	25.40	1.31	10.47
AlkM	1.00	1.20	4.80	1.80	0.50	6.10	3.00

for pseudosiallites, 5 % MgO [302]. However, later, our Uralian practice showed a great rarity of true sedimentary and metasedimentary siallites, which would contain more than 3 % MgO; usually all such rocks turned out to be pyrogenic (tuffoids). In order to increase the “sensitivity” of tuffoid diagnostics (which is especially important for predicting the ore content of sedimentary strata), the pseudosialites boundary was also lowered to 3% MgO [74, 297, 300, 308].

The prefix "pseudo" itself, with which we wanted to emphasize the specificity of the magnesian rocks composition, their difference from "normal" sedimentary rocks, can also be disputed. Perhaps it would be more correct to call them simply “magnesium-silites (-siallites, -hydrolysates)”. However, today we see no compelling reason to change both the boundary and the name of the aluminosilicate magnesian rocks.

The increased against the siallite standard magnesia content in non-carbonate (aluminosilicate) rocks can be caused by the presence of the following minerals: a) montmorillonite (especially its magnesian variety sepiolite), and sometimes glauconite enriched with a smectite component; b) chlorite – both endogenous 14-angstrom and exogenous 7-angstrom; c) palygorskite; d) magnesium sulfates and halides; e) magnesium carbonates – dolomite or even magnesite; f) amphiboles and pyroxenes; g) vermiculite, "hydrochlorites".

The presence of each of these minerals usually carries genetic information. Thus, the presence of amphiboles, pyroxenes, and 14- angstrom chlorite is possible either in petrogenic greywackes of the first cycle rock type or in pyrogenic tuffoids of basic and ultrabasic composition. Vermiculites and hydrochlorites are characteristic minerals of weathering crusts for the basic and ultrabasic substrates, and chamosite is a product of authigenic resynthesis from the material of erosion and near redeposition of such crusts.

Although montmorillonite clays are polygenetic, the peculiarities of the composition of montmorillonite make it possible to reveal two basic genetic lines: galmyrolysis of volcanic ash and weathering crust over the basic substrate [163]. Palygorskites also reveal two basic genetic lines – arid lithogenesis and halmyrolytic transformation of the basic pyroclastics in the modern ocean [160]. The formation of epigenetic dolomite, as shown by B.R. Shpunt using the example of the Riphean of Yakutia [279], is often an excellent lithological tuffoids indicator.

Finally, the presence of magnesium salts is the most striking indicator of arid lithogenesis – the final stage of the evaporite process.

Pseudosilites. These are such magnesian rocks in which the low HM module value is due not so much to the accumulation of SiO_2, as in real silites, but to the deficiency of alumina and iron. In particular, such formations as picrite tuffs can be pseudosilites. Many pseudosilites can be found among the ancient (Late Archean and Early Proterozoic – Karelian) black shales, and a significant part of iron in them may be present in the sulfide form [300]. Oddly enough, pseudosilites even include some clay rocks, for example, sepiolite–palygorskite argillites from Kizelovsky (C_1v) horizon of Bashkiria. Judging by the three analyzes given by R.T. Valiullina [41, p. 102], they have an average composition shown in table 65. The fact that the clay rocks turned out to be not siallites, but silites, is explained by their poor alumina, which, at a silica content normal for clays, gives a lower HM corresponding to silites.

In more rare cases, pseudosilites are clay rocks with montmorillonite and chlorite. Table 66 processed five analyzes of the Lower–Middle

Table 65

Average chemical composition of sepiolite–palygorskite argillites. *According to R.T. Valiullina, 1966 [41, p. 102]*

Oxides	Content,%	Oxides	Content,%
SiO_2	57.19	LOI	12.63
TiO_2	0.45	Total	100.58
Al_2O_3	8.17	H_2O^+	4.20
Fe_2O_3	2.20	H_2O^-	6.39
FeO	1.35	CO_2	1.97
MnO	0.01	HM	0.21
MgO	12.88	FM	0.29
CaO	2.94	TM	0.047
Na_2O	0.21	NKM	0.10
K_2O	0.59	AlkM	0.10

Table 66

Average chemical composition of the Jurassic clays of Moldova. *Compiled according to M.I. Zherou, 1978 [105, p. 144]*

Oxides and modules	I	II
	Clays and argillites	
	Pseudosilite	Pseudohydrolisate
n	3	2
SiO_2	60.17	48.32
TiO_2	0.48	1.01
Al_2O_3	11.72	20.57
Fe_2O_3	1.60	4.53
FeO	1.75	2.66
MgO	3.61	3.31
CaO	5.02	2.69
Na_2O	0.35	0.90
K_2O	0.71	3.85
LOI	10.46	11.43
Total	95.87	99.25
HM	0.26	0.60
FM	0.12	0.22
AM	0.19	0.43
TM	0.042	0.049
FerM	0.28	0.34
NKM	0.03	0.05
AlkM	1.80	0.30

Jurassic clays of Moldova (southern part of the Dnieper–Prut interfluve) [105]. These rocks form two groups, differing in alkalinity and HM. Cluster I (pseudosilites) has a low alkali content and a high silica content. Obviously, there is a lot of quartz here, and the clay matter is dominated by kaolinite, montmorillonite and chlorite, i.e., minerals with little or no alkali. Cluster II (pseudohydrolysates) differs by significantly higher Al_2O_3 and K_2O content. There is less quartz, and the leading clay minerals are hydromica, mixed-layer hydromica-montmorillonite, and chlorite.

Some *metamorphic* pseudosilites can be genetically associated with evaporite carbonates, which lost CO_2 during metamorphism. Table 67 shows the compositions of ancient apatite-bearing quartz-diopside rocks of the Archean Slyudyanka Group (Cisbaikalia), containing from 2 to 9 % P_2O_5 [286]. They are certified as pseudosilites, with very different alkalinity. Cluster I is represented by hypoalkaline pseudosilites (NKM 0.2), while cluster II, on the contrary, is hyperalkaline (NKM 1.8–3.1). The composition of the sample no. 3 with even higher alkalinity (NKM = 6.4) is outside the clusters. It seems that the primary substrate of these metamorphites was phosphate-bearing silica-carbonate sediments, since diopside could have formed from dolomite and quartz:

$$CaMg[CO_3]_2 + 2SiO_2 = CaMg[Si_2O_6] + 2CO_2.$$

However, where did such a high alkalinity come from? Even in alkali-rich rocks such as arkose, alkalinity generally does not rise above 0.60. In a 1:1 mixture of albite and orthoclase, the NKM is theoretically only 0.70 [295, p. 32]. No other alkaline silicates will also be able to provide such high NKM values that we see here. Therefore, it is necessary to admit the presence of evaporite minerals in the primary sediment, for example, chlorides or sulfates of Na and K. Perhaps it is no coincidence that the most alkaline compositions of cluster II and sample no. 3 contain notable sulphate impurities admixtures (there is little Cl in the rocks). This assumption is not trivial, since it does not fully agree with the paleogeographic reconstruction of N.I. Yudin and A.A. Arsenyev, according to which silica phosphate-bearing carbonate sediments belonged to the coastal marine facies [286, p. 99]. However, paleogeographic reconstructions for the Archean cannot claim to be reliable; one can't exclude that in that epoch, evaporite formation could have taken place in marine facies, and not only in lagoon ones, as in the Phanerozoic.

Pseudosiallites. Pseudosiallites include many bentonite clays composed mainly of minerals of the smectite subfamily. For example, out of 11 analyzes of industrial world bentonites, given by M.S. Merabishvili [176, p. 16–17], 7 are certified as pseudosiallites, since they contain 3.58–6.06 % MgO.

As one knows, among smectites there is a group of dioctahedral montmorillonite and trioctahedral saponite. In the first, the three-layer members belong to the pyrophyllite type, and in the second, to the talc.

Table 67

Chemical composition of apatite-bearing quartz–diopside rocks of the Slyudyanka Group of the Archean southwestern Cisbaikalia.

Compiled according to N.I. Yudin and A.A. Arseniev, 1970 [286, p. 86–87]

Oxides and modules	I	II	3
	Phosphate psemolite		
n	2	2	
SiO_2	60.59	69.71	66.68
Al_2O_3	1.08	0.07	0.11
Fe_2O_3	0.23	0.54	1.12
FeO	0.24	0.23	0.29
MnO	0.01	0.01	0.01
MgO	6.41	5.72	4.00
CaO	20.72	15.26	15.01
Na_2O	0.13	0.00	0.13
K_2O	0.11	0.17	0.58
H_2O	0.13	0.52	0.66
CO_2	0.83	3.65	2.55
P_2O_5	8.13	3.39	6.56
SO_3	0.00	0.23	0.16
F	0.66	0.52	1.34
C	0.01	0.01	0.02
Total	99.25	100.02	99.22
HM	0.03	0.01	0.02
FM	0.11	0.09	0.08
AM	0.02	0.00	0.00
FerM	0.44	12.00	12.91
NKM	0.22	2.54	6.45
AlkM	1.20	0.00	0.20

Montmorillonite group

Montmorillonite: $0.33Na \cdot 4H_2O \{(Al_{1.67}Mg_{0.33}) \cdot 2\ [Si_4O_{10}]\ (OH)_2$.

Beidellite: $0.5(1/2Ca, Na) \cdot 4H_2O \{Al_2[Al_{0.50}\ Si_{3.50}O_{10}] \cdot (OH)_2\}$.

Nontronite: $0.33Na \cdot 4H_2O \{Fe^{3+}{}_2\ [Al_{0.33}Si_{3.67}O_{10}) \cdot (OH)_2\}$.

Saponite group

Saponite: $0.33(1/2Ca, Na)\ 4H_2O \{(Mg_{3-2.25}Fe^{2+}{}_{0.-0.75})\ [Al_{0.33}Si_{3.67}O_{10}]\ (OH)_2\}$.

In the montmorillonite structure, an excess negative charge of three-layer packs is created due to the octahedral Al replacement by Mg, and in the other smectites structure, by the incorporation of a part of Al (and rarely Fe^{3+}) into silicon-oxygen tetrahedra. As you can see, in bentonites, the basic Al carriers are beidellite and montmorillonite, the Fe carrier is nontronite, Ca is beidellite, and Mg is saponite.

Obviously, the magnesian content of bentonites is related to the saponite amount. It should be the more, the more magnesian minerals (olivine, serpentine, Mg-pyroxenes and amphiboles, biotite) were in the substrate. Indeed, as A.D. Savko and A.D. Dodatko, who studied the Middle Devonian weathering crusts over the serpentinites of the Voronezh massif basement (Podkolodnov intrusion), point out *"if serpentinite prevails in the composition of the original rocks, then saponite prevails in the weathering crust among montmorillonites, if dark-colored minerals, then dioctasdric montmorillonite"* [233, p. 199].

A typical feature of industrial bentonites (Table 68) is low TM value and alkalinity (NKM): 10 analyzes out of 11 refer to hypotitanic (TM < 0.035) and 9 – to hypoalkaline (NKM < 0.20). In addition, one composition (coal-bearing strata of the Georgian Akhaltsykh deposit) is hydrolysate. It probably contains a kaolinite admixture.

Although palygorskite clays sometimes turn out to be pseudosilites, nevertheless most of them are certified as pseudosiallites. For example, of the 18 young and ancient palygorskite clays compositions given by O. S. Lomova, 13 are pseudosiallites [160].

Like pseudosilites, some *metamorphic* pseudosiallites can be associated with ancient evaporites. Table 69 and Fig. 60 give very unusual compositions of the high-pressure Archean talc-distene "white shales" of the Pamirs, described by T. F. Budanova (samples 10, 13). The reason for this is the enormous MgO content, reaching 26.8 % (sample 7). It may seem that this indicates a hyperbasic substrate of metamorphic rocks. However, this is clearly contradicted by their low titanium and iron value. Therefore, one should agree with T. F. Budanova, who accepts the interpretation of these shales as metaevaporites – "metaghalopelites" [33, p. 49]. Apparently, these were clay-magnesite sediments, and the clay matter was hydrolysate (otherwise it is difficult to explain the formation of the distene).

Pseudosiallites are often greywackes. For example, judging by 30 analyzes of the Lower Cretaceous flysch greywackes and the associated clay rocks of Kamchatka (Ilpinsky Peninsula) [169, p. 58–59], then 26 compositions are certified as pseudosiallites due to the increased MgO content (3–5.8 %) and only 4 – as normosiallites. This feature clearly highlights the specificity of these rocks as the basic greywackes, with a fifth of all compositions being superiron.

Oddly enough, pseudosiallites are even tillites, for example, given in the book by F. Pettijon [207, p. 227]. They are certified (Table 70) as hypo- and normotitanium pseudosiallites (except for obviously sandy rocks – an. 4, Brazil) – tab. 70.

Quite curious (not noticed by Pettyjohn) is a clear difference between the Permocarbonic tillites of Gondwana (South Africa and Brazil) from the Precambrian (Huronian) tillites of Laurasia. The former (cluster I) have a much lower total alka-

Table 68

Chemical composition of bentonite clays from exploited deposits.
Compiled according to M.S. Merabishvili, 1962 [176, p. 16–17]

Oxides and modules	Russia		Ukraine		Azerbaijan	Georgia			California	Colorado	Bavaria
	Super-siallite	Pseudo-siallite	Pseudo-siallite	Super-siallite	Pseudo-siallite	Hypo-siallite	Pseudo-siallite	Hypohydro-lisate	Pseudosiallite		
SiO_2	56.01	56.50	51.80	52.82	53.64	56.94	53.14	46.92	53.02	53.96	54.28
TiO_2	0.98	0.02	0.20	0.35	0.26	0.31	0.38	0.64	0.13	0.19	0.20
Al_2O_3	19.10	12.40	17.90	19.27	16.39	15.15	17.54	22.90	18.50	15.44	17.92
Fe_2O_3	8.88	6.18	2.09	7.58	2.73	2.57	4.08	3.22	2.33	1.12	3.88
FeO	-	0.57	-	-	-	0.12	0.22	2.08	0.13	0.01	-
MgO	2.33	6.06	3.58	1.80	4.32	2.59	4.64	2.02	4.04	6.99	3.76
CaO	2.07	3.75	1.75	1.53	2.12	1.36	2.91	1.94	0.80	0.80	1.80
Na_2O	0.08	1.90	0.50	0.20	1.19	0.14	1.82	1.24	3.80	0.94	0.10
K_2O	2.21	0.68	0.30	0.01	0.77	1.06	0.64	1.18	0.16	0.54	0.25
SO_3	0.31	0.18	0.19	0.01	0.06	0.50	0.07	0.26	-	-	-
H_2O	-	6.18	14.80	9.38	11.04	13.46	8.15	10.40	11.69	14.22	10.84
LOI	8.08	5.27	6.40	7.40	7.36	6.09	6.71	7.76	5.44	6.34	7.32
Total	100.05	99.69	99.51	100.35	99.88	100.29	100.30	100.56	100.04	100.55	100.35
HM	0.52	0.34	0.39	0.51	0.36	0.32	0.42	0.61	0.40	0.31	0.41
FM	0.20	0.23	0.11	0.18	0.13	0.09	0.17	0.16	0.12	0.15	0.14
AM	0.34	0.22	0.35	0.36	0.31	0.27	0.33	0.49	0.35	0.29	0.33
TM	0.051	0.002	0.011	0.018	0.016	0.020	0.022	0.028	0.007	0.012	0.011
FerM	0.44	0.54	0.12	0.39	0.16	0.17	0.24	0.23	0.13	0.07	0.21
NKM	0.12	0.21	0.04	0.01	0.12	0.08	0.14	0.11	0.21	0.10	0.02
AlkM	0.00	2.80	1.70	20.00	1.50	0.10	2.80	1.10	23.80	1.70	0.40

Table 69

The chemical composition of Archean talc–distene “white shales” of the southwestern Pamirs.

Compiled according to T. F. Budanova, 1991 [33, p. 48]

Oxides and modules	I	II	III	7	10	12	13
	Pseudo-silite	Pseudo-siallite	Alcaline pseudosiallite	Pseudo-silite	Pseudo-hydrolisate	Pseudo-silite	Pseudo-hydrolisate
n	4	3	2				
SiO_2	58.53	50.37	43.45	52.80	43.50	67.50	37.70
TiO_2	0.60	0.43	0.45	0.30	1.20	0.30	1.00
Al_2O_3	15.38	15.90	15.10	8.80	25.30	13.90	39.00
Fe_2O_3	0.65	0.70	1.60	0.70	1.40	0.20	0.30
FeO	1.18	0.67	0.65	0.60	3.60	1.10	0.80
MgO	13.28	21.53	26.00	26.80	18.00	9.20	10.60
CaO	1.15	2.33	1.15	2.40	0.30	1.10	0.80
Na_2O	0.95	0.87	1.00	1.00	0.80	0.60	0.60
K_2O	1.03	0.97	4.25	0.20	2.80	2.20	3.90
P_2O_5	0.13	0.07	0.11	0.09	0.20	0.03	0.20
LOI	6.93	5.93	5.95	6.10	2.60	3.90	5.70
Total	99.78	99.77	99.71	99.79	99.70	99.93	100.60
HM	0.30	0.35	0.41	0.20	0.72	0.23	1.09
FM	0.26	0.45	0.65	0.53	0.53	0.16	0.31
AM	0.26	0.32	0.35	0.17	0.58	0.21	1.03
TM	0.039	0.027	0.030	0.034	0.047	0.022	0.026
FerM	0.11	0.08	0.14	0.14	0.19	0.09	0.03
NKM	0.13	0.12	0.35	0.14	0.14	0.20	0.12
AlkM	0.90	0.90	0.20	5.00	0.30	0.30	0.20

linity and sodium content than the latter (cluster II), which contain 6.6–7.5% alkalis. It can be assumed that original (including sodium-rich?!) weathering crusts served as the starting material for the older tillites.

Pseudohydrolysates. Typically, among the pseudohydrolysates, two genetic lines can be distinguished. The first is volcano-sedimentary or non-sedimentary rocks. In particular, judging by the average figures calculated by A. A. Beus, basalts of platforms and geosynclines (HM 0.60), as well as their metamorphic analogs, amphibolites and eclogites[7] (HM 0.59), are certified as pseudohydrolysates [18, p. 283, 286]. The second line is the magnesian products of the weathering crust over magnesian-ferruginous basic or ultrabasic rocks.

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[7] Note that eclogites turn out to be supertitanium rocks (TM 0.083). Therefore, O. M. Rosen's ingenious idea, suggesting that dolomite montmorillonite clays could have been the primary substrate of eclogites [222], seems questionable. Such clays are usually certified as hypotitanic (more rarely, normotitanium) siallites, and not as hydrolysates.

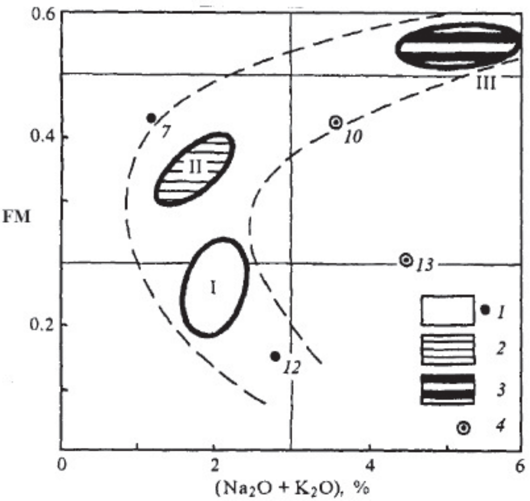

Fig. 60. Module diagram for the Archean talc–distene "white shales" of the southwestern Pamir. *Compiled according to T. F. Budanova, 1991 [33, p. 48].*
1 – pseudosilites, 2 – pseudosiallites, 3 – alkaline pseudosiallites, 4 – pseudohydrolysates

Such, in particular, are the montmorillonite clays of the Upper Jurassic carbonate volcanic formation in Armenia [205]: 4 out of 5 compositions given by I. Kh. Petrosov (Table 71) unexpectedly turn out to be pseudohydrolysates (and not pseudosiallites, which would be clearer). Perhaps this is one of the specific features of the apobasite montmorillonites enriched in iron? This assumption is consistent with normal (and not decreased) TM value (TM in four analyzes 0.043–0.051) and increased FerM value of three compositions (FerM 0.56–0.75). Note that the composition of the palygorskite "mountain skin" (sample 6) is clearly distinguished by the minimum TM, HM, and NKM values of.

The same genetic line is also seen in the composition of *glauconites* – hydrolysate formations associated with underwater weathering. Those of glauconite rocks in which the proportion of the smectite component is increased (and, accordingly, the proportion of the Fe-hydromica component is decreased), may turn out to be magnesian. Their distinctive feature is their high total alkalinity (alkaline pseudohydrolysates). Such compositions can be found, for example, in the V. I. Muravyev's work on glauconites from the Cretaceous and Paleogene deposits of the Russian platform [182, p. 96–97].

An important tendency in the prevalence of pseudohydrolysates genetically associated with terrestrial weathering crusts should be noted: they are characteristic of ancient WCrs (Precambrian and Lower Paleozoic) and are not characteristic of younger WCrs, where, apparently, magnesium was removed more intensively.

Table 70

Chemical composition of tillites.

Compiled according to F. Pettijohn, 1981 [207, p. 227]

Oxides and modules	I	II	4
	Pseudosiallite	Alcaline pseudosiallite	Myosilite
n	2	3	
SiO_2	60.45	62.75	80.34
TiO_2	0.53	0.52	0.42
Al_2O_3	13.46	16.11	7.66
Fe_2O_3	2.05	2.01	1.39
FeO	4.63	4.55	0.72
MnO	0.45	0.09	-
MgO	3.51	3.43	0.83
CaO	3.80	0.66	1.51
Na_2O	2.13	3.62	2.13
K_2O	2.40	3.51	1.94
P_2O_5	0.24	0.21	0.01
H_2O^+	-	2.44	-
CO_2	-	0.22	-
LOI	7.76	0.22	2.63
Total	101.39	100.33	99.58
HM	0.35	0.37	0.13
FM	0.17	0.16	0.04
AM	0.22	0.26	0.10
TM	0.039	0.032	0.055
FerM	0.51	0.40	0.26
NKM	0.34	0.44	0.53
AlkM	0.90	1.00	1.10

An example is the Early Paleozoic chlorite-montmorillonite weathering crusts described by A.D. Savko [232] for the Precambrian basic rocks of the Voronezh anteclise, where the initial decomposition products are certified as pseudosiallites. We deal with this issue in more detail in Ch. 8. It is obvious that t*he presence of true hydrolysate formations among the "pseudohydrolysates"* does not at all embellish this term. Therefore, it would be highly desirable, leaving the subtype of pseudohydrolysates in the classification, to divide the taxon of "true hydrolysates" into two classes – magnesian and all others:

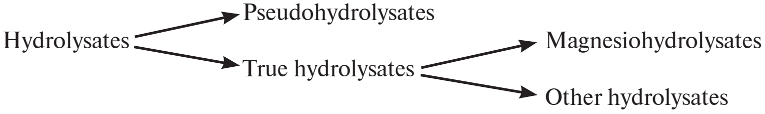

Table 71

Chemical composition of montmorillonite clays of the Upper Jurassic carbonate–volcanogenic formation in Armenia.
Compiled according to I. Kh. Petrosov, 1983 [205, p. 86]

Oxides and modules	1	11	3	6
	Pseudohydrolisate		Pseudohydrolisate	Pseudosiallite
n	2	2		
SiO_2	43.75	38.94	43.04	50.76
TiO_2	0.76	0.66	0.83	0.28
Al_2O_3	16.67	16.92	16.23	10.60
Fe_2O_3	8.45	4.22	11.50	4.68
FeO	1.34	2.12	1.32	-
MnO	0.06	0.46	0.04	0.04
MgO	3.51	3.49	4.14	8.90
CaO	2.63	9.72	3.17	0.91
Na_2O	0.50	0.69	0.81	0.77
K_2O	0.93	3.32	1.01	0.00
H_2O	12.13	6.18	10.25	9.28
LOI	9.82	13.79	8.14	14.04
Total	100.51	100.48	100.48	100.26
HM	0.62	0.63	0.70	0.31
FM	0.30	0.25	0.39	0.27
AM	0.38	0.43	0.38	0.21
TM	0.046	0.039	0.051	0.026
FerM	0.56	0.39	0.75	0.43
NKM	0.09	0.24	0.11	0.07
AlkM	0.50	0.20	0.80	-

The problem, however, is that we do not have a formal criterion to distinguish magnesiohydrolysates from pseudohydrolysates. Therefore, there is still no reason to change the scope of the term “pseudohydrolysates”, already so widely used for diagnostics of pyrogenic and petrogenic rocks [74, 297].

6.6. Alkalites

Alkalites include rocks containing more than 8% alkalis. Since some of these rocks are rich in mica (an alumina mineral), then, according to the HM module, they can turn out to be hydrolysates, and dawsonite rocks – simultaneously alkalites, hydrolysates, and carbonatolites. Nevertheless, the parameter $Na_2O + K_2O$ in this case is "older", and all such rocks are certified as alkalites.

Note that many magmatic rocks are also alkalites, in particular, alkaline volcanics of folded regions, studied by A.S. Ostroumova and N.A. Rumyantseva [198]. For example, trachyliparites, biotite-sanidine trachytes of the Caucasus, and epileucite porphyrites of the Pambak Ridge are certified as hypotitanium alkalites (TM_{av} 0.014–0.026, $(Na_2O + K_2O)_{av}$ 9.60–13.56 %), while trachyandesite porphyries of the Eastern Urals turn out to be normotitanium alkalites (TM_{av} 0.042, $(Na_2O + K_2O)_{av}$ 9.36 %).

Among sedimentary and metamorphic alkalites, at least five genetic lines can be distinguished:

a) potassium *micaceous* (hydrolysate) alkalites, as a rule, associated with the formations of the humid (laterite) weathering crust, often over the ash substrate (metabentonites); rarely, such rocks turn out to be high-temperature K-metasomatites.

b) potassium *mica-orthoclase* alkalites are characteristic of ancient red-colored strata and represent very remarkable sedimentites – high-potassium arkoses or high-potassium clays, products of specific arid weathering of an acidic substrate [298].

c) sodium–potassium *feldspar* alkalites, most often represented by acidic or alkaline tuffoids and less often metasomatites.

d) sodium alkalites – *albitolites*; these are Na-metasomatites or (less often) exotic diarenetic formations associated with evaporite facies.

e) sodium *carbonate* alkalites – dawsonite rocks associated with the epigenetic transformation of sodium pyroclastics.

Potassium micaceous alkalites. On the ridge Maldynyrd (the Subpolar Urals) one knows aporiolite alkalite-*sericitolite*. These can be both metasomatites and formations of the ancient weathering crust over Vendian rhyolites [111, 304, 308]. Although the initial rhyolites contain 3–4 % Na_2O, a characteristic feature of the Maldy sericitolites is the almost complete absence of sodium – these are quartz-sericite shales connected by transitions with pyrophyllite and diasporic shales. In this case, we have an example of a difficult genetic problem – distinguishing between endogenous and exogenous highly alkaline formations. We discuss this problem in detail in Ch. 9.

Strong accumulations of potassium are characteristic of apo-ash bentonites. For example, as can be seen from the J. Bowles and D. Coombs' source materials [322, p. 164], among 17 analyzes of zeolitized Triassic tuffs of New Zealand, 6 according to the NKM module are certified as super- and hyperalkaline, and among tuffogenic bentonites there is also one alkalite ($Na_2O + K_2O = 8.27$ %) – a product of allochemical degeneration of tuffs.

Table 72 and in Fig. 61 considers the compositions of the Silurian metabentonites of Ireland and their host shales [324]. Of the 11 analyzes of metabentonites, 8 are certified as potassium alkalites with a K_2O content of up to 9.1 %. This alone is enough to correctly diagnose these rocks as volcanogenic-sedimentary and distinguish them from the host turbidite shale. However, the latter also have a volcanic admixture: four out of five compositions are certified as pseudosiallites.

Table 72

Chemical composition of the Silurian metabentonites and the host shales of Northern Ireland.

Compiled according to T. Cameron and T. Anderson, 1980 [324, p. 66–67]

Oxides and modules	Ia	Ib	IIa	IIb	IIc	15
	Shales		Metabentonites			Shale
	Carbonate pseudosiallite	Pseudo-siallite	Alkalite		Alkaline hypohydrolysate	Pseudo-siallite
n	2	2	6	3	2	
SiO_2	52.85	52.95	53.73	52.72	52.23	61.60
TiO_2	0.70	0.94	0.78	1.05	1.49	0.84
Al_2O_3	10.74	17.37	25.19	24.74	25.04	15.80
Fe_2O_3+ FeO	5.03	8.77	2.53	3.80	3.65	7.38
MnO	0.12	0.06	0.03	0.01	0.04	0.05
MgO	3.20	6.33	2.66	3.27	2.25	4.15
CaO	12.40	2.73	1.06	0.63	0.64	0.94
Na_2O	2.02	1.10	0.68	0.12	2.49	1.15
K_2O	1.64	3.26	8.08	8.32	5.50	2.70
P_2O_5	0.16	0.20	0.17	0.20	0.42	0.17
CO_2+ H_2O	11.75	7.04	5.19	5.08	5.31	4.53
Total	100.60	100.72	100.09	99.93	99.05	99.30
HM	0.31	0.51	0.53	0.56	0.58	0.39
FM	0.16	0.29	0.10	0.13	0.11	0.19
AM	0.20	0.33	0.47	0.47	0.48	0.26
TM	0.065	0.054	0.031	0.042	0.060	0.053
FerM	0.45	0.48	0.10	0.15	0.14	0.45
NKM	0.34	0.25	0.35	0.34	0.32	0.24
AlkM	1.20	0.30	0.10	< 0.10	0.50	0.40

Curiously, on the HM – TM graph, one cannot achieve complete discrimination of lithotypes: cluster Ib of host shales and cluster IIc of bentonites are very close. On the other hand, in terms of iron content, bentonites are very distinct: if for the host shales the FerM is 0.44–0.49, then for metabentonites it is only 0.06–0.16. And since the titanium value in most of these bentonites is noticeably lower, the best plot is TM – FerM, where 5 clusters and one partially anomalous composition of the host shales are distinguished (sample 15). It is remarkable that in bentonites there is a positive correlation TM–FerM, and in shales – a negative one. In addition, bentonites exhibit a bright specificity in trace elements. They are characterized by geochemical anomalies of barium (600–2000 versus background for shales 350–830 ppm), zirconium (600–900 versus 150–200 ppm, respectively) and yttrium (80–100 versus 30–40 ppm). Note that the Zr accumulation due to diagenetic hydrolysis of volcanic ash was also noted by St. Petersburg geologists for the Vendian tuffoids of the Russian Platform [27].

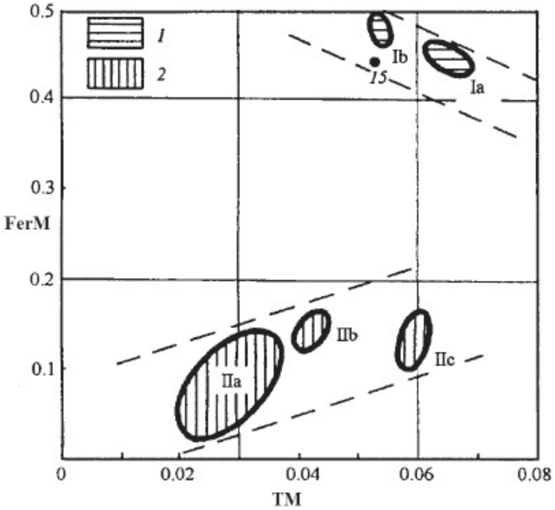

Fig. 61. Module diagram for Silurian metabentonites (1) and host shales (2), Northern Ireland. *Compiled according to T. Cameron and T. Anderson, 1980 [324, p. 66–67]*

Feldspar alkalites. Feldspar potassium alkalites are alkaline metasomatites on the rhyolite substratum in the Northern Urals – this is the so-called *Syvyaga apovolcanites type* identified by B.A. Goldin and colleagues. With the SiO_2 contents 72.0–76.7, Al_2O_3 10.5–15.0 %, they contain 6–9 % K_2O and 1.5–2.1 % Na_2O, so that the total alkalinity reaches 10.6 % [8].

Feldspar alkalites are sometimes found among psammites. Concerning the origin of the rare lithotype of feldspar sandstones (feldspars 75 % and more, up to 90–95 %), V.N. Shvanov notes: "*Apparently, such rocks can be formed due to local erosion of magmatic average and alkaline rocks, especially due to the washing of crystalline pyroclastics" especially due to the washing of crystalline pyroclastics*" [276, p. 120].

According to P. V. Markevich, in the upper section of the Lower Cretaceous arkoses of the Sikhote-Alin (the Yuzhny Luzhkin formation and the Uktur formation of the Northern Sikhote-Alin), the sandstone composition slightly increases the content of acute-angled fragments and whole crystals of feldspar and decreases the quartz grains content. In his opinion, this "*may testify in favor of some volcanic processes' influence*" [169, p. 30]. Accordingly, he considers it possible to qualify such rocks no longer as sandstones, but as "psammitic crystal-clastic tuffites". Indeed, in the "sandy-clay flysch" strata of the Uktur formation, we find an average composition (n = 5), in which the Na_2O content is 6.63 % and K_2O is 1.67 %. Thus, this sodium alkalite is probably substantially albitic. Such a specific composition can be considered confirmation of the diagnosis by P. V. Markevich.

Alkalites are often acidic Precambrian metamorphites – *leptites*. Thus, of the 24 analyzes of the Katarchean leptite gneisses and porphyroids of the Amedichin complex (Aldan shield), given by L.M. Reutov, 17 are certified as alkalites, while others are hyperalkaline myosilites with a total alkalinity of 7–8 %. A sharp K_2O accumulation (up to 8.8%) and extreme NKM values – up to 0.78 – are typical. L.M. Reutov considers these rocks as metariolites and acidic metatuffs [221].

A very peculiar type of alkalite is *metasomatites on the substrate of sedimentary rocks*. Table 73, 11 analyzes of alkaline metasomatites were pro-

Table 73

Chemical composition of alkaline metasomatites and original sandstone. *Compiled according to A. M. Blokh and I. V. Daraeva, 1984 [20, p. 97]*

Oxides and modules	I	IIa	IIb	1	11
	Feldspar metasomatite (alkaline myosilite)	Potassium feldspar metasomatite (alkalite)		Sandstone (normosilite)	Feldspar metasomatite (alkalite)
n	3	4	3		
SiO_2	74.30	75.77	67.40	74.86	68.57
TiO_2	0.41	0.41	0.44	0.23	0.63
Al_2O_3	12.27	10.67	13.58	10.46	15.73
Fe_2O_3	2.52	1.97	2.66	2.12	3.62
MnO	0.02	O.O!	0.03	0.05	0.14
MgO	0.18	0.20	0.59	0.94	0.10
CaO	0.59	0.39	1.06	2.15	0.28
Na_2O	4.65	0.22	0.13	1.80	6.10
K_2O	3.19	9.32	11.77	2.92	3.35
P_2O_5	0.06	0.03	0.04	0.04	0.04
BaO	0.08	0.09	0.11	0.08	0.07
LOI	1.59	0.93	2.54	4.11	1.36
Total	99.87	100.01	100.33	99.76	99.99
CO_2	0.75	0.44	1.45	2.50	0.10
HM	0.20	0.17	0.25	0.17	0.29
FM	0.04	0.03	0.05	0.04	0.05
AM	0.17	0.14	0.20	0.14	0.23
TM	0.033	0.039	0.032	0.022	0.040
FerM	0.20	0.18	0.19	0.20	0.23
NKM	0.64	0.89	0.88	0.45	0.60
AlkM	1.5	< 0.10	< 0.10	0.60	1.80

cessed on the substrate of Jurassic arkose sandstones of the Pristanovoy trough [20], and Fig. 62 shows them in comparison with the original sandstone composition.

It turns out that essentially potassium metasomatites can be distinguished from two-feldspar: the former are certified as alkalites, the latter as alkaline myosilites (the only exception is anomalous sample 11, which also turned out to be alkalite). The original arkose sandstones are classified as normosilites. A distinctive feature of metasomatites in comparison with their sedimentary substrate can be considered high alkalinity and a significant scatter of HM values (from 0.17 to 0.29 versus 0.17 in the substrate). The latter caused the looseness of cluster I and the formation of two isolated groups in cluster II: IIa and IIb. Obviously, at the first stage of feldspathization, the quartz amount does not change significantly (HM almost does not increase), and then the alkalis addition is accompanied by the silica removal. The NKM value changes especially sharply – from 0.60 to 0.89 versus 0.45 in the substrate.

In this case, it is of exceptional interest that the feldspathization process developed over the substrate of unmetamorphosed sedimentary rocks! It turns out that such cases are by no means rare: "*In many cases, feldspathization in unmetamorphosed sedimentary deposits is of endogenous nature and corresponds to the tectonic–metasomatic activation stage of the region. Needless to say, how important it is for a correct understanding of the studied object's geological history, the ore concentrations genesis, which are often confined to feldspathic rocks, and, accordingly, for the selection of the most effective methods for*

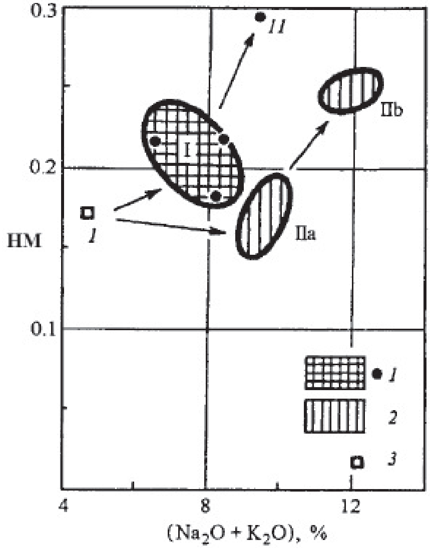

Fig. 62. Module diagram for alkaline metasomatites on the substrate of the Lower Jurassic sandstones; Pristanovoy trough, south of the Aldan shield.
Compiled according to A.M. Blokh and I.V. Dagaeva, 1984 [20, p. 97].
1, 2 – two-feldspar (1) and K-feldspar (2) metasomatites; 3 – original arkose sandstone of the Yukhta Formation

mineral deposits prospecting, to be able to distinguish endogenous manifestations of newly formed feldspars from authigenic ones” [20, p. 90].

A.M. Blokh and I.V. Dagaeva made a very useful summary (Table 74) showing important diagnostic differences between authigenic (hypergenic, low-temperature) feldspars and endogenous (high-temperature) feldspars.

Among the feldspar Na-alkalites are rare rocks described by Slovak geologists – *sedimentary albitolites* [328].

Table 74

Signs of authigenic and endogenous feldspathization
in unmetamorphosed sedimentary strata.
According to A.M. Blokh and I.V. Dagaeva, 1984 [20, p. 91]

<table>
<tr><th>Feature categories</th><th>Authigenic feldspathization</th><th>Endogenous feldspathization</th></tr>
<tr><td>Temperature</td><td colspan="2">No evidence of temperature increases during the formation of newly formed feldspars</td></tr>
<tr><td>Quantitative</td><td>Newly formed feldspars almost never become the main component of altered rocks: they account for no more than 5% of the feldspar material available in the rock.
Potassium feldspar is more often formed in sandstones, albite - in greywackes.</td><td>Striving for the formation of monomineral potassium feldspars and albitites; the share of newly formed feldspars accounts for up to 80% of the feldspar material present in the rock.
The composition of the newly formed feldspars does not depend on the primary composition of the altered rocks.</td></tr>
<tr><td rowspan="4">Mineralogical</td><td colspan="2">Fouling around detrital grains and in the form of newly formed crystals without traces of pre-existing nuclei</td></tr>
<tr><td>Random distribution of crystals in the rock, which usually "float" in cement of different composition</td><td>Preferential development in the form of microcrystalline cement, subordinate value of idiomorphic crystals</td></tr>
<tr><td colspan="2">Albite crystals are larger than potassium feldspar crystals. Albite grows without celonucleation, less often around detrital grains of any composition; potassium feldspar almost always grows around debris grains of the same composition</td></tr>
<tr><td>High degree of ordering of potassium feldspar.
Transparent appearance of crystals of potassium feldspar.
The majority of albite inclusions are not twinned.</td><td>Intermediate degree of ordering of potassium feldspar.
Turbid (pelitized) appearance of crystals of potassium feldspar.
The majority of albite inclusions are twinned.</td></tr>
<tr><td>Geochemical</td><td>Lack of impurities of foreign elements</td><td>The presence of impurities of foreign elements</td></tr>
</table>

They form small concretions, macroscopically almost indistinguishable from the host Permian lilac-grey siltstones, and gradually pass into them. Therefore, their morphology and distribution in the section were not precisely established. It is assumed that they are distributed irregularly, accumulating in separate layers and interlayers. Such formations with a thickness of up to 2 m and more are described in the Northern Hemerides in two areas, in mine workings and boreholes. The concretions are composed of albite (70–80 %) and Fe-carbonate such as mesitite or ankerite (30–20 %). Chlorite, illite are present as a small impurity, and tourmaline, apatite, pyrite, chalcopyrite, barite and low-temperature cristobalite are present in accessory amounts. Albite has all the characteristics of an authigenic low-temperature mineral: small crystal sizes (< 1 mm), their idiomorphism, characteristic quaternaries of the Rock-Tournais type, 2V 78–80°, high purity (only 3 % An). All these features, combined with the increased contents of strontium and boron in the rocks (up to 1500 and 882 ppm, respectively), indicate a relationship between albitization and evaporite facies, moreover, under conditions of extremely weakened terrigenous drift (absence of clastic material).

For albite formation, highly alkaline waters with high concentrations of Na^+ and SiO_2 were needed. Slovak geologists suggest that the albitization process took place in early diagenesis, although a later process is not excluded, since albite veins have also been described in addition to concretions. Nevertheless, the idea of syngeneticity of albitolites is generally accepted [328].

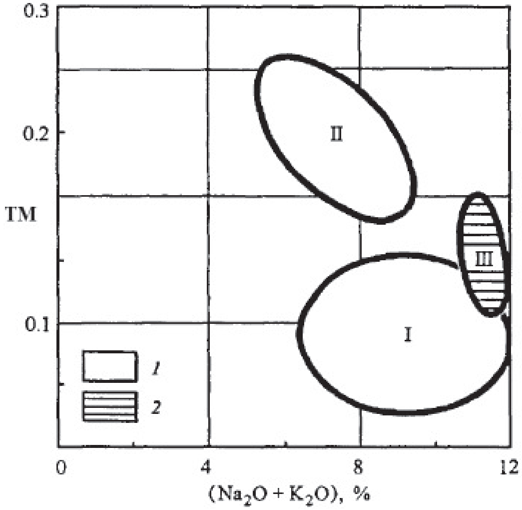

Fig. 63. Module diagram for Perm albitolites from the Northern Hemerida, Slovakia. *Compiled according to I. Tsurlik et al., 1984 [328, p. 732].*
1 – rocks, 2 – insoluble residues

On the module diagram (Fig. 63), one can distinguish clusters I–II of the rocks themselves (differing in carbonate content, which can be judged here by the LOI, FeO, MgO values), and also show the average composition of their insoluble residues (cluster III). It is curious that in the most carbonate rocks of cluster II the alkalinity (NKM) is noticeably lower than in the insoluble residues (Table 78). This can be explained by the heterogeneity of the statistical sample (i.e., it is possible that these rocks are actually more clay than in cluster I), and the presence of non-silicate aluminum (?!) in them. This assumption is not trivial and deserves attention.

Tabl

Dawsonite alkalites. Dawsonite rocks, which combine high alkalinity, carbonate and hydrolysate content at the same time, represent an extremely unique class of alkalites. As one can see from the table 76 and fig. 64, 18 analyzes of Tournaisian dawsonite rocks of the Pripyat depression [89] form

Table 75

Average chemical composition of Permian albitolites from Northern Hemerides, Slovakia.
Compiled according to J. Tsurlik et al., 1984 [328, p. 732]

Oxides and modules	I	II	III
	Albite rocks		Insoluble residues (alkalite)
	Alkalite	Alkaline pseudosiallite	
n	3	4	3
SiO_2	63.38	53.10	67.10
TiO_2	0.31	0.70	0.59
Al_2O_3	17.43	14.53	19.09
Fe_2O_3	1.29	2.39	0.43
FeO	1.43	4.05	0.30
MnO	0.10	0.20	0.01
MgO	0.94	5.32	0.35
CaO	1.55	1.99	0.10
Na_2O	9.48	6.03	11.18
K_2O	0.28	1.14	0.22
P_2O_5	0.07	0.18	0.02
LOI	4.33	11.65	0.80
Total	100.60	101.28	100.19
HM	0.32	0.41	0.30
FM	0.06	0.22	0.02
AM	0.27	0.27	0.28
TM	0.018	0.048	0.031
FerM	0.16	0.44	0.04
NKM	0.56	0.49	0.60
AlkM	33.50	5.30	50.10

Table 76

Chemical composition of the Tournaisian dawsonite rocks of the Pripyat Depression.
Compiled according to F.L. Dmitriev et al., 1975. [89, p. 296–297]

Oxides and modules	I	Ib	IIa	IIb	III	IV	V	6	18
	Carbonate alkalite		Titanium alkalite	Titanium carbonate alkalite	Sulfurous carbonate alkalite	Alkaline carbonatolite	Alkalite-carbonatolite	Sulfurous carbonate alkalite	Sulfurous alkaline carbonate pseudohydrolysate
n	2	2	2	2	4	2	2		
SiO_2	21.43	19.53	15.46	10.42	5.36	9.63	5.25	2.49	4.26
TiO_2	1.16	1.13	2.23	2.07	1.39	1.12	1.14	0.97	0.91
Al_2O_3	33.39	36.06	24.28	30.82	19.78	20.10	35.23	18.55	12.66
Fe_2O_3	3.36	1.26	23.73	10.02	19.31	2.87	1.14	32.84	15.40
FeO	3.07	0.00	0.09	0.18	8.17	21.76	0.01	0.64	16.97
MnO	0.05	0.02	0.01	0.01	0.04	0.13	O.O!	0.01	0.03
MgO	0.12	0.00	0.18	0.28	0.69	1.58	0.11	0.08	3.99
CaO	0.30	0.28	1.51	0.97	4.76	3.34	0.43	5.75	5.83
Na_2O	8.41	11.71	8.82	14.19	9.10	6.29	17.67	9.77	5.58
K_2O	0.12	0.29	0.17	0.12	0.15	0.14	0.10	0.12	0.12
P_2O_5	0.13	0.12	0.06	0.05	0.05	0.10	0.05	0.03	0.03
SO_3	0.33	0.00	1.39	1.45	6.02	1.00	1.18	8.99	6.76
LOI	27.57	29.55	21.85	29.33	24.61	31.77	37.66	19.38	26.89
Total	99.41	99.94	99.75	99.89	99.40	99.80	99.94	99.62	99.43
CO_2	14.19	16.78	9.30	15.35	13.64	24.10	25.30	10.16	12.43
HM	1.91	1.97	3.26	4.14	9.09	4.78	7.15	21.29	10.79
FM	0.31	0.06	1.55	1.01	5.26	2.72	0.24	13.48	8.54
AM	1.56	1.85	1.57	2.96	3.69	2.09	6.72	7.45	2.97
TM	0.035	0.031	0.092	0.067	0.070	0.056	0.032	0.052	0.072
FerM	0.19	0.03	0.90	0.31	1.30	1.17	0.03	1.72	2.39
NKM	0.26	0.33	0.37	0.46	0.47	0.32	0.50	0.53	0.45
AlkM	73.10	41.10	51.90	118.20	59.60	44.90	176.70	81.40	46.50

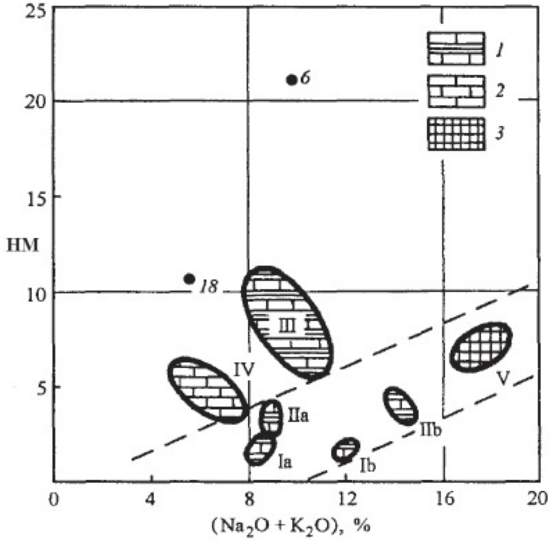

Fig. 64. Module diagram for dawsonite rocks C_1t of the Pripyat depression.
Compiled according to F. L. Dmitriev et al., 1975 [89, p. 296–297].
1 – carbonate alkalites, 2 – alkaline carbonatolites, 3 – carbonatolites–alkalites

a series of clusters and individual points, rather chaotically distributed on the module diagram, which reflects significant variations in composition.

In this case, a remarkable situation arises with the formal lithochemical certification of rocks. Clusters Ia, b, IIb, III can be classified as carbonate alkalites (and in terms of HM they are also carbonate hyperalkaline hydrolysates); rocks of cluster IV are certified as carbonatolites ($CO_2 > 20$ %), and rocks of cluster V are both carbonatolites ($CO_2 > 20$ %) and alkalites ($Na_2O + K_2O > 8$ %). Thus, we have a classification incident – a case when Nature decided to play a trick on the authors of this book...

Let us note three more lithochemical features of dawsonite rocks: a) increased TM value, which apparently indicates their genetic relationship with basites (half of the compositions are certified as super- and hypertitanic, with TiO_2 contents reaching 2.81 %); b) increased iron content (half of the samples are ferruginous, and the FerM reaches 2.4, and the Fe_2O_3 content – up to 33.3 %); c) high SO_3 content (up to 9 %) due to the presence of anhydrite. According to V.P. Kurochka, dawsonite in these rocks is epigenetic, and the sequence of mineral formation is drawn as a very complex, six-stage one [89]. Although the problem of dawsonite formation continues to be a subject of discussion, two alternative lines can be distinguished in it:

1) the formation of dawsonite on the substrate of syngenetic alumina minerals – kaolinite, boehmite, gibbsite; 2) the formation of hydrolysate

minerals as a result of the dawsonite decomposition in an acidic medium. V.P. Kurochka develops this very idea.

It is possible that the division of the module diagram into two parts (correlated series of clusters Ia, IIa ⇒ Ib ⇒ IIb ⇒ V and uncorrelated clusters IV, III) reflects the polygeneticity of dawsonite rocks.

6.7. Carbonatolites

In nature, the most widespread are limestones, dolomites and calcareous-dolomite rocks, which form the first three classes of carbonatolites, distinguished in the FCM triangle.

The classes are calcium (1), magnesium-calcium (2) and calcium-magnesium (3). Let us consider the typification of carbonatolites most widespread in the sedimentary shell of the first three classes using the example of flysch carbonates on the southern slope of the Ukrainian Carpathians. According to the I. M. Afanasyeva's description [11], there are limestones, sandy and silty limestones, marls and clay limestones, calcareous tuffs and carbonate concretions. An attempt of typing carbonatolites by their *silicious component* is shown in the NKM–AM diagram (Fig. 65). We see, firstly, a clear trend

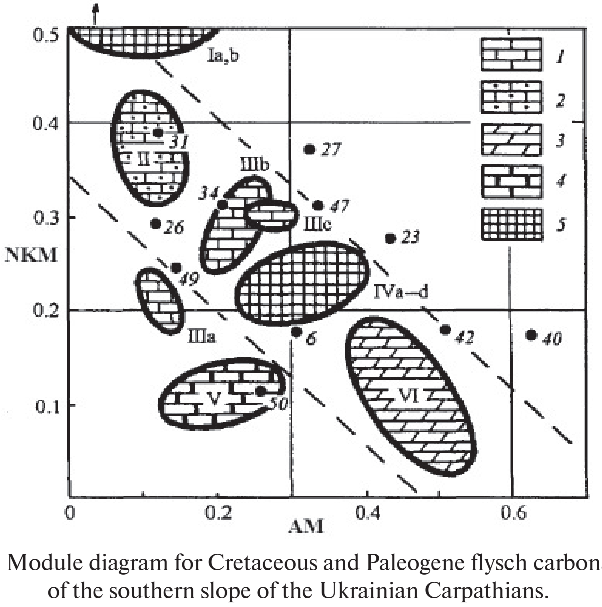

Fig. 65. Module diagram for Cretaceous and Paleogene flysch carbonatolites of the southern slope of the Ukrainian Carpathians.

Compiled according to the data of I. M. Afanasyeva, 1979 [11, p. 188–195].

Carbonate rocks: 1 – calcite, 2 – the same, manganese, 3 – dolomite, 4 – siderite and ankerite, 5 – mixed composition band for the lithotypes prevailing in the section, and secondly, non-trivial features of the composition are clarified in table 77.

Thus, “recrystallized limestones” are actually dolomites (cluster VI). Their falling into the negative correlation band together with limestones may indicate an epigenetic process. The special position of “sandy-silty limestones” of cluster IIIa and siderite, ancerite concretions of cluster V reflects the specifics of their formation.

The use of the FCM triangle (Fig. 66), where clustering is performed according to the *carbonate component* composition, makes it possible to better discriminate dolomite, siderite and ankerite rocks (clusters IV b, c, d that are indistinguishable on the AM–NKM diagram are well distinguished), but on the other hand it leads to the loss of information in relation to limestones and (unification of clusters I–III, IVa).

In addition, it turns out that the "limestones" composition is strongly dependent on their lithological characteristics. In 6 samples of 11 ones the M parameter is only 1.2–6.5 %, and in 5 others – 20.0–27.2 %. It turns out that all the first (except one) are "cryptocrystalline limestones", and all the second ones are "recrystallized limestones". As noted by I.M. Afanasyeva, "*the highest contents of iron and magnesium carbonates are typical for the limestone of those stratigraphic horizons, which are characterized by an increased content of organic material ...*" [11, p. 196].

Among the four analyzes of travertines (calcareous tuffs), two show significant Mg value (grade 3) and two are purely calcareous (grade 1). All sandy and silty carbonatolites are also in this class, but only half of the clay (marles), while others are more magnesian. In any case, it is hardly accidental that the rocks with the maximum values of the M parameter – 16.4 and 33.0 % – turned out to be the most silica. However, the latter can also be explained by analytical errors – the inclusion of silicate iron and magnesium into the MgO_{carb} and FeO_{carb} composition conventionally accepted by us [302, p. 23][8].

Fe–Mn class 6 includes exclusively concretions: there is not a single bed-like carbonate with such a composition. However, even among the concretions, 6 samples have Mg–Ca and Ca compositions scattered in classes 1–3 and indistinguishable from stratal carbonates.

Let us touch upon the significant for historical geochemistry issue of the magnesium-calcium carbonatolites distribution in ancient strata, in particular, in the Riphean strata. If we follow the A.V. Sochava and V.N. Podkovyrov’s logic [247, p. 22], the intensification of continental weathering leads to an increase in the Mg/Ca ratio in water runoff from the continents and, accordingly, increases Mg/Ca in ocean water. This conclusion

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[8] The fact is that in the absence of phase "carbonate" analyzes in the primary source, we were forced to use complete silicate analyzes [11, p. 188—195], taking as 100 % the sum of the data in the analysis of FeO, MnO, MgO, CaO. For pure carbonate rocks, this method is legitimate, but for marls it can lead to errors if they contain a lot of chlorites [295, p. 26].

Table 77

Chemical composition of Cretaceous and Paleogene flysch carbonatolites on the southern slope of the Ukrainian Carpathians.

Compiled according to I.M. Afanasyeva, 1979 [11, p. 188–195]

Oxides and modules	Ia	Ib	II	IIIa	IIIb	IIIc	IVa	IVЬ	IVc	IVd	V	VI
	Cacarbonatolite		Mn carbonatolite	Cacarbonatolite				Mg carbonatolite	Mg-Fe carbonatolite	Mn carbonate pseudohydrolisate	Mn-Fe carbonatolite	Mg carbonatolite
	2	2	5	2	5	2	4	5	3	3	3	4
SiO_2	20.68	7.08	39.25	38.86	23.27	33.52	23.62	26.52	20.67	30.47	25.03	8.86
TiO_2	0.17	0.03	0.30	0.20	0.28	0.46	0.34	0.30	0.29	0.38	0.26	0.12
Al_2O_3	0.54	0.88	4.02	5.00	5.26	9.32	7.53	8.69	6.01	8.95	5.27	3.92
Fe_2O_3	5.42	0.80	1.09	0.89	1.35	1.50	1.50	2.41	3.60	6.68	6.45	1.20
FeO	1.79	0.92	1.58	1.08	2.70	2.17	1.81	2.18	16.68	20.11	25.37	3.56
MnO	0.39	0.13	1.12	0.06	0.33	0.47	0.17	0.47	0.72	1.57	1.12	0.25
MgO	1.39	1.13	1.50	1.51	1.11	2.32	3.21	9.88	5.23	3.55	4.76	10.82
CaO	37.02	47.82	26.09	26.12	33.50	23.56	30.98	19.39	16.15	5.16	6.86	31.15
Na_2O	0.43	0.47	0.88	0.51	0.49	0.88	0.88	0.97	0.40	0.97	0.20	0.18
K_2O	1.00	0.53	0.62	0.58	1.07	1.99	0.90	1.15	0.90	1.10	0.45	0.40
P_2O_5	0.38	0.10	0.37	0.19	0.20	0.08	0.26	0.26	1.01	0.73	0.63	0.32
SO_3	0.40	0.59	0.54	0.17	0.54	0.76	0.61	0.37	0.18	0.23	1.05	0.06
CO_2	27.45	38.34	21.59	22.47	27.38	20.56	26.33	23.76	27.19	17.21	21.08	37.44
H_2O	3.55	0.91	1.72	1.88	2.68	3.18	2.66	4.03	1.26	3.28	2.13	2.17
Total	100.58	99.71	100.66	99.48	100.17	100.76	100.77	100.37	100.29	100.40	100.64	100.43
HM	0.40	0.39	0.21	0.19	0.43	0.41	0.48	0.53	1.32	1.24	1.54	1.02
AM	0.03	0.12	0.10	0.13	0.23	0.28	0.32	0.33	0.29	0.29	0.21	0.44
TM	0.315	0.034	0.074	0.040	0.054	0.049	0.045	0.034	0.048	0.043	0.049	0.030
NKM	2.65	1.13	0.38	0.22	0.30	0.31	0.24	0.24	0.22	0.23	0.12	0.15
AlkM	6.40	0.90	1.40	0.90	0.50	0.40	J.00	0.80	0.40	0.90	0.40	0.40

Table 77 (continuation)

Oxides and modules	6	23	26	27	31	34	40	42	47	49	50
	Carbonatolite	Carbonate hypohydrolisate	Pseudosilite	Carbonatolite	Carbonate pseudohydrolisate	Carbonatolite					Mncarbonate pseudohydrolisate
SiO_2	29.17	29.33	55.75	28.39	23.95	13.99	16.98	25.99	18.65	26.72	26.21
TiO_2	0.45	0.43	0.26	0.30	0.23	0.15	0.29	0.31	0.27	0.19	0.20
Al_2O_3	9.04	12.78	6.78	9.35	3.05	2.98	10.62	13.30	6.28	3.98	6.83
Fe_2O_3	3.40	0.33	0.64	1.08	27.39	8.46	4.29	6.83	1.16	6.60	3.22
FeO	6.82	4.02	2.30	2.24	0.75	0.29	6.31	14.28	4.45	23.85	12.56
MnO	0.20	0.21	0.07	0.11	0.26	0.51	0.30	0.80	0.46	0.88	15.50
MgO	2.15	2.28	4.07	1.75	8.02	3.06	2.26	0.50	7.27	4.20	7.63
CaO	24.19	24.50	18.46	28.47	11.21	35.91	27.42	9.80	27.38	7.09	5.03
Na_2O	0.46	0.70	1.12	1.55	0.40	0.25	0.50	0.60	0.62	0.19	0.37
K_2O	1.18	2.91	0.90	1.97	0.80	0.70	1.40	1.85	1.37	0.80	0.45
P_2O_5	0.98	0.10	0.27	0.17	0.09	0.54	0.26	2.30	0.37	1.57	1.26
SO_3	0.09	0.08	0.23	0.10	0.66	0.13	0.15	0.37	0.44	0.07	O.O!
CO_2	21.30	19.80	8.78	23.00	16.20	30.35	27.50	20.64	30.77	21.06	17.75
H_2O	0.77	2.85	0.48	1.81	6.98	2.70	1.64	1.73	0.80	3.48	3.44
Total	100.20	100.32	100.11	100.29	99.99	100.02	99.92	99.30	100.29	100.68	100.46
HM	0.68	0.61	0.18	0.46	1.32	0.89	1.28	1.37	0.68	1.33	1.46
AM	0.31	0.44	0.12	0.33	0.13	0.21	0.63	0.51	0.34	0.15	0.26
TM	0.050	0.034	0.038	0.032	0.075	0.050	0.027	0.023	0.043	0.048	0.029
NKM	0.18	0.28	0.30	0.38	0.39	0.32	0.18	0.18	0.32	0.25	0.12
AlkM	0.40	0.20	1.20	0.80	0.50	0.40	0.40	0.30	0.50	0.20	0.80

Note. Limestones – clusters Ia, b, II, IVa, b; sandy–siltstone limestones – clusters IIIa, b; clay limestones – clusters IIIc, samples no. 23, 26, 27; recrystallized limestones – clusters VI, sample 6; calcareous tuffs – samples 31, 34; carbonate concretions – clusters IVc, d, V, samples 40, 42, 47, 49, 50

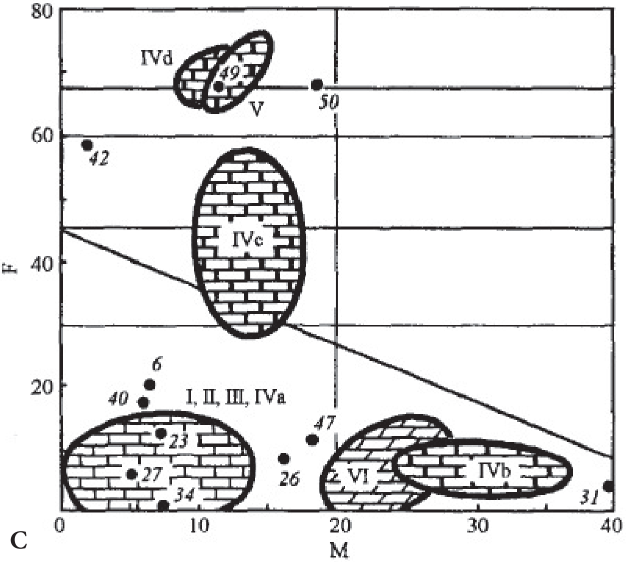

Fig. 66. Composition clustering of Cretaceous and Paleogene flysch carbonatolites of the Ukrainian Carpathians on the FCM triangle. Legend – see fig. 65

looks plausible, since an increase in P_{CO2} and surface temperatures (due to the greenhouse effect), according to the model by J. Walker et al. [358], leads to an increase in continental weathering and, accordingly, to an increase in the rate of carbonate formation [247, p. 22]: *“Note that calcium is sufficiently fully extracted from the rocks of the source areas with an average degree of weathering. The expansion on the continents of the weathering crusts development zones, in which the degree of transformation of the primary rocks approaches the kaolinite stage, will lead to an increase in the flux of alkaline earth elements into the ocean, largely due to an increase in the magnesium content in it. The Mg/Ca ratio in this flux should increase, approaching that of the parent rocks* <...> This should also, ultimately, contribute to the increasing role of dolomite in marine sediments*”* [247, p. 22, highlighted by us].

However, the plausibility of this conclusion is testable. Obviously, all other things being equal, the HM of dolomites should, on average, be higher than the HM of limestones; dolomites in the sections should be more often associated with hydrolysate terrigenous sediments than limestones. As far as can be judged from the data at our disposal, none of these assumptions is supported by factual material.

Magnesium class (4). Table 78 gives the *average* chemical magnesite ores compositions of the Southern Urals, containing 38–46 % MgO in carbonate form [258]. The most alumina compositions form cluster I, which

Table 78

Chemical composition of the southern Urals magnesite ores.
Compiled according to L.P. Urasina et al., 1993 [258, p. 90–91]

Oxides and modules	1	2	4	5
т	153	13	62	41
п	2			
SiO_2	0.95	1.20	2.10	2.60
TiO_2	0.01	0.01	0.04	0.04
Al_2O_3	0.35	0.30	0.50	0.50
Fe_2O_3	0.25	0.20	0.70	0.60
FeO	1.00	0.50	3.00	3.60
MnO	0.04	0.03	0.10	0.10
MgO	45.15	45.70	43.10	38.40
CaO	1.65	0.90	1.40	6.30
Na_2O	0.04	0.03	0.06	0.67
K_2O	0.03	0.02	0.10	0.12
LOI	50.50	50.90	48.60	47.20
Total	99.97	99.79	99.70	100.13
HM	1.74	0.87	2.07	1.86
AM	0.37	0.25	0.24	0.19
TM	0.029	0.033	0.080	0.080
NKM	0.19	0.17	0.32	1.58
AlkM	1.60	1.50	0.60	5.60

unites magnesites of the Satka and Elnya deposits (a total of 153 analyzes). In other magnesites, the AM value is noticeably lower, and the ores of the Semibratsk deposit are distinguished by an increased NKM value – up to 1.58 (analysis 5 is the average of 41 analyzes).

It is curious that the most alkaline compositions (analyzes 4 and 5) are also the most TM (0.080 versus 0.029–0.033 in other deposits). However, the aluminum and titanium contents are so negligible that it is better to refrain from interpreting these figures due to the danger of analytical errors.

Ferruginous and/or manganese classes (5, 6 and 7). Modules AM and NKM are also suitable for clustering the compositions of Fe-Mn carbonatolites, since alumina, silica, and alkalis can be considered noncarbonate components. As can be seen from Fig. 67, the AM of the Precambrian siderites is much lower than the Phanerozoic (among which one is Silurian and five Jurassic). The fact is that in the Precambrian there is much more low-alumina non-carbonate admixture because they are closely related to ferruginous

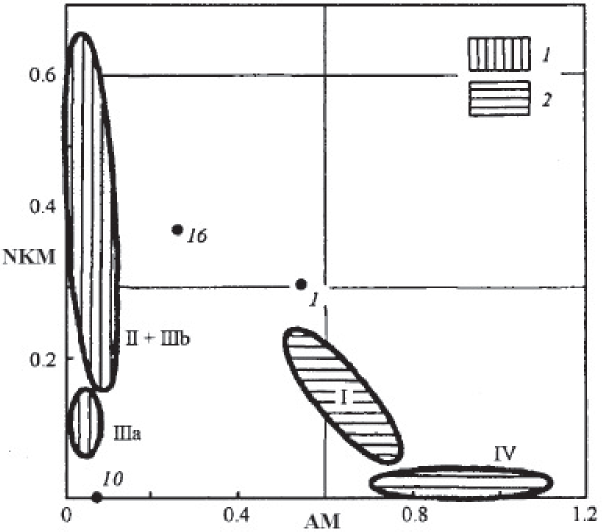

Fig. 67. Module diagram for some Phanerozoic (2) and Precambrian (1) siderite rocks. *Compiled according to H. James, 1966* [337, p. W25–W26]

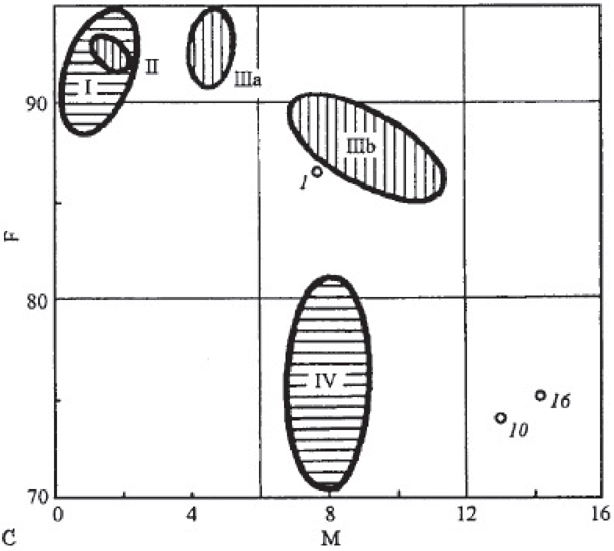

Fig. 68. Clustering of siderite rock compositions using the FCM triangle. *Compiled according to H. James, 1966* [337, p. W25–W26]. See the legend in Fig. 67

quartzites. The titanium module also partially retains its significance; thus, the extreme TM value for Jurassic siderite from Sweden (sample 4, table 79) requires some explanation. Using the FCM triangle (Fig. 68), it is possible to clearly discriminate cluster IIIb (Wisconsin and Wisconsin-Michigan Precambrian siderites), but the Krivoy Rog Precambrian siderites (cluster II) fall into the contour of cluster I (Jurassic siderites of Sweden).

The reader can find numerous examples of the calcium-manganese (manganocalcite and rhodochrosite) and calcium-magnesium-iron manganese (mangano-ankerite or manganodolomite) carbonatolites composition in the specialized literature (e.g., [297]). Let us note only the most characteristic feature of such carbonatolites – as a rule, they are concretional or concrezoidal, and not purely sedimentary formations.

Table 79

Chemical composition of some siderite rocks.
Compiled from the data of H. James, 1966 [337, p. W25–W26]

Oxides and modules	I	II	IIIa	IIIb	IV	1	10	16
	Carbonatolite	Carbonate hypohydrolisate	Mn carbonaceous carbonatolite	Mn carbonatolite	Carbonatolite		Mn carbonatolite	Mn-S carbonatolite
n	3	2	2	6	2			
SiO_2	8.22	48.40	24.97	31.89	8.13	7.56	39.26	13.91
TiO_2	1.02	0.03	0.10	0.09	0.27	0.18	0.07	0.09
Al_2O_3	5.57	1.88	1.19	1.47	7.24	4.10	2.88	3.63
Fe_2O_3	5.05	3.65	2.95	4.11	1.74	1.83	0.63	3.28
FeO	43.62	24.49	36.47	31.36	36.26	43.86	24.94	28.62
MnO	0.47	0.03	3.53	1.65	0.40	0.13	1.23	1.73
MgO	0.57	0.46	2.01	3.24	3.89	3.92	4.62	5.73
CaO	3.76	1.56	1.07	1.13	8.04	2.90	4.62	4.34
Na_2O	0.06	0.33	0.05	0.03	0.04	0.11	0.00	0.94
K_2O	0.52	0.08	0.08	0.12	0.10	1.13	0.00	0.45
H_2O^+	2.54	0.66	0.26	0.68	4.10	0.81	1.23	1.30
H_2O^-	1.00	2.01	0.14	0.23	10.00	0.28	0.11	0.10
P_2O_5	0.47	-	0.33	0.35	1.29	0.11	0.11	0.23
CO_2	26.37	16.01	26.35	22.86	22.98	32.84	20.46	27.06
S	0.12	-	-	0.06	0.08	-	0.04	0.43
C	0.50	-	2.02	0.79	0.32	-	0.0..7	-
Total	99.85	99.56	101.50	100.05	104.84	99.76	100.27	99.84
HM	6.78	0.62	1.77	1.21	5.65	6.63	0.76	2.69
AM	0.68	0.04	0.05	0.05	0.89	0.54	0.07	0.26
TM	0.184	0.013	0.084	0.064	0.037	0.044	0.024	0.025
FerM	7.45	14.82	33.29	23.82	5.12	10.71	9.08	9.04
NKM	0.10	0.22	0.11	0.10	0.02	0.30	0.00	0.38
AlkM	0.10	4.10	0.70	0.30	0.40	0.10	-	2.10

6.8. Phosphatolites

Considering the relative abundance of various phosphates, practically the only representative of sedimentary phosphatolites can be considered phosphorites, composed mainly of calcium carbonate-fluorine-apatite – francolite.

Table 80 processed the analyzes of different-aged phosphorites and phosphate rocks from different regions, compiled by N.G. Brodskaya [30]. The Lower Cambrian phosphorites of the Western Okhotsk region (cluster I) are distinguished by the highest alkalinity and TM value, are hypertitanic and same-aged (?) Strongly phosphatized limestones and silica of Kazakhstan (samples 5 and 6). Miocene phosphorites of Poland (cluster II) and Oligocene phosphorites of Bulgaria (cluster III) differ little in alkalinity and TM value from the Upper Cretaceous phosphate rocks of the Polish Carpathians (IV) and from the Eocene phosphate rocks of Colorado, USA (Va and Vb).

Noteworthy is the unusual AM value in oligocene phosphorites in Bulgaria – 0.91. If the analysis is to be believed, this may mean the presence of a hydrolysate admixture in these phosphorites (from the weathering crust?). Unusual and the value of the NKM (~1) of the Lower Cambrian phosphorites of the Western Okhotsk region (sample 10), exceeding the norm for alkaline feldspars; again, if this is not an analytical error, then it requires the presence of some low-alumina alkaline phase.

Among industrial phosphorites, it is customary to distinguish between varieties *by structure*; it is interesting to find out if they have any specific chemical composition. Table 81, the compositions of some phosphorites and phosphate rocks with a *psephite* structure are given: conglomerates, pebbles, shell conglomerates, and concretion pseudo-conglomerates [241]. On a formal basis (P_2O_5 > 21 %), only Cambrian phosphorite conglomerates are certified as phosphatolites, the rest are phosphate silites, and two concretionary pseudo-conglomerates (Vyatsko-Kamsky swell and Egoryev deposit) are even siferlites. For all phosphate rocks, high FerM values are noted (0.85–2.58) and for half of them – hyperalkaline composition (NKM = 0.61–0.92). The former can be partly due to the presence of pyrite, while the latter is due to feldspars. However, in the Upper Cretaceous samples without pyrite, the FerM remains elevated (perhaps due to the admixture of glauconite?).

Ya.Ya.Maldre calculated the average composition of the Lower Ordovician obolus phosphorites of Estonia using 17 analyzes (Table 82) [165]. If, according to these data, the composition of the phosphorites' silicate part is estimated, then it will unexpectedly be represented by Fe-hydrolysate (HM 0.80, FerM 5.7). Obviously, this reflects the presence of pyrite (as evidenced by the noticeable sulfate content). In addition, TM value (0.246) and sodium content (AlkM > 10) are abnormally high. The last two signs may indicate

Table 80

Chemical composition of uneven-aged phosphorites.
Compiled according to N.G. Brodskaya, 1974 [30]

Oxides and modules	I	II	III	IV	Va	Vb	5	6	7	10	11	14	15
	F phosphatolite			Phosphate hypohydrolisate	Phosphate pseudosilite	Phosphate alkaline normosiallite	F-P myosilite	F-carbonate supersiallite	Carbonatolite	F phosphatolite	Phosphate normohydrolysate	F phosphatolite	Phosphate alkaline normosiallite
n	2	2	2	2	2	2							
SiO_2	7.86	6.35	2.55	41.15	32.45	44.10	46.74	21.83	14.52	43.26	34.00	11.03	50.25
TiO_2	0.21	0.05	-	0.61	0.28	0.36	0.33	1.55	0.29	0.03	0.62	0.00	0.56
Al_2O_3	0.79	1.73	2.31	15.07	6.85	11.65	3.86	6.92	2.07	1.26	22.92	3.69	14.4S
Fe_2O_3	0.39	0.32	0.59	8.24	2.40	2.70	5.41	0.47	0.17	0.25	9.12	1.00	1.22
FeO	0.30	0.07	0.13	0.66	0.84	0.31	0.28	1.69	1.51	0.55	0.91	2.38	0.86
MnO	0.01	0.06	-	0.48	0.17	0.15	0.00	0.23	0.14	0.03	0.14	0.01	0.04
MgO	1.43	0.34	0.39	1.88	3.35	1.80	0.00	0.14	0.39	0.56	1.66	0.56	1.44
CaO	47.60	48.73	50.88	11.19	21.80	13.25	21.66	34.93	44.57	30.26	10.90	42.57	8.47
Na_2O	0.53	0.60	0.15	0.18	2.50	2.10	0.57	2.61	0.44	0.08	0.43	0.27	5.26
K_2O	0.30	0.12	-	2.36	1.43	4.30	0.54	0.78	0.10	0.11	2.99	0.26	0.09
H_2O	-	2.74	1.90	5.83	3.95	5.25	1.71	0.32	0.77	-	7.15	2.56	5.78
CO_2	4.95	3.27	1.42	0.66	8.95	5.70	0.22	19.10	33.68	-	1.42	0.30	3.02
P_2O_5	32.25	32.97	36.45	8.23	10.60	5.15	17.00	8.86	1.30	19.98	7.83	31.84	7.10
F	3.40	2.46	3.54	-	-	-	1.21	0.82	-	1.56	-	2.66	-
C_{org}	-	0.00	-	0.50	0.50	0.50	1.18	0.01	0.00	-	-	2.39	0.00
Total	100.00	99.78	100.29	97.01	96.06	97.32	100.71	100.26	99.95	97.93	100.09	101.52	98.54
HM	0.22	0.35	1.19	0.61	0.32	0.34	0.21	0.50	0.29	0.0S	0.99	0.64	0.34
AM	0.10	0.27	0.91	0.37	0.21	0.26	0.08	0.32	0.14	0.03	0.67	0.33	0.29
TM	0.266	0.026	0.000	0.040	0.041	0.030	0.085	0.224	0.140	0.024	0.027	0.000	0.039
FerM	0.70	0.25	0.31	0.60	0.48	0.26	1.36	0.28	0.77	0.64	0.43	0.92	0.14
NKM	1.04	0.41	0.06	0.17	0.57	0.55	0.29	0.49	0.26	0.15	0.15	0.14	0.37
AlkM	1.80	5.20	-	0.10	1.80	0.50	1.10	3.30	4.40	0.70	0.10	1.00	58.40

Table 81

Chemical composition of psephite and pseudopsephite phosphorites of the USSR.
Compiled according to A.I. Smirnov, 1972 [241, p. 22–23]

Oxides and modules	I	II	III	4
	F phosphatolite	P-S siferlite	P supersilite	
n	2	3	4	
SiO_2	8.03	35.91	56.55	55.33
Al_2O_3	0.97	5.94	2.79	2.32
Fe_2O_3	0.77	7.27	3.03	2.52
FeO	1.16	1.73	O.O!	-
MnO	-	0.13	0.04	0.05
MgO	1.92	0.61	0.51	0.76
CaO	47.14	21.18	17.06	18.12
Na_2O	0.50	0.80	0.81	1.02
K_2O	-	1.86	1.08	-
P_2O_5	30.02	13.07	10.18	12.70
SO_3	-	0.80	1.73	0.53
CO_2	6.35	3.55	2.07	1.74
FeS_2	-	3.55	0.13	2.08
F	2.41	1.41	1.17	1.01
LOI	-	3.22	2.47	0.75
Total	99.25	101.04	99.62	98.93
HM	0.36	0.42	0.10	0.09
FM	0.48	0.27	0.06	0.06
AM	0.12	0.17	0.05	0.04
FerM	1.98	1.54	1.10	1.11
NKM	0.52	0.45	0.68	0.44
AlkM	-	0.40	0.80	-

Table 82

Average chemical composition of shell phosphorites.
Compiled according to Ya.Ya. Muldre, 1979 [165]

Oxides	Content, %	Oxides	Content, %
SiO_2	2.49	Na_2O	0.61
TiO_2	0.06	K_2O	-
Al_2O_3	0.26	P_2O_5	33.97
Fe_2O_3	1.67	CO_2	3.39
FeO	4.06	F	2.64
MnO	0.18	SO_3	0.99
MgO	0.46	H_2O^-	1.91
CaO	47.38		

an active hydrodynamic environment of sediment accumulation with washing out of the clay fraction. However, an interpretation in terms of weathering is also possible: the phosphorites sulfuric weathering process could be accompanied by the Al and K removal in the form of soluble alum. Finally, the least probable (albeit very attractive) paleo-biological interpretation: perhaps, obolid brachiopods in the process of their vital activity had the ability to accumulate Ti and Na or, conversely, to somewhat discriminate Al and K?

Table 83 shows the phosphorites and phosphate rock compositions with the *psammites* structure. It turns out that they are characterized by the same lithochemical features as for phosphate psephites.

Table 83

Chemical composition of psammitic and psammite-like phosphorites of the USSR and North Africa.

Compiled according to A.I. Smirnov, 1972 [241, p. 27–29]

Oxides and modules	I	II	III	IV	1	6	9
	$€_2$	$J_3–K_1V$	$K_2–P$	O_1	O_1	P	K_2sn
	Age						
	Phosphatolite	P, S siferlite	Phosphatolite	Phosphate hypersilite	Pseudosilite	Phosphate normosilite	Fcarbonate phosphatolite
n	5	2	2	2			
SiO_2	23.29	49.86	3.79	72.46	55.12	54.82	2.04
Al_2O_3	2.59	9.16	0.63	0.85	5.54	4.19	0.08
Fe_2O_3	1.09	12.60	1.03	0.98	5.56	1.80	1.59
FeO	1.02	-	-	0.15	1.02	-	-
MnO	0.08	0.10	-	0.04	0.07	-	-
MgO	2.05	0.51	1.50	1.46	3.98	0.72	5.17
CaO	35.00	7.90	47.53	11.65	9.28	18.35	44.75
Na_2O	0.47	0.76	1.23	0.18	0.05	0.96	1.02
K_2O	0.73	3.62	0.12	0.25	4.02	1.07	0.08
P_2O_5	21.91	4.48	28.69	7.20	2.62	7.82	24.91
SO_3	0.34	0.57	2.89	0.13	0.03	0.93	1.57
CO_2	5.59	1.22	7.03	3.68	9.46	5.67	12.83
FeS_2	0.65	2.50	-	0.05	0.60	-	-
F	1.97	0.48	2.65	0.59	0.20	0.66	3.05
LOI	2.58	5.73	3.22	0.53	2.03	2.85	3.50
Total	99.34	99.46	100.28	100.18	99.58	99.84	100.59
HM	0.20	0.44	0.44	0.03	0.22	0.11	0.82
FM	0.18	0.26	0.67	0.04	0.19	0.05	3.31
AM	0.11	0.18	0.17	0.01	0.10	0.08	0.04
FerM	0.85	1.39	1.63	1.37	1.20	0.43	19.88
NKM	0.46	0.48	2.13	0.51	0.73	0.48	13.75
AlkM	0.60	0.20	10.70	0.70	0.00	0.90	12.80

The extreme alkalinity and sodium values in the Cenomanian granular-detrital rite phosphorite of the Hamruin Egyptian deposit (sample 9) may be associated with the presence of halite (?!) or authigenic albite, which may occur in evaporite facies. This assumption is consistent with the high sulfate content (in the absence of pyrite?). If this guess is correct, then all compositions of North African phosphorites with high NKM can be interpreted as formations of arid evaporite basins of phosphate accumulation. This is consistent with A.I. Smirnov's conclusions, to which he came by comparing the carbon and sulfur content in natural phosphorites with experimentally obtained phosphate sediments [241].

As in the case of psephitic phosphate rocks, it is also possible to form clusters I and II, corresponding to the Cambrian and Upper Jurassic–Cretaceous phosphorites, respectively, and cluster IV, to the Lower Ordovician. However, cluster III is already mixed (Cretaceous and Paleogene), and several compositions (samples 1, 6, 9) are outside the clusters.

6.9. Evaporites

Usually, one must deal with only two classes of evaporites – sulfatolites and halolites, which in the sections of saline arid strata are in paragenesis with various carbonate and terrigenous deposits. Diagnostics of such strata is not always an easy task, and lithochemical methods can be of great help, as one can see from the example of the Devonian of Western Yakutia. In Fig. 69 and Tab. 84 shows 64 processed analyzes of rocks from three wells drilled in the Chayandin area in the western part of the Vilyui syneclise (materials by G.V. Ivensen). According to the collector's description of the core, these are sandstones, siltstones and argillites; one sample (sample 1, borehole Ch–15, depth 1787.4 m) was named dolomite and another (sample 46, borehole Ch–20, depth 1854 m) – anhydrite. Analyzes show that we are dealing with saline evaporite strata. This is evidenced by the following signs.

a) High chlorine contents, on average for clusters – from 0.38 to 5.44, up to 7.98 % (sample 51); with chlorine content above 0.1 % (i.e., when the "noise" introduced by the analysis errors can be neglected) they are very closely correlated with the sodium content, which indicates the form of chlorine occurrence – halite.

b) The presence of hyperalkaline compositions with NKM > 1, which cannot be attributed to either feldspars or zeolites (clusters III, IV and samples 1, 2, 3, 5, 37, 45, 47, 51); it is obvious that such compositions can only be due to the presence of salts. The high total alkalinity of many "sandstones" is also indicative (clusters III–V, VI–VII, samples 25, 32, 37, 45, 51), which, in combination with other features, indicates the presence of salts. Anomalousness of such rocks is also shown by the fact that they do

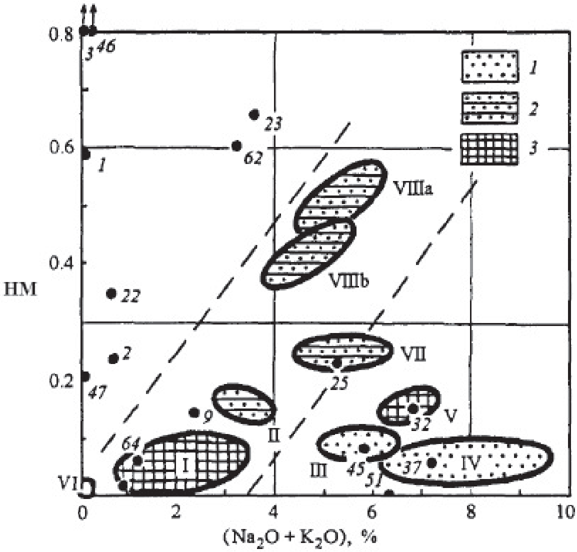

Fig. 69. Module diagram for saline terrigenous–carbonate deposits of the Devonian in the western part of the Vilyui syneclise.

Compiled based on the G.V. Ivensen's materials, 1997 (private message).

Litotypes (according to the reservoir description of the core): 1 – sandstones, 2 – siltstones, 3 – mixture of lithotypes

not fall into the "normal" (due to clay matter) band of positive correlation "Alkali – HM" on the module diagram (Fig. 69).

c) The presence of sulfate compositions (to which we referred here compositions with SO_3 content > 3 %); even on average, in the "sandstones" (cluster VI), the amount of SO_3 reaches 15–16 %, and some samples with an SO_3 content > 20 % (samples 1, 46) are certified as sulfatolites.

d) Increased magnesium content of some samples, where a high content of dolomite is evident, as well as, quite possibly, soluble magnesium salts and/or high-magnesium silicates (the latter is also characteristic of evaporite strata).

Let's add two more features of this strata here.

e) Unusually acidic composition of some "siltstones", which are certified as hyper- and supersilites (clusters Ia, Ib) and contain on average from 80 to 90 % SiO_2. Since for "siltstones" such contents seem strange (they are typical only for well-washed quartz sandstones), a doubt arises – are these siltstones? Perhaps we are dealing with authigenic silica formations, which are so characteristic of alkaline media of arid (evaporite) lithogenesis?

f) The presence of, albeit few, but still distinct geochemical anomalies of manganese (more than 0.2 % MnO), reaching 1.45–1.87 % in "sandstone" (sample 22)

Chemical composition of saline terrigenous
of the western Vilyui syneclise part. *Compiled*

Oxides and modules	I	Ib	II	III	IV	V	VI	VII	VIIIa	VIIIb	1	2	3
	Sandstones (hypersilite)	Siltstones		Sandstone (CI alkaline supersilite)		Aleurosandstones (alkaline normosilite)	Sandstones (sulfate carbonate pseudolite)	Siltstone (alkaline myosilite)	Argillites		Dolomites		
		Supersilite	Normosilite						Alkaline pseudosiallite	Sulfate normosiallite	Sulfatolite	Carbonatolite	Sulfate carbonatolite
n	15	4	3	2	10	4	2	3	3	2			
SiO_2	89.74	80.53	73.80	76.75	73.99	68.92	45.37	69.52	53.37	55.86	0.46	4.86	0.78
TiO_2	0.15	0.50	0.80	0.30	0.05	0.47	0.01	0.64	1.10	0.90	0.08	0.24	0.02
Al_2O_3	2.63	2.69	7.63	4.95	4.25	9.05	0.01	13.63	19.76	12.65	0.01	0.24	0.01
Fe_2O_3	0.45	1.04	1.88	1.60	0.60	1.36	0.35	2.46	3.42	9.37	0.12	0.12	0.44
FeO	0.28	0.54	1.05	0.40	-	0.82	-	0.69	2.24	0.72	-	0.43	0.43
MnO	0.02	0.14	0.09	0.06	0.04	0.13	0.14	0.03	0.26	0.07	0.06	0.14	0.26
MgO	0.34	0.88	0.45	0.48	0.29	0.90	6.80	1.51	3.28	1.24	19.68	40.78	20.36
CaO	1.11	4.37	3.08	2.11	2.90	4.36	16.83	0.97	1.15	2.77	25.06	2.08	26.41
Na_2O	0.42	0.18	0.25	3.20	4.91	0.58	0.07	0.38	0.46	0.31	0.05	0.06	0.04
K_2O	1.78	1.47	3.14	2.59	2.95	6.34	0.06	4.85	4.85	4.42	0.03	0.64	0.04
P_2O_5	0.05	0.06	0.06	0.03	0.06	0.06	-	0.08	0.11	0.08	0.03	0.06	0.03
SO_3	0.76	1.36	2.53	0.38	2.07	1.23	15.86	2.47	1.02	4.08	26.97	2.53	17.40
CO_2	0.73	4.33	2.35	1.10	0.88	3.16	-	0.55	1.67	4.98	-	-	-
Cl	0.38	0.49	0.55	3.45	5.44	0.55	0.01	0.65	0.85	0.34	0.13	0.15	0.15
LOI	4.20	8.34	6.47	3.01	2.93	2.14	14.03	7.93	20.52	10.43	27.86	47.49	34.49
HM	0.04	0.06	0.16	0.10	0.07	0.17	0.01	0.25	0.50	0.42	0.59	0.24	1.49
AM	0.03	0.03	0.10	0.06	0.06	0.13	0.00	0.20	0.37	0.23	0.02	0.05	0.01
TM	0.058	0.186	0.105	0.061	0.012	0.052	1.000	0.047	0.056	0.071	8.000	1.000	2.000
FerM	0.27	0.54	0.36	0.39	0.15	0.24	24.50	0.22	0.28	0.75	2.00	1.44	37.67
NKM	0.83	0.61	0.44	1.17	1.85	0.76	12.00	0.38	0.27	0.37	8.00	2.92	8.00
AlkM	0.20	0.10	0.10	1.20	1.70	0.10	1.20	0.10	0.10	0.10	1.70	0.10	1.00

Note. The materials were presented by G.V. Ivensen at the All-Russian School of Lithochemistry, conducted by us in Syktyvkar (May 1997)

Table 84

—carbonate deposits of the Devonian

according to G.V. Ivensen, 1997 (private message)

5	9	22	23	25	32	37	45	46	47	51	62	64
Siltstones		Sandstone (Mn sulfate carbonate pseudosiferlite)	Argillite (sulfate hypohydrolysate)	Sandstones		Sandstones		Anhydrite (sulfatolite)	Sandstones		Siltstones	
Hypersilite	Sulphate normosilite			Sulphate alkaline myosilite	Alkaline normosilite	Clalkaline pseudosilite	Clalkaline supersilite		Sulfate carbonatolite	Cl alkaline hypersilite	Mnsulfate carbonate pseudohydrolisate	Sulphate supersilite
94.19	75.68	47.60	49.63	54.25	73.55	78.08	68.69	0.48	3.96	83.49	31.28	66.93
0.30	0.38	0.02	1.11	0.18	1.56	0.02	0.06	0.01	0.01	0.01	0.70	0.32
0.08	3.73	1.30	20.15	6.40	8.80	4.44	3.60	0.16	0.01	0.24	8.36	3.68
1.09	6.52	0.97	3.08	4.67	1.18	0.60	1.36	0.16	0.32	0.02	1.98	0.11
0.28	0.43	13.08	8.18	0.98	-	-	0.67	-	-	-	6.08	0.57
0.00	0.08	1.45	0.29	0.32	0.03	0.04	0.17	0.30	0.49	0.00	1.87	0.06
0.30	0.35	5.53	0.93	0.62	0.39	3.28	2.98	28.90	23.01	0.00	13.53	0.00
0.36	3.03	7.50	1.05	8.53	1.58	1.65	5.24	15.73	22.68	0.91	4.05	9.73
0.20	0.30	0.09	0.27	1.27	0.41	4.02	3.65	0.06	0.06	6.30	0.35	0.12
0.75	2.09	0.62	3.33	4.04	6.45	3.21	2.23	0.03	0.02	0.09	2.90	1.44
0.06	0.05	0.10	0.03	0.03	0.06	0.06	0.03	0.03	-	0.03	0.11	0.08
1.85	4.60	3.37	5.74	9.96	1.90	0.18	2.15	22.38	15.71	0.40	7.03	13.64
0.55	2.21	-	2.22	-	0.55	1.65	6.76	-	-	-	-	-
0.29	0.43	0.17	0.59	1.72	0.27	4.34	3.80	0.53	0.00	7.98	0.68	0.19
0.26	0.08	17.40	3.85	7.70	2.68	-	-	32.03	33.49	5.08	20.92	3.94
0.02	0.15	0.35	0.66	0.23	0.16	0.07	0.09	1.31	0.21	0.00	0.61	0.07
0.00	0.05	0.03	0.41	0.12	0.12	0.06	0.05	0.33	0.00	0.00	0.27	0.05
3.750	0.102	0.015	0.055	0.028	0.177	0.005	0.017	0.063	1.000	0.042	0.084	0.087
3.61	1.71	11.74	0.54	0.91	0.12	0.14	0.60	2.71	40.50	0.08	1.10	0.19
11.88	0.64	0.55	0.18	0.83	0.78	1.63	1.63	0.56	8.00	26.63	0.39	0.42
0.30	0.10	0.10	0.10	0.30	0.10	1.30	1.60	2.00	3.00	70.0	0.10	0.10

and “siltstone” (sample 62), which makes these rocks to be certified as "manganese". All rocks with such anomalies contain dolomite. It can be assumed that we have here a type of manganese accumulation described by K. Wedepohl for the German Zechstein: accumulation of Mn^{2+} in stagnant waters of stratified salt-bearing lagoons with subsequent deposition in dolomite [360].

The compositions of evaporites published in the literature are often incomplete, which makes it impossible to calculate the values of all modules, but even from the available data, values are often obtained that are difficult to give a reasonable interpretation. Such, for example, is the average composition of the Devonian anhydrite rocks of the Dnieper-Donets depression (Table 85), calculated by us from four analyzes given by V.A. Khomenko [266].

The absence of alumina in these analyzes does not allow us to estimate the values of the HM, NKM and FerM modules. However, the hydrolysability of the sulfate-free part of these rocks is interesting. On average, it turns out HM = 1.54, and according to individual analyzes – from 1.18 to 3.13! Note that in the previous example (sulfate carbonatolite, sample 3), we encountered an unusually high HM value (1.49). The reason for this is poorly understood. Apparently, in such rocks, there is no terrigenous admixture at all, and both silica and iron oxides are chemogenic.

Table 86, the mean compositions of Neogene sulfatolites of the Fergana Valley calculated by O.M. Rosen [223] are given: gypsum, anhydrite (cluster II) and genetically related terrigenous (an. 3, cluster I) and carbonate (an. 6) rocks enriched in sulfates. Although the modules, in which there is no sulfur or sulfate, do not provide clear information about the specificity of these rocks, attention is drawn to the hyperalkalinity: NKM – from 0.58 to 0.93 in sulfatolites. This fact can "alert" the researcher and make him pay attention to the sulfur or

Table 85

Average chemical composition of anhydrite rocks
of the Dnieper–Donetsk depression.
Compiled according to V.A. Khomenko, 1977 [266, p. 26–27]

Oxides	Content, %	Components and modules	Content, %
SiO_2	0.54	SO_3	52.55
TiO_2	0.05	H_2O^-	0.06
Fe_2O_3	0.19	LOI	1.70
FeO	0.41	CO_2	1.58
MnO	0.01	C	0.26
MgO	0.75	Cl	0.11
CaO	41.34	F	0.02
Na_2O	0.23	Total	100.37
K_2O	0.30	HM	1.54
P_2O_5	0.09	FM	2.49

Table 86

Chemical composition of sulfatolites and related sulfate-bearing rocks in the Neogene sediments of Fergana.

Compiled according to O.M. Rosen, 1979 [223, p. 451].

Oxides and modules	1	11	3	6
	Sandstones and siltstones (sulfate myosilite)	Gypsum and anhydrite (sulfatolite)	Clays (Cl sulfate pseudosiallite)	Limestone (carbonatolite)
m	10	7	14	2
n	2	2		
SiO_2	48.05	9.13	41.11	9.70
TiO_2	0.36	0.22	0.57	0.14
Al_2O_3	7.88	2.34	13.04	1.99
Fe_2O_3	1.14	0.63	2.70	0.20
FeO	1.53	0.62	2.10	0.60
MnO	0.07	0.02	0.08	0.12
MgO	1.91	1.71	5.08	0.98
CaO	15.82	30.32	10.67	44.77
Na_2O	1.74	0.89	2.64	0.78
K_2O	1.43	0.55	2.12	0.49
P_2O_5	0.09	0.03	0.10	0.02
H_2O	5.33	9.54	6.20	2.05
SO_3	5.74	41.42	3.62	1.48
CO_2	9.24	3.67	8.80	35.80
Cl	0.50	-	1.06	-
Total	100.80	101.05	99.87	98.92
HM	0.23	0.42	0.45	0.31
FM	0.10	0.32	0.24	0.18
AM	0.16	0.26	0.32	0.21
TM	0.046	0.094	0.044	0.070
FerM	0.33	0.49	0.36	0.43
NKM	0.40	0.61	0.37	0.64
AlkM	1.20	1.60	1.20	1.60

sulfate content in the rocks. In addition, the hypertitanium value of gypsum and anhydrite (TM 0.476) is very curious (although not clear).

Sulfatolites associated with sulfuric weathering are a special variety. Genetically, they, of course, are not "evaporites" (i.e., the products of brines evaporation) and are categorized as such purely formally. Table 87 shows analyzes of very peculiar secondary formations containing substrate residues (quartz, carbonate, clay matter), metastable aluminum sulfate (aluminite), gypsum, and iron hydroxides. They were formed because of sulfuric weathering of sulfide-bearing sedimentary rocks of the Lower Vilyuikan horizon (D_1–D_2) in Western Yakutia [138]. A characteristic feature of rocks with sulfates is a high

Table 87

Chemical composition of sulfate rocks of the Lower Vilyukan horizon D_1–D_2 and underlying clays, Western Yakutia.

Compiled according to G.V. Kozlov et al., 1977 [138, p. 134].

Oxides and modules	1	2	3	4
	Sulphate rocks			Clay (sulfate normosiallite)
	Sulphatolite		Sulfide carbonatolite	
SiO_2	0.39	8.90	22.39	52.58
TiO_2	0.04	0.14	0.24	0.55
Al_2O_3	30.86	8.49	3.58	12.63
Fe_2O_3	1.00	10.40	8.08	9.70
MnO	0.01	0.13	0.73	0.0!
MgO	0.10	0.00	0.72	1.74
CaO	1.56	18.01	32.19	2.13
Na_2O	0.00	0.17	0.57	0.88
K_2O	0.00	0.46	1.20	2.53
P_2O_5	0.00	0.00	O.O!	0.04
SO_3	26.40	30.25	0.90	6.22
S	0.00	0.00	4.94	0.34
H_2O^+	16.95	13.94	0.31	4.05
LOI	22.26	8.83	26.17	6.44
Total	99.57	99.72	102.03	99.84
HM	81.82	2.15	0.56	0.44
FM	2.82	1.17	0.39	0.22
AM	79.13	0.95	0.16	0.24
TM	0.001	0.016	0.067	0.044
FerM	0.03	1.22	2.31	0.74
NKM	0.00	0.07	0.49	0.27
AlkM	-	0.40	0.50	0.30

HM – sulfate-free part of sample no. 1 and 2 could be qualified as a hydrolysate. It is possible that this feature, in the absence of other information, could help distinguish sulfatolites associated with pyrite oxidation from sulfatolites associated with the evaporite process.

6.10. Cahytolites

Cahytolites include sedimentary rocks of various compositions, containing C_{org} in an amount of 15 % or more. This type includes some "black shales", mainly those that are traditionally called *oil shale*, most coals of varying degrees of metamorphism, as well as some graphite rocks – products of the metamorphism of ancient black shales. As A.E. Kontorovich emphasized in his time [139], sedimentary rocks' OM belongs to two basic genetic lines – aquagenic and terrigenous, usually inaccurately referred to in the literature as “sapropel” and “humic” [300]. The material classes of cahytolites are oxygen (O), hydrogen (H) and nitrogen (N) – approximately correspond to the proper humic (arkonic), proper sapropel (aline), and mixed humus–sapropel (amikahyn) varieties of natural OM – sedicahytes [46].

However, the cahytolites characterization by the composition of only their "combustible" part is incomplete because it does not consider some chemical elements, which are also organic matter components. Elements such as Ca, Mg, Fe, Al, and even partly Si, form the *virtual components of cahytolites*, namely, the genetic classes of their "ash": plant (biogenic) and sorption. These issues are discussed in detail in the geochemistry of fossil coals [293, p. 34–58].

In 1978 we attempted the lithochemical characterization of coal ash using two modules: alumosilicon (M) and calcium-magnesium-iron (K), which is the ratio of the difference to the sum: $K = [(CaO + MgO) - Fe_2O_3]/(CaO + MgO + Fe_2O_3)$.

The complex structure of this module was designed to reflect the ratio of two mineralization types in the coal: carbonate and sulphide. It was assumed that the correlated appearance of the module diagram in the M–K coordinates reflects the syngenetic character of mineralization (aluminum, calcium, magnesium, and iron are part of the plant and sorption "ash" of the coal), and the appearance of uncorrelated swarms of points ("prominences") on the diagram reflects the presence of superimposed epigenetic "ash" – carbonate or sulphide mineralization [293, pp. 30–33]. The appearance of the plot should have been strongly influenced by the total ash content value of the coal since the correlated field is typical only for low ash coals.

More than 20 years later, our invention can be assessed.

1. Application of modules M (in lithochemistry – AM) and K (no analogue in lithochemistry) has not received any development in the geochemistry of coals; in any case, we are not aware of such works.

2. The idea of using an aluminum-silicon module for characterizing the coal ash composition is undoubtedly fruitful; this allows to evaluate the role of kaolinite in ash (for kaolinite, AM = 0.85) and the contribution of alumina from sorption ash in cases where the AM value exceeds the kaolinite norm.

3. The K module structure is probably not the best; therefore, further searches in this direction are legitimate. Firstly, instead of the difference in the numerator, it is better to simply use the value (CaO + MgO), and secondly, the Fe_2O_3 content in the ash does not give a correct idea of the pyrite content, since siderite also affects this value. Probably a more adequate measure of the pyrite content is the SO_3 content in the ash. Then the module K could have the form $(CaO + MgO)/SO_3$.

4. The chemical composition of *low-ash* coal ash is undoubtedly specific and has no direct analogs among normal sedimentary rocks.

Unlike coals, most *black shales* are not cahytolites ($C_{org} < 15$ %); therefore, their mineral matrix in composition usually differs little from the host non-carbonaceous deposits. However, some varieties of black shale, like coal, turn out to be "exotic" in composition due to the accumulation of iron sulfides, phosphorus, manganese carbonates, sometimes also barite and barium silicates, and from small components – molybdenum, vanadium and zinc. Such accumulations are *specific*, that is, they are genetically related to the organic matter of black shales [300; 303, p. 17].

6.11. Mixtolites

As noted in Ch. 2, mixtolites are such oxide and aluminosilicate rocks (mostly pyro-, petro-, and lithogenic), which contain a significant proportion of aquatic components – carbonate, phosphate, sulfate, carbonaceous, and less often others. The mixtolite taxon includes many sedimentary rocks that make up a very noticeable (but not yet accurately estimated) portion of the sedimentary shell. In the newest lithological "Systematics" great attention is paid to mixtolites; the problems associated with the terminology of such rocks are analyzed in detail [238].

Sometimes the very definition of a rock as a mixtolite carries genetic information. For example, in the analyzes of the Upper Devonian arkoses of the Dnieper–Donetsk depression, attention is drawn to the high content of sulfate sulfur, which is completely uncharacteristic of sandstones: in 5 out of 6 samples, the SO_3 content was 0.22–3.03%. The last figure is already acquiring a classification status and needs to be reflected in the name of the rock: "sulphurous alkaline hyposiallite". Referring to the petrographic description of V.A. Khomenko [266, p. 24], we understand the reason for the accumulation of sulphur; it turns out that these sandstones are characterized by cements with the participation of salts: micaceous-anhydrite-carbonate, carbonate-anhydrite-halite. Thus, the certification of these arkoses as sulphurous mixtolites indicates the process of sulfate epigenesis.

The practice of lithochemistry reveals two types of mixtolites, which can be conventionally designated as "nonspecific" and "specific". The former includes such mixtolites that simply inherit the compositional characteristics of their components and therefore do not carry any additional lithochemical information. For example, carbonate varieties of terrigenous rocks very often show higher TM values compared to non-carbonate ones, which is a simple consequence of the increased TM in carbonate matter. Similarly, phosphate mixtolites can have increased alkalinity (NKM) or sodium content (AlkM), again since such features are also inherent in pure phosphate matter. On the contrary, in specific mixtolites some new quality (emergence) appears, which was not present in their components. It can be assumed that nonspecific mixtolites are formed because of mechanical mixing (without chemical interaction) of a dissimilar material, whereas during the formation of specific mixtolites, allochemical processes could take place. For example, silica, carbonate, sulfate, or phosphate cement can fill the pores, but it can also metasomatically replace the aluminosilicate matrix [287].

Here are some typical examples, ranked in order of increasing complexity of the mixtolites composition.

Processing of the *average* compositions of the Upper Vendian clastic rocks of the Russian platform [72], where each analysis corresponds to a formation, allows us to distinguish three clusters of sandstones and two clusters of siltstones. At the same time, a cluster of *sandstones with carbonate cement* (about 18% $CaCO_3$) overlaps with carbonate-free sandstones in terms of HM and alkali content. The characteristic features of the composition of the former (increased FerM, NKM, and AlkM values) allow to assume that carbonate cement, during its formation, “ate up” an admixture of clay matter, reducing the alumina and potassium content in the rocks.

Table 88 and in Fig. 70 shows the processed compositions of 23 samples of Cenomanian nodular phosphorites of the Polpinsky deposit, located 30 km to the NE from Bryansk city [167]. Formally, only sample 10 is a phosphatolite, while others are certified as phosphate silites (the host rocks for them are quartz sands).

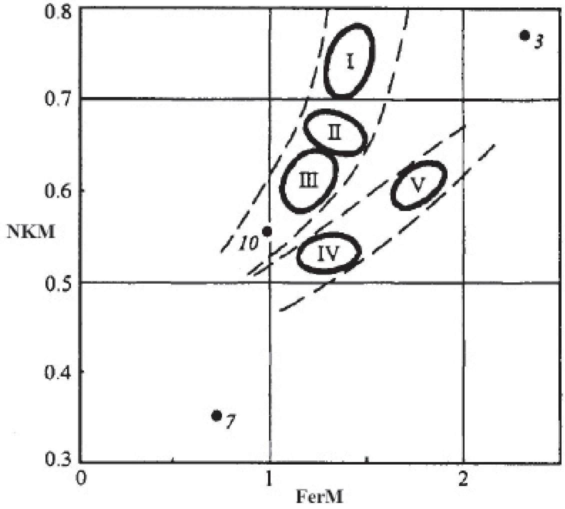

Fig. 70. Module diagram for Cenomanian nodular phosphorites. *Compiled according to S.V.Manukovsky and V.M.Podobnyi, 1993* [167, p.107]

Table 88

Chemical composition of Cenomanian nodular phosphorites.
Compiled according to S.V. Manukovsky and V.M. Podobny, 1993 [167, p. 107]

Oxides and modules	I	II	III	IV	V	3	7	10
	Phosphate supersilite	Phosphate normosilite		Phosphate supersilite	Phosphate normosilite			Phosphatolite
n	4	5	6	3	2			
SiO_2	41.83	39.87	34.82	42.20	38.22	43.58	34.70	22.52
Al_2O_3	1.77	1.83	2.10	1.81	2.09	1.77	3.73	2.31
Fe_2O_3	2.48	2.42	2.53	2.32	3.71	4.12	2.72	2.28
MgO	0.52	0.46	0.43	0.50	0.47	0.56	0.37	0.56
CaO	27.28	28.62	30.91	27.69	28.46	27.00	30.60	37.68
Na_2O	0.55	0.56	0.59	0.45	0.63	0.55	0.60	0.70
K_2O	0.76	0.66	0.70	0.51	0.65	0.81	0.72	0.58
P_2O_5	16.61	17.38	19.04	16.94	17.79	16.22	19.10	23.23
CO_2	3.26	3.23	3.37	3.24	3.30	3.12	3.39	3.86
LOI	6.27	5.88	6.44	5.68	5.97	5.71	6.70	7.20
Total	101.31	100.90	100.95	101.34	101.26	103.44	102.63	100.92
HM	0.10	0.11	0.13	0.10	0.15	0.14	0.19	0.20
FM	0.07	0.07	0.09	0.07	0.11	0.11	0.09	0.13
AM	0.04	0.05	0.06	0.04	0.05	0.04	0.11	0.10
FerM	1.40	1.33	1.21	1.29	1.78	2.33	0.73	0.99
NKM	0.74	0.67	0.62	0.53	0.61	0.77	0.35	0.55
AlkM	0.70	0.80	0.80	0.90	1.00	0.70	0.80	1.20

Judging by the high NKM values, the carriers of alkalis are feldspars, not micas. In addition, according to the siallite standard, all phosphorites are hyperferrous: FerM > 1, at a maximum of 1.84. On the module diagram NKM – FerM (Fig. 70), one can notice two trend bands, which, perhaps, correspond to some two types of phosphorites: sample ⇒ 10 clusters III, II ⇒ cluster I and cluster IV ⇒ cluster V.

In the first band, the clusters identification is somewhat arbitrary: it is possible to combine clusters III and II. Probably, the difference in alkalinity reflects the different ratio of sandy-silty and clay matter in these phosphorites. Outside the clusters, phosphorites are the most (sample 3) and least ferruginous (sample 7, 10). Since the latter are also distinguished by the maximum HM (0.19–0.20), it is obvious that these are the most clay phosphorites. Most likely, they come from the "first lower" productive layer (and there are four such layers in the field).

So, the Upper Cretaceous nodular phosphorites-mixtolites do not have their own lithochemical specificity; in any case, the identified clusters do not differ significantly in the P_2O_5 and CO_2 contents. Obviously, the high alkalinity and iron content of these phosphorites are simply inherited from the host rocks and are not inherent in the phosphate material itself.

The phosphorites of the Permian Phosphoria formation in the USA have a much more complex composition, which consist of at least five rock-forming components: 1) carbonate, represented by calcite and dolomite in variable proportions; 2) apatite–francolite; 3) organic matter; 4) terrigenous clay matter; 5) authigenic (biogenic) silica. The contents of all these components vary widely. In particular, the normative recalculation of the compositions of 21 samples from the section of the Montpellier canyon into state Idaho [342] gives the limits of the contents of these components, respectively: 0–60, 1–96, 0.5–11, 1–66, 0–71%.

On the NKM – HM module diagram, six clusters and four separate compositions can be identified (Fig. 71, Table 89). Rocks are certified as phosphatolites or carbonatolites if the P_2O_5 or CO_2 content reaches 20%. However, there are fewer such compositions than mixtolites, for example, carbon-phosphate siallites or silites, depending on the ratio in the non-phosphate part of clay matter and authigenic silica. The varieties of phosphate-containing rocks form two trends: with a linear decrease in HM and an increase in alkalinity with increasing phosphate content (a series of clusters I ⇒ II ⇒ III) and with a nonlinear change in HM with almost unchanged alkalinity (clusters IV ⇒ V ⇒ VI). Obviously, the first band of the trend is phosphate rocks with a substantially clay base, and the second – with a substantially silica base, and the nonlinearity of the change in the HM value may indicate an allochemical process (input–removal of silica during diagenesis).

Cluster I is formed by 6 samples of carbonaceous phosphate hyposiallites containing 14–18% P_2O_5, 22–32 SiO_2, 3–7 CO_2, and 3.1–6.6% C_{org}. In general, the

Table 89

Chemical composition of phosphate-bearing deposits of the Phosphoria Formation, Montpellier Canyon, Idaho, USA.

Compiled from the data of M. Medrano and D. Peiper, 1992 [342, p. A16–A17]

Oxides and modules	I	II	III	IV	V	VI	1	2	9	13
	Phosphate carbonaceous hyposiallite	Carbonacerous phosphatolite	Phosphatolite	Phosphate myosilite	Carbonacerous phosphatolite	Phosphate normosilite	Carbonatolite	Phosphatolite		Phosphate carbonate normosiallite
n	6	3	2	2	2	2				
SiO_2	27.75	18.03	10.39	26.60	20.65	37.40	3.88	5.00	3.70	12.10
TiO_2	0.25	0.15	0.08	0.20	0.13	0.11	0.00	0.07	0.01	0.11
Al_2O_3	6.42	3.90	1.79	4.26	2.86	2.81	0.17	1.29	0.35	2.98
Fe_2O_3	2.26	1.60	1.17	1.61	0.95	1.72	0.10	1.42	0.38	1.06
MnO	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01
MgO	0.94	0.51	0.29	1.70	0.39	0.47	0.41	0.28	0.17	1.11
CaO	26.95	34.74	44.77	30.32	36.44	29.84	54.04	49.10	51.75	37.09
Na_2O	0.35	0.39	0.34	0.44	0.26	0.45	0.04	0.65	0.16	0.24
K_2O	1.81	1.12	0.47	1.16	0.86	0.64	0.02	0.35	0.09	0.84
P_2O_5	15.64	22.47	30.07	17.28	24.52	18.98	12.61	32.22	37.38	16.07
CO_2	-	-	2.12	4.70	-	-	-	4.50	2.38	-
C_{org}	4.89	4.97	1.96	2.42	3.57	0.87	0.82	0.50	0.83	6.31
LOI	15.11	13.12	6.13	10.81	9.38	5.13	29.40	5.73	3.52	23.50
Total	102.37	101.01	99.54	101.48	99.97	98.42	101.51	101.12	100.73	101.42
HM	0.32	0.31	0.29	0.23	0.19	0.12	0.08	0.56	0.20	0.34
FM	0.12	0.12	0.14	0.12	0.06	0.06	0.13	0.34	0.15	0.18
AM	0.23	0.22	0.17	0.16	0.14	0.08	0.04	0.26	0.09	0.25
TM	0.038	0.038	0.042	0.046	0.044	0.039	0.000	0.054	0.029	0.037
FerM	0.34	0.40	0.63	0.36	0.32	0.60	0.71	1.05	1.08	0.35
NKM	0.34	0.39	0.45	0.37	0.39	0.39	0.35	0.78	0.71	0.36
AlkM	0.20	0.40	0.70	0.40	0.30	0.70	2.00	1.90	1.80	0.30

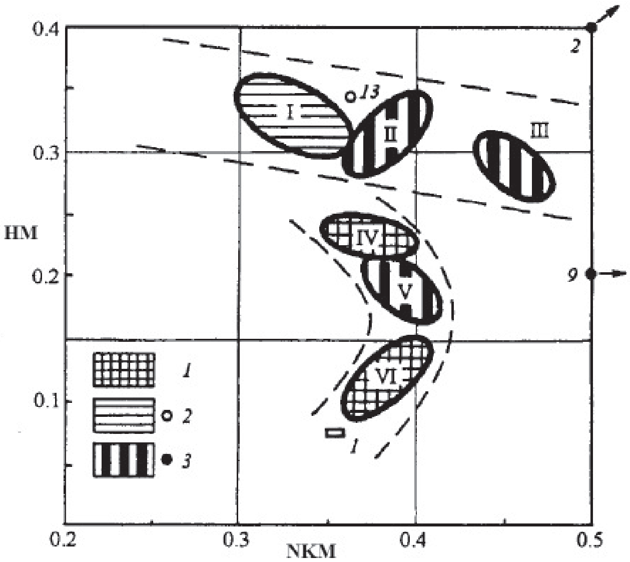

Fig. 71. Module diagram for phosphate-bearing sediments of the Phosphoria Formation, Montpellier Canyon, state Idaho, USA.

Compiled according to M. Medrano and D. Peiper, 1992 [342, p. A16–A17].

1, 2 – mixtolites: phosphate silites (1) and phosphate carbonaceous siallites (2); 3 – phosphatolite

phosphate mixtolites of cluster I are distinguished by the lowest NKM value and the highest HM value. It is quite obvious that these are relatively poor phosphorites, in which the non-phosphate material is mainly clay rather than silica.

Cluster II is formed by three samples of carbonaceous phosphatolites with increased alkalinity (NKM 0.40 versus 0.34 ± 0.02 in cluster I).

Cluster III is also formed by phosphatolites, which are somewhat more silica and alkaline, but much less carbonaceous (C_{org} 2 % versus 5.6 % in cluster II). Clusters IV and V form carbonaceous phosphate myosilites and carbonaceous phosphatolites. These are the same rocks as in clusters I and II, but more silica. Authigenic silica acts as a mechanical diluent, almost without affecting the NKM values. This means that the silicate matter composition in them is the same as in the rocks of clusters I and II.

Cluster VI is formed by the most silica rocks – phosphate normosilites.

Outside the clusters are, on the one hand, the most carbonate rocks (samples 1, 13), and on the other, the richest phosphorites (samples 2, 9). The latter differ not only in maximum alkalinity (NKM 0.71–0.78, while in others it is not higher than 0.50), but also in abnormal FerM value (~ 1 versus 0.30–0.40).

Thus, despite the diversity of the phosphate mixtolites composition, they do not show any specific features of their composition.

Probably, the carbonaceous mixtolites-siallites composition, which is represented by *atmospheric dust* collected in snow samples on the territory of the southern Ural industrial city of Miass, should be certified as specific [141]. The HM value in dust samples reaches almost to the border of hydrolysates, and the presence of a soil nature humic substance determines the carbon dust content; judging by the value of losses on ignition (minus CO_2 and H_2O), the OM content in the samples reaches 10 %.

However, the authors of the materials are mistaken, believing that "*the chemical dust composition corresponds to the basic rocks ...*" [141, p. 111] – this diagnosis does not agree with the low magnesium value of the dust. The nature of the increased hydrolysability is not clear from the above materials, because the mineralogical analyzes data do not show its carrier: quartz 2–3 %, calcite 1–14 %, dolomite, talc, feldspars, chlorites – 1–3 % each, other 1 % or less. Thus, the mixtolite dust composition is very peculiar and has no analogue among water-sedimentary formations.

PART II

PROBLEMS OF GLOBAL LITHOCHEMISTRY

Currently, five or six problems of global lithochemistry have emerged. Some of them are relatively new, previously not clearly formulated, while others have a rather long history. In general, lithochemical problems can be divided into two fields, descriptive and diagnostic: a) inventory of the traditional lithotypes compositions; b) diagnostics of rocks.

Inventory of the sedimentary rocks' chemical compositions given in the literature. The development of a databank by clustering the compositions of hundreds of statistical samples (formed according to a stratigraphic, geostructural or geographical principle) on module diagrams results in several thousand clusters – a set representing a chemotypes' variety. Next, this set should be subjected to statistical processing in order to find out whether there are "dips" on the frequency graphs, which should correspond to some natural (and not predetermined by the researcher) boundaries. For example, as shown in Chapter 3, the frequency HM value distribution in siallites revealed the absence of a clear boundary in the HM interval 0.50–0.55; this forced us to abandon the allocation of the "hypersiallites" class, which was practiced earlier – before statistical processing [301, 302]. Obviously, most chemotypes will closely or almost exactly match the known lithotypes. However, one certainly will not find a complete correspondence: as was shown in Ch. 5, the set of chemotypes is, as a rule, richer than the set of lithotypes.

As a result, one will obtain statistically reliable characteristics of the sedimentary rocks' chemical composition – this has long been done for magmatic rocks. *To bring lithochemical systematics to the level of petrochemical* – this is how this problem can be briefly formulated. To solve it, one will need to process a sufficiently large set of analyzes, in which sedimentary rocks of different ages and different regions should be presented.

Diagnostics of volcanic admixtures in sedimentary rocks. At the present time, this is, apparently, the most urgent problem [305], but it can be formulated more broadly: *diagnostics of pyrogenic rocks*. In addition, since some volcanoclastic greywackes are often difficult to distinguish from tuffoids, the problem actually embraces *diagnostics of petrogenic rocks*. As we will see below (Chapter 7), such characteristics as magnesiality, the presence of alkaline compositions up to alkalites, positive correlation FM–TM, FerM–TM, negative correlation NKM–FM and some others, make it possible to distinguish volcanogenic-sedimentary rocks from normal sedimentary.

Based on the databank, it is necessary to adjust diagnostic techniques and develop its methodology in the form of a clear recognition algorithm. The first results of such diagnostics, performed on the black shale strata of the Pai-Khoi and the Lemva zone of the Urals, turned out to be very successful [71, 74, 206, 297].

Geological evolution of hydrolysates. By now, quite a lot of data have been accumulated on the weathering crusts composition of different ages [21, 82, 200, 233]. It was found that the processes of subaerial weathering in the Archean, Proterozoic and Phanerozoic had their own specificity associated with the atmosphere and biosphere evolution. For example, one can consider it established that during the Karelian weathering of the Late Archean granite-greenstone regions, iron and silica were vigorously removed into the ocean – this process has never repeated in the history of the Earth.

In addition, we believe that in the epoch of the Precambrian supercontinents – ancient Pangaei – alkaline arid weathering prevailed on Earth with the potassium accumulation in the weathering crusts. Apparently, as a whole, arid geocratic epochs were longer than thalassocratic humid epochs, which was the reason for the thick continental red-colored strata formation composed of high-potassium rocks – arkoses and clays [298]. Apparently, the fact that the ancient weathering products of mafic rocks (that is, genetically undoubted hydrolysates) still retain a noticeable magnesiality ($MgO > 3\ \%$), which requires upgrading the classification and introducing a special taxon *magnesiohydrolysates* into it.

However, not only arid, but also ancient humid weathering had little resemblance to lateritic weathering; most likely, it resembled the modern gley (carbon dioxide) process, but much more intense. The task is to follow A. I. Pak [200], A.D. Savko and A.D. Dodatko [233] and some other researchers [21, 82] and to detail the evolution of weathering crusts by developing a data bank. This attempt, to its simplest extent, was undertaken in Ch. 8.

Diagnostics of metahydrolysates' convergent composition. When describing the taxon "hydrolysates" (Chapter 6), we have already noted that endogenous hydrolysates (metasomatic and hydrothermal rocks of the secondary quartzite formation, hydrothermal argillisites, and some other products of allochemical metamorphism) can have a chemical composition that is very close to the hypergene hydrolysates composition – crust weathering products. The problem of distinguishing them is extremely acute since the assessment of mineral resources directly depends on this.

For example, the unique manifestations of rare earth diaspora rocks in the Subpolar Urals [308] are hardly of practical interest if they are locally developed metasomatites with limited reserves. But the prospective assessment of these fossils could change radically – if it were possible to prove that rare earth diasporites are in fact metamorphosed Cambrian weathering crust [187]. The challenge is to find reliable diagnostic features to distinguish between endogenous and hypergenic hydrolysates. We try to solve this problem to its simplest extent in Ch. 9.

Diagnostics of the isochemical metamorphites' primary substrate. This is an old problem with which, in essence, the development of lithochemistry began in our country. Although this problem has undergone a thorough study in O. M. Rosen, A. A. Predovsky and A. N. Neelov's works [183, 184, 212], one cannot consider it completely solved. Successful experience in diagnostics of the Subpolar Urals metamorphic rocks [75, 111, 177, 178, 299, 304, 308, 310–312, 315] has shown that the methods of lithochemistry are quite effective for solving this traditional problem. In this book we give numerous examples of diagnostics of the metamorphites primary substrate in Ch. 7–9.

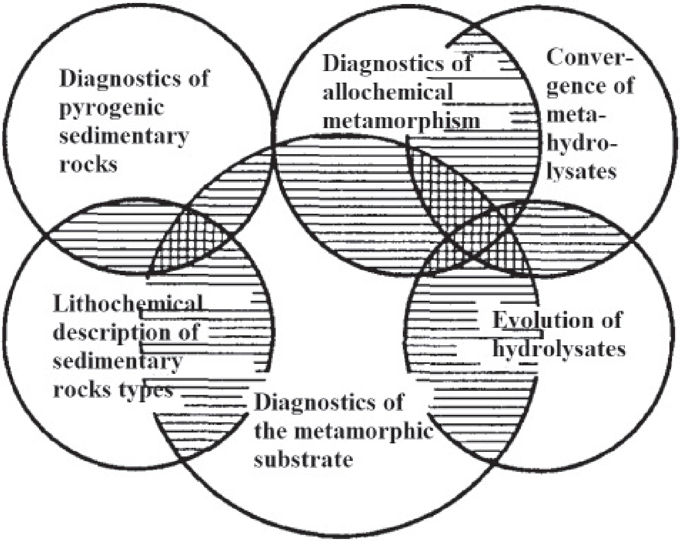

Fig. 72. Correlation of the lithochemistry problems, shown with the help of Euler's circles.
Areas of overlap (subject-logical connections) are shaded [301, p. 25]

Diagnostics of the allochemical metamorphism processes. This task was not posed at all: the "metamorphists'" works always postulated that the diagnostics of the metamorphic substrate can be correct only if the allochemical metamorphism processes can be neglected [284]. However, the experience of our work in the North Urals showed that the indicated processes manifested themselves much wider than it was imagined earlier, and at the usual scale of sampling it is in no way possible to neglect them [309]. At the same time, it unexpectedly turned out that allochemical processes can often be recognized by some features of module diagrams. The challenge is to accumulate more data and propose a recognition algorithm. The reader will find some examples of such recognition in Ch. 8 and 9 of this book.

All the listed lithochemistry problems are by no means separated by an abyss: they have areas of overlap – subject-logical connections (Fig. 72).

CHAPTER 7

DIAGNOSTICS OF A PYROGENIC IMPURITY

7.1. Tuffoids, their role in the sedimentary shell and problems of recognition

In Ch. 1 we have already mentioned four genotypes of sedimentary rocks: petrogenic (arkose and greywacke of the first cycle rock type), lithogenic (various recyclization products – second cycle rock, etc.), aquagenic, and pyrogenic. The last genotype, which is conveniently designated by the free use term, *tuffoids*, are pyroclastic rocks in traditional lithological classifications.

The newest "Systematics" distinguishes *«volcano-sedimentary rocks*", and among them, according to the formation method, they distinguish two groups: “effusive-clastic” and “explosive-clastic, or tuffs”. The former are additionally subdivided by genesis into lavoclastites and hyaloclastites, and the second largest by pyroclastics size – into agglomerate, lapillian, sandy, and silty. The last two varieties are usually called *ash tuffs* [238, p. 301]. If we add the products of volcanic exhalations to the detrital volcanogenic rocks, we get the following scheme:

Volcanogenic material	*Pyroclastic (hot): pyrogenic rocks*	Hyaloclastic Lavo-clastic Explosive-clastic Exhalative
	Volcanoclastic (cold): petrogenic rocks	Greywackes Arkoses

This division is based on *the mechanism of volcanic sediment formation.* During the formation of pyrogenic sediments, clastogenesis is explosive and effusive: fresh incandescent fragments enter the sediment (or coagulated suspensions are deposited), which stimulates powerful processes of authigenic mineral formation. During the formation of petrogenic sediments, the clastogenesis process is a low-temperature, hypergenic one. Unfortunately, the means of lithochemistry may not be sufficient to distinguish the indicated deposits genotypes; there is also no certainty that pyrogenic rocks can be reliably distinguished from petrogenic ones (for example, from volcanoclastic greywackes).

This problem is also relevant for lithology. As V.T. Frolov and M.N. Shcherbakova point out, "*ordinary exogenous-detrital volcanic sandstones or breccias, objectively indistinguishable from them, were often erroneously described as tuffs, which transfers the concept of "volcanic tuff" from petrographic to genetic: pyroclastic genesis of such layers is established most often only presumably, probabilistically, and this is contraindicated in petrographic concepts*" [238, p. 301].

This means that, while developing a technique for lithochemical diagnostics of pyrogenic rocks, we must leave the possibility that such a diagnosis may in fact also apply to petrogenic rocks. However, some differences between the one and the other, apparently, exist, and they will be discussed. In addition, we will not consider pyrogenic rocks of non-volcanic nature (xenotuffs, mud volcanic tuffs, kimberlites with an abundance of sedimentary and metamorphic rocks fragments, etc.).

Accurate lithological identification of tuffoids is a serious problem. What should be the minimum content of pyrogenic material to call a rock tuffoid: 50, 30, 10%? This boundary is uncertain since it clearly depends on the contrast between the pyroclastics composition and the host sediment. Let us assume that andesitic pyroclastic material enters the polymictic flysch sediment. In this case, the compositions of the endogenous and exogenous clastic can be so close that even the presence of a significant admixture of the former will have little effect on the sediment bulk composition. And vice versa, if, for example, acidic pyroclastics gets into a carbonate sediment, then the addition of even 10% of such material can already noticeably increase the alkali content and quite noticeably raise the NKM module value.

These examples show that it is very difficult to give an exact definition of tuffoids, but an imprecise definition is as follows: *tuffoids are sedimentary or sedimentary-metamorphic rocks with a noticeable admixture of pyrogenic material.* The word "noticeable" means that the tuffoids composition has features of *anomalousness* that distinguish it from the obviously sedimentary rocks. This approach was first implemented by us when processing analyzes of black shale strata in the Lemva zone of the North Urals: on the module diagrams, the composition points of the known tuffs jumped out of the contours of the normal sedimentary rocks' fields and, in this sense, were certified as “anomalous” [71]. Subsequently, this approach was successfully used by other researchers, for example, who studied the shungite strata of Karelia [192]. Thus, the diagnostic technique presupposed a preliminary study of a series of "training statistical samples" – analyzes of rocks for which their tuffoid nature was sufficiently reliably established by independent methods.

At present, none of the lithologists any longer doubts that pyrogenic material, along with terrigenous material, is a very important component of sediments, which together form strata hundreds and even thousands of meters thick. According to A.S. Kalugin, data on the Holocene eruptions frequency in North Kamchatka (Klyuchevsk group of volcanoes) show that at 42 km distance from volcanoes, the rate of ash layers accumulation is 12–14 cm per 100 years. “*With such a rate of accumulation, over a million years, an ash mass up to 1000 m thick can be deposited. The epochs of explosive volcanism last not only millions, but tens of millions of years, from which the possibility of ash accumulation up to tens and hundreds of meters thick even in areas remote from volcanoes at a distance up to hundreds of kilometers is obvious. Favorable for the ash accumulation is the leeward position of areas of possible ash falls, especially in zones of stable planetary winds, for example, near-latitude trade winds of the tropics. For the geological past, in particular, the position of reef bauxite-bearing sediments in the Devonian of the Urals and Salair in relation to the zones of synchronous explosive volcanism located to the east at distances of 50–150 km seems to be exactly this*” [125, p. 11]. Moreover, as the study of Cenozoic explosive volcanism shows, the paroxysms of eruptions are of a global nature. For example, a powerful activation of volcanism in the Eocene is recorded not only in ocean sediments, but also in sediments of the entire Alpine-Mediterranean fold belt [155]. It is known that the global epochs of the most powerful volcanism in the Phanerozoic were, for example, the Triassic, the Early Carboniferous and the Late Devonian, and in the Precambrian – Akitkanian (geochron, identified by L. I. Salop [234] and corresponding in an absolute scale to the period 1900–1600 Ma). The Triassic was characterized by basaltic volcanism, and Akitkanian by rhyolitic effusive and explosive volcanism of exceptional strength.

In general, the following rule is true*: the more detailed study of sedimentary strata, the greater is the role of pyrogenic deposits in them.* This can be seen in the well-studied Ordovician – Silurian strata of the Siberian Platform, where eight large cycles – sedimentary series – are found, and the horizons with acidic pyroclastics are located in the regressive parts of the sedimentary series, and there are no less than eight or nine such horizons. Horizons with basic pyroclastics are noted in transgressive facies (llandoveri), although they are much less common [14, p. 27–28].

Thick sedimentary strata of folded areas, as a rule, are much less studied than platform ones. Therefore, the role of pyrogenic deposits here can be underestimated. For example, in works devoted to flysch strata, we often find analyzes of "argillites" or "shales" containing 70–75 % SiO_2. Obviously, such a composition is impossible for normal clay siallite rocks. Therefore, it is necessary to admit either an admixture of authigenic (biogenic) silica (which looks strange for a flysch with its avalanche sedimentation), or an admixture of acidic pyroclastics. But in the latter case, the pelitic parts of flysch rhythms should be classified as tuffoids. This idea is quite correct, and even in 1969 A.S. Kalugin admitted: "*46 % of the ash mass of the North Kamchatka latest eruptions is deposited on land, and the remaining 54 % is deposited directly into the waters of the Pacific Ocean and the Sea of Okhotsk, despite the distance from volcanoes to the coasts of more than 80 km <...> As shown in the study of modern and ancient sediments, often undergoes further difficult transportation due to storm and seismic roiling, landslides, turbidity flows, bottom currents and other factors <...>*" [125, p. 9].

Based on these and other data, A.S. Kalugin concluded that "*among the basin sediments formed under conditions of repeated turbidity and gradational sedimentation, one can expect a noticeable ash admixture, most likely in the fine-grained fraction of layered rhythmic series, for example, the flysch type*" [125, p. 13].

How difficult it is to diagnose volcanic ash in terrigenous strata is evidenced by N.N. Karlov, who gave an excellent bibliography on the volcanic ash study in the European part of the USSR: "*At the beginning of XX century, most even experienced geologists could not distinguish ash from other rocks and constantly mixed them with sands, marls, etc.*" [126, p. 43].

As A.V. Van noted, who was the first to prove the wide distribution of tuffs in the Upper Devonian of the Kuzbass, "*due to deep changes, the external appearance of the tuffs macroscopically resembles normal sedimentary rocks, therefore, they were previously taken for terrigenous formations. Only detailed microscopic studies, supplemented by various types of analyzes, made it possible to reliably establish the pyroclastic origin of many of the rocks types under consideration*" [42, p. 35].

So, the difficulties in recognizing pyrogenic material in sedimentary strata have several objective reasons. First, even fresh tephra, getting into sediments, can "camouflage" in them, if its composition does not differ much from that of the sediment [144]. Second, ash tephra on its way into the sediment can undergo aeolian and water differentiation, as a result of which its composition can be very noticeably different from that of the original magma. Thirdly, ash tephra is a substance that is sharply out of equilibrium with the host sediment average and, as a result, is subject to significant allochemical changes.

7.2. Camouflage and differentiation of fresh pyroclastics

Camouflage of tephra in sediments. It is obvious that recognition of tuffoids among related petro-lithogenic (terrigenous) rocks is a much more difficult task than among aquagenic rocks, the composition of which usually contrasts with the composition of tuffoids. Another important factor in the diagnosis of tuffoids is the sedimentation rate. At minimum sedimentation rates in a deep-water basin, ash settling to the bottom is almost not diluted by terrigenous or biogenic matter; and at high rates, its strong dilution is inevitable. Therefore, an ash interlayer of the same age can be clearly visible in pelagic or bathyal strata, but it will be strongly "diluted" (and, as a result, camouflaged) in shelf sediments. In addition, if it is easy to recognize a light-colored interlayer of acidic tuff in the black-shale silica strata [71], then the same interlayer can be completely lost among light-colored alluvial, deluvial, or aeolian deposits. However, in black shale strata, lithological diagnostics of tuffoids can also be a difficult task.

For example, according to the testimony of Ukrainian geologists, "*oligocene deposits of the Carpathians with their monotony, uniformity of the appearance of sedimentary formations have long been considered devoid of pyroclastic rocks*". This situation had an objective reason – the difficulty of field diagnostics: "*The Oligocene sediments contain only ash material, most often of the pelitic dimension, and in only a few cases the rock can be called tuff; usually, these are tuffites, tuff argillites, tuffaceous sandstones. In addition, volcanic ash has been largely altered by post-sedimentary processes*" [210, pp. 20–21]. Only subsequent detailed studies made it possible to establish that in the Oligocene of the Ukrainian Carpathians there are four basic horizons of tuffs, tuffites and related rocks – tuff-argillites. Pyroclastics is mainly vitroclastic, and liparitic in composition, less often liparitic-dacitic and dacitic.

It is even more difficult to recognize pyrogenic rocks in *metamorphic strata*. 25 years ago, the Leningrad geologist V.K. Golovyonok (who tragically died in his prime of life in 1995), to whom lithochemistry owes a great deal, outlined the problem of tuffoid diagnosis in relation to metamorphic strata with great clarity: "*We can well distinguish volcanogenic sediments only in the areas of volcanism epicenters, where there are thick flows of lavas, lavobreccias, tuff-clumps, etc.*". Meanwhile to modern island arcs in the Pacific Ocean "*vast areas of the ocean floor adjoin, measured in tens of thousands of square kilometers, where there is a fine alternation of tuffaceous rocks with silica rocks in the northern part or with carbonate rocks in the more southern regions of the ocean. In these areas, only the finest ash material is deposited, carried by the winds from the volcanic ridges, and tuff breccias and lava rocks are completely absent. With intense metamorphism, such sediments will have the appearance of normal sedimentary and it is extremely difficult to recognize their primary nature <...> Apparently, it is necessary to try to find more subtle geochemical* *criteria that would make it possible to distinguish volcanic material from normal sedimentary material*" [83, p. 94].

Eolian and water ash differentiation. Usually a geologist, having a chemical analysis of the tuffoid, tries to compare it with the known effusive rocks' compositions. However, such a comparison very often turns out to be ineffective due to the mechanical (aeolian and/or water) differentiation of pyroclastics (tephra) prior to its burial in sediments. Therefore, for example, tuffs genetically related to andesites or rhyolites can be very different in composition from both.

According to the A.S. Kalugin's review, during the transport of volcanic ash through the air, *the glass proportion* in the ash *increases* first of all, with a corresponding decrease in the proportion of crystal-clastic material [125]. We find indirect existence confirmation of such a process, for example, in the Riphean tuffs of Podolia, the composition of which differs from the original basalts. With an approximate equality of the total iron content, it is much more strongly oxidized in tuffs: the redox module RM = 0.17–0.43 (on average 0.29) versus ~1 in basalts. With an approximate equality of the MgO contents, the ratio of MgO and CaO changes: in tuffs MgO > CaO, and vice versa in basalts. "*This can be explained by the increased content of chlorite-hydromica material in the tuffs and the absence of plagioclases*" [210, p. 92–93].

Another tendency of aeolian differentiation (seemingly not so clearly manifested) is the SiO_2 and K_2O increase in the ashes during their transfer, noted by A.S. Kalugin, and a decrease in the FeO content, which is explained by the gravitational differentiation of the ash cloud. "*Finally, one should assume that with the distance from the volcano, ash particles are gradually freed from readily soluble, in particular sorbed substances*" [125, p. 12].

According to our data, light interlayers of tuffoids in the Carboniferous black shale strata of the Lemva zone of the North Urals, as a rule, cannot be directly compared with the known compositions of effusive rocks. In particular, they were often characterized by *decreased* (rather than increased) SiO_2 contents in combination with unusually high alkali contents, which could exceed the alkalite boundary (8 %) [71, 74]. Geologists who studied the volcanic ash layers in the Quaternary deposits of Ukraine and southern Russia have long faced the same situation. They emphasized that the chemical composition of the ash is acquiring differences, "*because in the process of transporting the lava material sprayed by the eruption, larger particles were sifted out, first of all, minerals fragments with a large volumetric weight; therefore, the dusty glassy ash particles should differ from the composition of the parent lava*" [154, p. 53]. On this basis, they assumed that although the SiO_2 content in the ash interlayers studied by them is 55.0–58.8 %, it is greatly reduced due to the loss of quartz.

They consider the parent lava to be alkaline-dacitic, characteristic, for example, of the Caucasian volcano Alagez. "*Of course*," they note, "*it is impossible to indicate exactly which minerals and in what quantity were eliminated during transportation, but one thing is indisputable – the ash composition cannot be unconditionally comparable with lava of a similar composition*" [154, p. 54]. Indeed, as can be seen from Table 90, young ash rocks studied by Ukrainian geologists are *alkalites*. Even if they were devoid of bright lithological features (light color, looseness, low density, lack of bedding), which may well be erased during lithogenesis (which we have in ancient strata), they could be accurately distinguished from the host rocks (loesslike loam) only in chemical composition.

Table 90

Average chemical composition of volcanic ash from Quaternary deposits of Ukraine (n = 4) and pumice from Alagez volcano in the Lesser Caucasus. *According to V.I. Lebedinsky and L. Ya. Khodyush, 1959 [154, p. 52]*

Oxides	Ashes	Pumice
SiO_2	57.02	61.28
TiO_2	0.42	0.88
Al_2O_3	18.42	17.77
Fe_2O_3	2.63	3.06
FeO	1.89	0.51
MnO	0.18	0.08
MgO	0.79	0.85
CaO	2.08	1.72
Na_2O	4.46	3.68
K_2O	5.23	4.50
P_2O_5	5.36	4.57
H_2O^+	1.95	1.04
Сумма	100.43	99.94

A.R. Geptner made interesting observations on the Icelandic shelf. It turns out that basaltic tephra does not travel long distances through the air; the main mechanism of its transportation is the spreading of underwater eruption products by sea currents – "hydroexplosive pumice" and "pulverized volcanoclastics". On the contrary, acid ashes are carried by air for tens and hundreds of kilometers outside the volcanic regions. Being (relative to basaltic tephra) insignificant in mass, they form the main horizons in shelf sediments[1].

Getting into the aquagenic environment, volcanic ash undergoes further differentiation – the same as terrigenous clastic. This can be observed in the

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[1] *Geptner, A.R.*, Influence of island basalt and volcanism on sedimentation, // Geology of oceans and seas. Abstract of the report, 8th All-Union school of sea geol. Vol. 2. - M., 1988. - P. 25-26.

volcanic areas alluvium, where the eolian ash differentiation is small due to the short transport distance, and pyroclastics, which are close in composition to the original, fall out onto the earth's surface.

It turns out that *the ash water differentiation of Kamchatka volcanoes in modern alluvium depends significantly on the eruption composition*. As N.P. Kuralenko showed, the composition of *basalt tephra* in alluvium remains almost unchanged, which is explained by "*the closeness of the composition of the basic sediments components – litho-vitro- and crystal-clastic materials – and a small content of the crystalline phase*" [150, p. 29]. A different picture is for andesite material. There is a great difference in the densities of porous volcanic glass and phenocrysts, which entails their significant sorting, up to the ore concentrate formation in the riverbed shoals of the river Kamchatka: "*Sandy sediments, markedly enriched in crystals (up to 75 %), have a more basic andesite-basaltic composition in comparison with the original andesite pyroclastics. In this case, the* SiO_2 *content decreases from 60 to 54.5 %. At the same time, the K content decreases slightly and the Al, Fe, Ca and Mg content increases (due to an increase in the relative amount of plagioclases and mafic minerals). In the transition to aleuritic and aleuropelite sediments of drying streams, their gross chemical composition, on the contrary, becomes more acidic (*SiO_2 *62–63 %) due to a decrease in the content of the same minerals and a sharp increase in acid glass particles. At the same time, the alkalis content increases and Al, Fe, Mg, Mn, Ca content decreases*" [150, p. 31].

So, water sorting of andesite tephra leads to the fact that the sands become more basic, and the silts become more acidic than the initial andesites.

As for tuffites (i.e., tuffoids with a high proportion of non-volcanic sedimentary material), an idea of their formation is given by the alluvium of the upper reaches of the river Kamchatka. Here, in the greywacke sands, "*all components are divided into two approximately equal groups: 1) terrigenous (quartz and fragments of metamorphic rocks) and 2) volcanoterrigenous (feldspars and fragments of intermediate and basic igneous rocks). The third, insignificant (about 5%) group is formed by clearly diagnosed pyroclastic material: fragments of basic, average and acidic glasses*" [150, p. 33]. It turns out that an increase in the terrigenous material proportion changes the alluvium differentiation process: "*the sands are relatively more acidic <...>, and aleuropelites and clays are more basic*" [150, p. 38]. At the same time, the alkalinity of sands is noticeably higher than that of aleuropelites: NKM 0.34 versus 0.22, respectively, which is quite natural – the sands have a higher feldspar/clay matter ratio. Note that thinner sediments are also more femic. It is difficult to say to what extent N.P. Kuralenko's last observation is maintained in more ancient sediments, but we have at least one confirmation: the Middle Riphean dellenite and liparite tuffoids of the Puyva formation of the Subpolar Urals really differed from the parent porphyries and obvious tuffs in greater femicity (FM) and especially TM [310].

The influence of tephra water differentiation on the tuffoids composition is very clearly manifested in the Riphean deposits of Podolia [210], where "tuff gravelites" differ greatly from "tuffs" by the increased dispersion of all modules. In particular, at least 6 analyzes of tuff gravelites out of 15 have anomalous TM, which can be attributed to the Migdisov's law – the process of natural schliching with the accumulation of heavy titanium minerals in gravelites.

7.3. Allochemical alteration of pyroclastics

At present, a lot of data have been accumulated that reveal pyroclastics allochemical changes (with the addition-removal of components); the most common processes of this change are claying, silicification, carbonatization, and zeolitization.

Claying and silicification. Claying of volcanic ash is understood as the process of replacement of initial magmatic minerals with hypergene clay and micaceous minerals: montmorillonite, hydromica, chlorite, and kaolinite. In particular, bentonites are characterized by the process of montmorillonitization, which is almost always accompanied by silicification due to the SiO_2 release. Acidic vitroclastic tuffs, according to A.V. Van, are transformed in terrestrial conditions into chlorite-hydromica or kaolinite-hydromica aggregates, and in submarine ones, "*they turn into a cryptocrystalline microfelzite mass, which is undetectable under a microscope, consisting of the smallest grains of quartz, albite or adularia. The author proposes to call the rocks formed by this mass and completely lost their primary structure tuffogenic microfelite*" [42, p. 40].

Table 91 and in Fig. 73 show the compositions of tuffaceous Paleogene deposits of the Carpathians, among which I.M. Afanasyeva [10] distinguishes bentonites, silicified tuffites and tuffs. It is obvious that bentonites are products of clay formation in tuffs, and silicification accompanies the clay formation process. A characteristic feature of the module diagram is the significant number of points that go beyond the clusters. This may have two reasons: a) the strong heterogeneity of the primary composition of the tuffs, b) the phenomenon of allochemical change. We see the latter on the silicification example.

On the module diagram, tuffs form a correlated set, but it is possible to distinguish several varieties (clusters III, IIa, b and individual compositions). Tuffs are highly differentiated in alkalinity, up to alkalites (samples 14, 15). There are also carbonate compositions (probably, with siderite – sample 8); the composition of sample 1 is very exotic: pseudohydrolysate with a strong titanium anomaly (TiO_2 = 5.18 %, TM = 0.428). Silicified tuffites are also characterized by increased TM.

Table 91

Chemical composition of the Paleogene pyroclastites of the flysch strata on the northern slope of the Ukrainian Carpathians.

Compiled according to I.M. Afanasyeva, 1983 [10, p. 48–49]

Oxides and modules	1	IIa	IIb	III	1	6	7	8	12	14	15
	Bentonite (normo-siallites)	Tuffs			Bentonite (pseudohydrolisate)	Silicified tuffites		Tuffs			
		Normosilite	Alkaline normosilite	Normosilite		Hypersilite	Supersilite	Carbonate normohydrolysate	Myosilite	Alkaline myosilite	Alkalite
n	4	2	3	2							
SiO_2	52.59	65.40	71.06	82.15	46.06	91.35	80.42	38.66	61.90	62.80	69.42
TiO_2	0.25	0.29	0.19	0.33	5.18	0.25	0.27	0.62	0.13	0.27	0.39
Al_2O_3	17.08	8.66	11.86	6.59	12.10	2.52	2.27	11.67	5.45	13.61	12.66
Fe_2O_3	4.19	2.28	1.92	0.81	11.20	0.75	0.83	3.58	11.09	2.04	0.79
FeO	1.47	1.04	1.01	1.14	0.29	0.36	1.15	20.13	1.15	1.19	1.12
MnO	0.07	0.08	0.02	0.01	0.06	0.01	0.03	0.12	0.13	0.06	0.06
MgO	2.53	1.67	0.78	0.30	3.04	0.40	0.78	1.87	0.72	1.67	0.39
CaO	2.17	5.00	1.65	0.34	2.51	0.29	4.97	2.26	1.26	2.14	1.61
Na_2O	0.31	0.60	3.98	0.16	0.13	0.08	0.37	0.35	0.40	1.48	4.76
K_2O	1.16	2.22	2.29	0.93	1.20	0.50	0.80	2.35	0.40	6.05	5.06
P_2O_5	0.04	0.12	0.15	0.13	0.23	0.10	0.12	0.12	0.10	0.07	0.05
S	0.29	0.39	0.11	0.72	0.82	0.04	0.18	-	8.68	0.37	0.12
CO_2	1.62	8.89	0.73	0.82	0.34	1.02	2.90	-	-	-	-
LOI	16.73	3.43	5.37	5.84	16.77	2.01	3.41	17.40	9.91	8.79	3.88
Total	100.49	100.04	101.11	100.23	99.93	99.68	98.50	100.13	102.32	100.54	100.31
HM	0.44	0.19	0.21	0.11	0.63	0.04	0.06	0.93	0.29	0.27	0.22
FM	0.16	0.08	0.05	0.03	0.32	0.02	0.03	0.66	0.21	0.08	0.03
AM	0.32	0.13	0.17	0.08	0.26	0.03	0.03	0.30	0.09	0.22	0.18
TM	0.015	0.033	0.016	0.049	0.428	0.099	0.119	0.053	0.024	0.020	0.031
FerM	0.33	0.38	0.24	0.28	0.67	0.40	0.79	1.94	2.22	0.24	0.15
NKM	0.09	0.33	0.53	0.16	0.11	0.23	0.52	0.23	0.15	0.55	0.78
AlkM	0.30	0.30	1.70	0.20	0.10	0.20	0.50	0.10	1.00	0.20	0.90

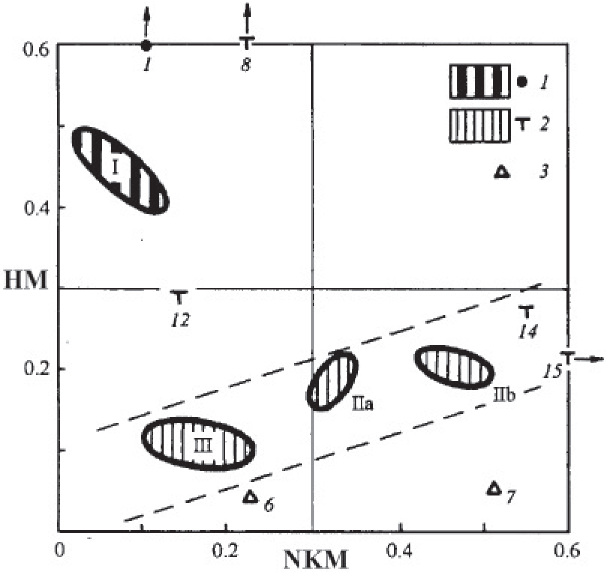

Fig. 73. Module diagram for Paleogene pyroclastites in the flysch strata of the northern slope of the Ukrainian Carpathians.
Compiled according to the I.M. Afanasyeva's data, 1983 [10, pp. 48–49].
1 – bentonites, 2 – tuffs, 3 – silicified tuffites

Bentonites form cluster I; they are characterized by low TM and alkalinity, but, in contrast to tuffs, they are more hydrolysate and femic. Characteristic and important for diagnosis is the presence of magnesian rocks – pseudosiallites among them (three analyzes out of five).

Sometimes tuffs claying is combined not with silicification, but with zeolitization. Such are the bentonites occurring among the zeolitized Triassic tuffs of New Zealand [322, p. 164]. They differ from acidic and average tuffs in HM, FM, and FerM; in TM the discrimination is worse, but still the titanium composition (TM 0.081, TiO_2 1.30) is bentonite.

In the Jurassic of the Lesser Caucasus, R.A. Mandalyan described peculiar sandy and sandy-silty rocks closely related to pillow andesite-basalts – clay hyaloclastites. They form interlayers with a thickness of 3–4 cm to 12–15 m and consist of "*angular and semi-angular, intensely chloritized and partly montmorillonitized glassy fragments, frequently containing relics of plagioclase, and sometimes a dark-colored mineral. Whole globules and semi-spheres of hyalobasalt are rare. The filler is represented by the same glassy, but to a greater extent, clay material of pelitic-fine-silt dimension. It also contains zeolites, chalcedony, leucoxene*" [166, p. 82]. As can be judged from five analyzes, these rocks turn out to be *pseudohydrolysates* with a constant HM

0.60–0.62 and MgO contents from 4.8 to 9.6 % (which allows us to distinguish varieties that are less and more magnesian with average MgO contents of 5.11 and 8.54 %). They differ from their parent rocks (andesite-basalts) by a low content of SiO_2, which R.A. Mandalyan explains by two reasons: "*the presence in a large amount (up to 15 %) of bound and hygroscopic water and the silica removal due to basalt glass montmorillonitization*" [166, p. 82].

A spectacular example of clay and silicification is some Upper Vendian (Redkinsk) tuffs, regionally developed on the Russian Platform. The horizons thickness of the Redkinsk tuffs reaches tens of meters, and among them there are two contrasting petrochemical varieties: a) silica (predominant), containing SiO_2 71–82, Al_2O_3 7–15 %, and b) high-alumina, SiO_2 50–58, Al_2O_3 21.0–29.5 %. Particularly noteworthy is the second variety, in which the contents of trace elements-hydrolysates Zr, Hf, Y, and Th are 1.5–2 times higher than in the host Redkinsk argillites. Because of the obvious dissimilarity of the Redkinsk tuffs and modern (and Holocene) acid volcanic ashes' compositions, St. Petersburg geologists came to the conclusion that the Redkinsk pyroclastic material underwent a process of halmyrolysis, which was the reason for its chemical composition differentiation: "*The most probable reason for the variations in the volcanic tuffs composition of the Redkinsk time is the redistribution of elements during the inflow of pyroclastic material into the sedimentation basins of the Russian Platform as a result of reaction with seawater*". It is assumed that the process proceeds along two lines: hydrolysate products such as montmorillonite clays are formed with parallel silicification of the host terrigenous sediments due to the removed silica. "*Since volcanic zircon is preserved during halmyrolysis and leaching, one should expect an increased zirconium content in high-alumina tuffs*" [27, p. 40].

As one can see from the module diagram (Fig. 74), the average compositions of argillites and two varieties of tuffs are easily recognized by the hydrolysate module HM value. A similar discrimination is also possible here for the aluminum-silicon module AM (the authors themselves used the Si/Al value). High-alumina tuffs are certified as alkaline hypohydrolysates (HM 0.56–0.62), and silica tuffs – as myosilites (HM 0.20–0.28). Argillites are normally siallites, in this case alkaline. However, the fact that, on the module diagram, argillites form a single mixture with tuffs, may indicate the presence of pyroclastic admixtures in argillites. Interestingly, silica tuffs (NKM 0.31–0.35) have the highest alkalinity; they are also more titanium: TM = 0.045–0.061 versus 0.046–0.053 in argillites (Table 92). At the same time, the minimum TM (0.021) is shown by the composition of sample 4 with the highest total alkalinity and alumina value. Obviously, this essentially hydromica rock was formed after the most acidic tuff. Outside the clusters, there is also sample 3; it has an intermediate composition and can probably be attributed to tuff argillites.

Table 93 and Fig. 75 processed 15 analyzes of Kamchatka Miocene silica rocks and associated tuffs of varying alteration degrees [87]. Tuffs are

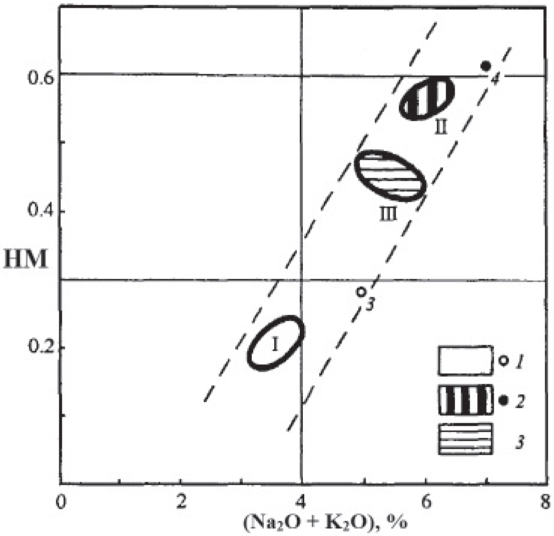

Fig. 74. Module diagram for tuffs and argillites of the Redkinsk horizon of the Russian Platform. *Compiled according to D.V. Borkhwardt and S.B. Felitsin, 1992 [27].*
1, 2 – silica (1) and aluminous (2) tuffs; 3 – argillites

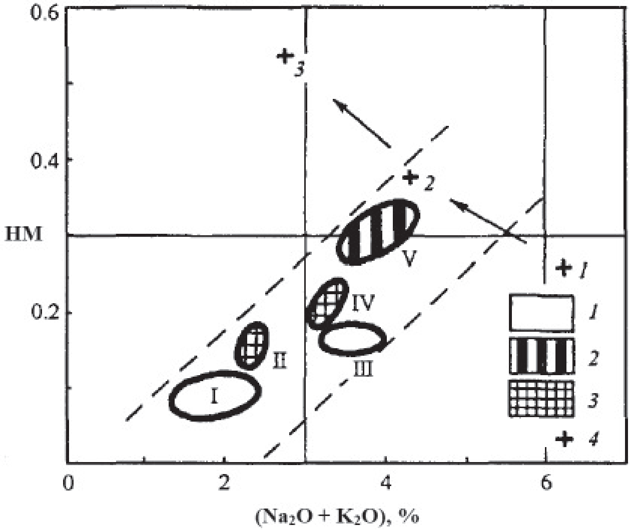

Fig. 75. Module diagram for Miocene silica rocks and associated tuffs. *Compiled according to V.I. Grechin's data, 1971 [87, p. 118–119].*
1 – opokas and recrystallized opokas, 2 – tuff diatomites, 3 – mixture of lithotypes (1 + 2), 4 – tuffs. The arrows show the growth of clay formation in the original dacite tuff

Table 92

Chemical composition of volcanic tuffs and host argillites
of the Redkinsk horizon of the Russian Platform.
Compiled according to D. V. Borkhwardt and S.B. Felitsin, 1992 [27]

Oxides and modules	1	11	III	3	4
	Siliceous tuffs (myosilite)	Alumina tuffs (alkaline hypo-hydrolysate)	Argillites (alkaline normosiallite)	Siliceous tuff (alkaline myosilite)	Alumina tuff (alkaline hypo-hydrolysate)
n	2	2	3		
SiO_2	77.54	57.90	62.88	71.43	55.45
TiO_2	0.52	0.98	0.97	0.86	0.60
Al_2O_3	10.70	22.19	19.55	14.13	28.34
Fe_2O_3 +FeO	4.68	9.45	7.34	5.09	5.20
MnO	0.12	0.05	0.14	0.16	0.07
MgO	1.92	2.52	2.35	2.27	2.24
CaO	0.92	0.79	0.70	0.97	0.95
Na_2O	1.10	1.48	1.60	2.29	0.39
K_2O	2.44	4.55	3.84	2.71	6.64
P_2O_5	0.08	0.12	0.11	0.11	0.08
Total	100.02	100.03	99.48	100.02	99.96
HM	0.21	0.56	0.45	0.28	0.62
FM	0.09	0.21	0.15	0.10	0.13
AM	0.14	0.38	0.31	0.20	0.51
TM	0.049	0.044	0.050	0.061	0.021
FerM	0.43	0.41	0.36	0.35	0.18
NKM	0.33	0.27	0.28	0.35	0.25
AlkM	0.50	0.30	0.40	0.80	0.10

clearly distinguished by two features: increased total alkalinity and increased HM. At the same time, in the series of changes "crystal-vitroclastic tuff ⇒ clay tuff ⇒ highly clay tuff" (samples 1 ⇒ 2 ⇒ 3), the alkali content decreases, while the HM value increases. Judging by the moderately low TM value, the pyroclastics had a dacitic composition; this is confirmed by the V.I. Grechin's petrographic data of [87, p. 118].

As for the actual silica rocks – opokas and recrystallized opokas, they do not differ in chemical composition since they give mixed clusters I and III. The appearance of pyroclastics in the silica sediment primarily increases the HM (compare clusters I–II, III–IV), almost without increasing the total alkalinity. The reason for this strange phenomenon lies in the allochemical nature of the tuffs degeneration (claying): in this case, alkalis are clearly removed. This can be seen both in the decrease in the total alkalinity (sample 1 ⇒ 2 ⇒ 3) and in the decrease in the normalized alkalinity NKM as HM grows. The rocks identified as "tuff diatomites" (silica tuffoids – myosilites) form clus-

Table 93

Chemical composition of Miocene silica rocks and associated tuffs of Western Kamchatka. Compiled according to V.I. Grechin, 1971 [87, p. 119]

	1	II	III	IV	V	1	2	3
	Opokas and tuff diatomites					Tuffs		
	Supersilite	Normosilite		Myosilite		Alkaline myosilite	Normosiallite	Pseudosiallite
N	4	2	2	2	2			
SiO_2	82.88	74.85	74.11	69.65	62.61	66.48	54.86	42.09
TiO_2	0.32	0.49	0.51	0.49	0.68	0.51	0.51	0.68
Al_2O_3	5.36	8.85	8.34	9.84	13.63	14.30	14.75	17.68
Fe_2O_3	1.30	1.42	2.39	2.07	3.57	1.02	3.87	2.46
FeO	0.80	0.66	0.88	2.02	1.13	0.89	1.02	1.36
MnO	0.01	0.03	0.02	0.05	0.03	0.08	0.02	0.11
MgO	0.50	0.61	0.92	1.51	1.26	0.53	2.55	4.15
CaO	1.25	1.41	1.56	1.89	3.61	2.03	2.16	6.85
Na_2O	0.94	1.04	2.10	1.57	2.32	2.81	3.43	1.41
K_2O	0.96	1.32	1.51	1.70	1.60	3.41	0.88	1.35
P_2O_5	0.08	0.05	0.08	0.08	0.12	0.09	0.07	0.09
H_2O	4.84	7.75	6.30	6.82	8.03	7.25	15.69	15.98
CO_2	0.02	0.00	0.00	0.36	0.00	0.08	0.00	5.36
C	0.44	0.53	0.58	0.51	0.26	0.08	0.00	0.00
$S + SO_3$	1.07	2.36	1.88	2.34	1.99	0.13	-	-
Total	100.74	101.32	101.15	100.86	100.81	99.69	99.81	99.57
HM	0.09	0.15	0.16	0.21	0.30	0.25	0.37	0.53
FM	0.03	0.04	0.06	0.08	0.10	0.04	0.14	0.19
AM	0.06	0.12	0.11	0.14	0.22	0.22	0.27	0.42
TM	0.059	0.055	0.061	0.049	0.050	0.036	0.035	0.038
FerM	0.37	0.22	0.37	0.40	0.33	0.13	0.32	0.21
NKM	0.35	0.27	0.43	0.33	0.29	0.43	0.29	0.16
AlkM	1.00	0.80	1.40	0.90	1.40	0.80	3.90	1.00

ter V, which is very close to "clay tuffs". In addition, in clusters II and IV, tuff diatomites are indistinguishable from opokas and recrystallized opokas. All of this, plus the hit of all sedimentary and volcanic-sedimentary rocks in the band of positive correlation "alkali – HM", indicates an admixture of pyroclastics in all (or almost all) silica rocks.

Finally, the formation of highly specific *chamosite*[2]*-silica concretions* – the products of the basaltic pyroclastics transformation – is a remarkable illustration of the conjugate process of claying-silicification. We described in detail such concretions, consisting mainly of chamosite and microcrystalline quartz (with noticeable admixtures of apatite, pyrite, and carbonates), in the Devonian and Permian deposits of the Lemva zone of the North Urals [74], and other geologists – in the Caucasus, Tuva and Moldavia volcanic-sedimentary strata of different ages [29, 88, 105].

Carbonatization. A notable feature of many epigenetically altered tuffoids is their essentially carbonate composition. Such rocks were described by B.R. Shpunt in the Riphean of Yakutia [279] and by A.V. Van in the Upper Devonian of the Kuznetsk basin. In Kuzbass, carbonate tuffites, as a rule, "*occur in the upper and middle parts of sedimentary rhythms, above which there is a gradual transition of carbonate tuffites to limestones. The rock-forming component in carbonate tuffites consists of volcanogenic clastic material (50–90 %) and carbonate admixtures (< 50 %). The latter is most often presented in the form of a binder mass*". It turns out that a significant part of this binding mass is authigenic, which arose during the degeneration of particles of the basic volcanic glass, which is shown by direct observations in thin rock sections: "*Some lumpy limestones gradually pass into the basic vitroclastic tuffs and, apparently, owe their origin to them <...> Limestone lumps shape is very similar to the vitric fragments shape in tuffs. Individual lumps have vaguely pronounced concentric circles, the core of which are fragments of plagioclase crystals, less often quartz, clots of iron hydroxides, or grains of monocrystalline calcite with a shape characteristic of volcanic ash. The formation of concentric circles is probably associated with the desorption of elements (iron, manganese, etc.) that were part of the ash particles or enveloped them in the form of a film <...> After the removal of calcite, clay or ferruginous minerals or fine-crystalline albite aggregates remain in the thin section, forming complex patterned or looped patterns that fix the initial contours of the dissolved lumps. <...> Therefore, one of the possible ways of forming problematic round-shaped formations (this can include some coprolites, oolites, clots) may be the volcanic ash decomposition*" [42, p. 42–43].

As one can see from the Table 94, the compositions of these rocks form two clusters, differing in femicity and alkalinity. In this case, a direct (and

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[2] Note-2022. In 2000, we (like many other geologists) called "shamosite" a two-layer 7-Å "septechlorite", which is now called ***bertierine***. In modern mineralogy, shamosite is only a 4-layer 14-Å chlorite.

not inverse, as in normal sedimentary rocks) correlation (FM, HM)–NKM is found. Such a picture can take place when alkalis are included in the composition of dark-colored minerals (biotite, amphibole).

In the Oligocene menilite shales of the Carpathians, the leading processes of tuffoids allochemical alteration are bentonitization and the accompanying silicification, but carbonatization is also noted. "*The latter is widely developed in the tuffs and tuffites of the Upper Benilite subformation (Chechva), occurring among calcareous argillites. Here, even during sedimentogenesis, the normal sedimentary admixture to the pyroclastic material was essentially carbonate, but the basic replacement processes undoubtedly took place later. As a result, the rock often corresponds in composition to marl, but the relict pyroclastic structure and textural features indicate its true genesis*" [164, p. 87].

Carbonate content can be a decisive sign in situations where lithochemical diagnostics of tuffoids is very difficult.

Table 94

Average chemical composition of tuffs and tuffites in sediments D_3, Kuznetsk Basin. *Compiled according to A.V. Van, 1969 [42, p. 41]*

Oxides and modules	I	II
	Carbonate myosilite	Normosiallite
n	3	3
SiO_2	48.88	50.63
TiO_2	0.51	0.71
Al_2O_3	7.93	13.59
Fe_2O_3	3.84	3.01
FeO	0.65	3.42
MnO	0.17	0.13
MgO	1.12	2.13
CaO	17.70	10.62
Na_2O	0.10	1.83
K_2O	0.94	2.24
P_2O_5	0.18	0.25
SO_3	0.07	0.10
LOI	18.17	11.33
Total	100.26	99.99
CO_2	11.05	7.91
H_2O	0.50	2.26
HM	0.27	0.41
FM	0.11	0.17
AM	0.16	0.27
TM	0.064	0.052
FerM	0.55	0.46
NKM	0.13	0.30
AlkM	0.10	0.80

For example, among the Oxfordian-Neocomian silica rocks and associated tuffoids of the Somkheto-Karabakh zone of the Lesser Caucasus, the latter are recognized precisely by their carbonate content (up to 20–25 % carbonates) [230]. In addition, silica tuffoids have an increased TM = 0.078 versus 0.011–0.018 in other silicites. Apparently, pyroclastics had an andesite composition. The same case is presented by pyroclastites of the Upper Cretaceous and Eocene of the Ukrainian Carpathians [210, p. 20], in the statistical sample of which only two analyzes of Cretaceous (samples 2 and 4) and one analysis of Eocene rocks (sample 6) clearly differ from normal sedimentary rocks in their alkalinity, TM, or Mg values (Table 95). At the same time, the genetic diagnosis of the other four compounds is no longer so indisputable. For example, sample 1 ("brown spread glass enriched with carbonates") is certified as tita-

Table 95

Chemical composition of Cretaceous and Paleogene pyroclastic rocks of the Ukrainian Carpathians.

Compiled according to L.G. Tkachuk et al., 1977 [210, p. 20]

Oxides and modules	1	2	3	4	5	6	7
	Ti-carbonate hypohydrolisate	Ti-alkaline normosiallite	Myosilite	Alkaline normosiallite	Normohydrolisate	Pseudohydrolisate	Carbonate supersiallite
SiO_2	30.73	57.00	70.05	56.06	38.66	42.70	40.12
TiO_2	4.05	3.20	0.53	0.80	0.62	1.52	1.44
Al_2O_3	10.38	14.20	12.96	16.52	11.67	17.60	14.67
Fe_2O_3	7.20	8.91	4.56	2.31	3.58	0.83	4.32
FeO	1.87	0.43	1.03	5.01	20.13	9.90	1.43
MnO	0.07	0.02	0.32	0.11	0.12	0.25	0.17
MgO	2.26	0.75	0.89	1.58	1.87	3.49	1.62
CaO	16.90	4.09	0.91	5.13	2.26	9.70	16.63
Na_2O	0.13	5.05	0.78	6.74	0.35	1.09	1.87
K_2O	2.45	1.03	3.31	0.17	2.35	1.44	0.93
P_2O_5	0.29	0.62	0.09	0.37	0.12	0.18	0.26
H_2O	6.85	0.70	1.62	0.37	1.19	0.45	0.50
CO_2	-	-	0.01	3.22	-	6.98	12.33
LOI	17.11	3.67	3.05	2.10	17.21	4.34	3.25
Total	100.29	99.67	100.11	100.49	100.13	100.47	99.54
HM	0.77	0.47	0.28	0.44	0.93	0.70	0.55
FM	0.37	0.18	0.09	0.16	0.66	0.33	0.18
AM	0.34	0.25	0.19	0.29	0.30	0.41	0.37
TM	0.390	0.225	0.041	0.048	0.053	0.086	0.098
FerM	0.63	0.54	0.44	0.43	1.94	0.57	0.37
NKM	0.25	0.43	0.32	0.42	0.23	0.14	0.19
AlkM	0.10	4.90	0.20	39.60	0.10	0.80	2.00

nium carbonate hypohydrolysate. Myosilite (sample 3), Fe-normohydrolysate (sample 5) and carbonate supersiallite (sample 7) can be taken for the weathering crust formation, if not for the strange combination of "*hydrolysateness* + *carbonateness*", not typical for Phanerozoic humid weathering crusts, during formation of which Ca is removed.

Zeolitization. Table 96 shows the average composition of mordenite rocks of Transcaucasia, California and Japan, which are zeolitized acid tuffs [180]. Mordenite is a zeolite with the formula (Ca, Na_2, K_2)[$AlSi_5O_{12}$] $7H_2O$. It is formed during the diagenetic degeneration of acidic volcanic glass in seawater.

As one can see, the composition of mordenite rocks corresponds to normosilites, however, with two features that do not allow them to be mistaken for ordinary siltstones: a) very poor TM (only 0.006), characteristic only of acidic effusive rocks or their derivatives; b) an increased CaO content without an equivalent amount of CO_2 or SO_3, which indicates the silicate form of calcium – a clear diagnostic sign of a petrogenic or pyrogenic rock.

A similar case is presented by the Jurassic mordenite rocks of the Karadag, which are locally called "trasses" – the zeolitization products of acidic ash vitroclastic tuffs [278]. The relatively low alkalis content in the trasses (about 4.5 %) is not diagnostic – such a composition could correspond to siltstones. The only but decisive feature is again the poor TM of the trasses (0.006–0.007), which is possible only for acidic pyroclastics.

Sometimes one can observe a particularly complex case of staged tuffs alteration – clay formation in the weathering crust of already zeolitized tuffs. Such are the zeolitized Upper Neogene basalt tuffs, andesite-basalt pumice and the bentonites of Vietnam formed from them (Phu Luong section). In these rocks, zeolites (heulandite, phillipsite, chabazite, erionite) replace volcanic glass and, in part, feldspar crystal clasts, fill the voids in pumice. A stratum of tuffs and pumice was accumulated in a freshwater lake and

Table 96

Average chemical composition of mordenite rocks (*n* = 4).
According to A.S. Mikhailov, 1975 [180]

Oxides	Contents, %	Oxides and modules	Contents, %
SiO_2	66.35	K_2O	1.02
TiO_2	0.14	H_2O^+	8.12
Al_2O_3	11.67	H_2O^-	4.61
Fe_2O_3	1.21	Total	99.93
FeO	1.21	HM	0.20
MnO	0.21	TM	0.006
MgO	0.02	NKM	0.30
Na_2O	0.68	AlkM	2.7

was covered by a thick shield, poorly permeable to heat – a cover of basalt. Therefore, one believes that zeolites were formed mainly almost without the substance introduction, according to "geoautoclave" mechanism [195].

All pyrogenic lithotypes and their derivatives are perfectly distinguished on the module diagram (Fig. 76): compared to pumice and andesite-basalt, tuffs are much more hydrolysate and titanium formations. Additional diagnostic features of these rocks can be (Table 97) manganese and carbonate content of pumice (cluster I) and noticeable phosphatization of tuffs (clusters IIa and b).

Bentonites (cluster III) are certified as titanium pseudohydrolysates, which confirms their interpretation as weathering crust formations on the substrate of zeolitized tuffs and pumice. Since this cluster also included one analysis of "tuff," one can assume that the replacement of zeolites by smectites described by the authors is not always macroscopically recognized [195].

7.4. Evidence for the exhalative material presence

A particular, but very important case of a pyrogenic admixture in sedimentary strata is an admixture of exhalations, which cannot be called pyroclastic, since there was no clastogenesis process. As observations in the rift zones of the Ocean show, a coagulated suspension of iron or iron and

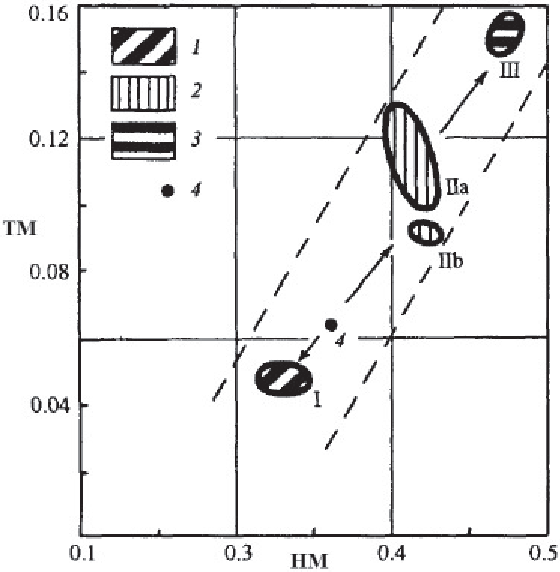

Fig. 76. Module diagram for Neogene tuffs and bentonites of Vietnam.
Compiled according to V.V. Petrova et al., 1997 [195].
1 – pumice, 2 – tuffs, 3 – bentonites, 4 – andesite-basalt

Table 97

Chemical composition of the Neogene tuffs and bentonites of Vietnam.
Compiled according to V.V. Petrova et al., 1977 [195, p. 167]

Oxides and modules	**1**	IIa	IIb	III	4
	Pumice	Tuffs			Basalte
	Pseudosiallite (75 %)	Supersiallite (3-30 %)	Pseudosiallite (8-30 %)	Tihypohydrolysate (2-8 %)	Normosiallite (10-15 %)
n	2	3	2	2	
SiO_2	47.57	47.82	47.14	45.87	56.76
TiO_2	0.69	1.71	1.51	2.58	1.01
Al_2O_3	13.92	15.33	16.16	16.84	15.47
Fe_2O_3	1.78	8.14	8.06	10.00	7.57
FeO	0.00	0.35	0.13	0.30	0.14
MnO	0.91	0.04	0.07	0.05	O.O\
MgO	3.26	2.00	3.23	2.11	1.83
CaO	9.70	5.35	5.67	5.94	1.59
Na_2O	1.09	0.63	1.17	1.53	0.12
K_2O	1.93	1.10	3.06	0.81	0.74
P_2O_5	0.76	1.45	1.66	0.84	0.03
LOI	18.36	15.53	12.72	13.68	14.03
Total	99.94	99.45	100.55	100.53	66.30
H_2O^+	5.36	6.06	5.71	5.19	6.70
CO_2	7.50	-	-	-	-
HM	0.36	0.53	0.55	0.65	0.43
FM	0.11	0.22	0.24	0.27	0.17
AM	0.29	0.32	0.34	0.37	0.27
TM	0.050	0.112	0.093	0.153	0.065
FerM	0.18	0.50	0.47	0.53	0.47
NKM	0.22	0.11	0.26	0.14	0.06
AlkM	0.60	0.60	0.40	1.90	0.20

Note. Zeolite content is in parentheses.

manganese hydroxides is introduced into the sediment. Many elements-impurities from seawater – Ni, Co, Mo, As, etc., can be sorbed on such a suspension, giving the sediment (and subsequently sedimentary rock) features of “geochemical specialization” [297]. Until recently, geologists did not know how to distinguish exhalative products in sedimentary strata, but today, in connection with the plate tectonics concept development, such a diagnosis has ceased to be a rarity.

Exhalative material is usually associated with silica rocks – jasper, flints, and phtanites, as well as with compositionally specific carbonates. For example, in the Upper Eocene of the Ukrainian Carpathians, the flysch variegated *Vyshkovskaya strata* is known [254]. These are argillites, limestones, and silica-rhodochrosite rocks – apparently, concrezoids and concretions, partly oxidized, with the phosphorus accumulation (up to 1.26 % P_2O_5) characteristic of carbonate concretions. The volcanogenic nature of these formations is evidenced by two diagnostic features: manganese content and magnesium content. Even argillites have elevated MnO contents (up to 1.80 %); limestones are certified as manganese (MnO 2.82 %), and in silica-rhodochrosite rocks the MnO content reaches 28 %. Argillites are certified as pseudosiallites and pseudohydrolysates, which allows them to be considered primary montmorillonite. The fact that, in addition to MnO, the FeO content is quite high in carbonate-bearing rocks, most likely indicates an exhalative process. Ukrainian geologists hold the same opinion [254].

Table 98

Chemical composition of Permian hydrothermal silicites of Central Japan.
Compiled according to K. Sugitani et al., 1991 [355]

Oxides and modules	I	II	III	IV	3	7	17
	Mn supersilite	Mn normosilite	Mn supersilite	Mn myosilite	Hypohydrolisate	Supersilite	Mn normosilite
n	5	4	2	2			
SiO_2	87.43	86.12	91.76	75.21	57.83	91.26	87.05
TiO_2	0.16	0.05	0.01	0.05	1.22	0.01	0.01
Al_2O_3	2.73	0.76	0.38	0.80	7.16	0.07	0.33
Fe_2O_3	1.62	4.93	2.67	7.86	21.46	6.16	3.51
FeO	0.45	0.94	0.12	3.17	2.88	0.38	0.16
MnO	2.09	5.23	2.65	8.48	0.96	0.14	5.40
MgO	0.66	0.19	0.14	0.38	1.19	0.10	0.44
CaO	0.63	0.26	0.22	0.27	0.19	0.35	0.48
Na_2O	0.37	0.44	0.42	0.33	0.32	0.50	0.53
K_2O	0.90	0.15	0.13	0.05	2.90	0.02	0.08
P_2O_5	0.10	0.02	0.04	0.05	0.06	0.02	0.06
H_2O	1.01	0.72	0.28	0.82	2.72	0.23	0.64
CO_2	0.52	0.10	0.46	0.00	0.00	0.00	0.59
LOI	0.94	0.74	0.91	0.72	0.25	0.58	1.39
Total	99.61	99.91	100.17	98.16	99.14	99.82	100.67
HM	0.08	0.14	0.06	0.27	0.58	0.07	0.11
FM	0.03	0.07	0.03	0.15	0.44	0.07	0.05
AM	0.03	0.01	0.00	0.01	0.12	0.00	0.00
TM	0.058	0.063	0.026	0.063	0.170	0.143	0.030
FerM	1.44	13.82	13.95	22.94	3.02	83.50	26.68
NKM	0.46	0.78	1.43	0.47	0.45	7.43	1.85
AlkM	0.40	3.00	3.40	7.30	0.10	25.00	6.60

Table 98 shows the compositions of the very remarkable Permian iron-manganese silicites of Japan, which lie directly above the basalts [355]. Four clusters can be distinguished on the FerM—NKM module diagram; two analyzes jump out of clusters due to extreme FerM and NKM values and one analyze due to increased HM.

Cluster I is represented by supersilites-radiolarites with HM = 0.08. However, these rocks are hyperferrous and superalkaline (FerM 1.46, NKM 0.46) and are enriched in manganese (MnO ~2 %). Clusters II and III are represented by normo- and supersilites, but much more ferruginous (FerM 14) and alkaline, especially the latter (NKM 14.3). The MnO content is 2.6 and 5.2 %, and for some samples – up to 11 %. Cluster IV is close to cluster I in alkalinity but differs in strong iron content (FerM ~23) and, accordingly, in extreme "ore" MnO contents – up to 17 %. Abnormal samples 3, 7 and 17 are also manganese. The first of them is iron ore (Fe_2O_3 + FeO ~ 24 %), in addition, it contains more alumina (7.16 against the background of 0.4–2.7 % in clusters), so the rock turns out to be Fe-hypohydrolysate (HM 0.58). On the FerM – NKM graph, this point practically falls into the contour of cluster I, which emphasizes the relationship of iron ores with silite-radiolarites; indeed, these rocks are interbedded in the section. Exotic compositions 7 and 17 are distinguished by extreme alkalinity (NKM 7.4 and 1.8) and iron content (FerM 83 and 27). In this case, samples 3 and 7 are abnormal in TM: 0.170 and 0.143 against background values 0.030–0.060. This fact did not remain unnoticed by Japanese researchers, who operated on the Al_2O_3/TiO_2 value (i.e., 1/TM). According to K. Sugitani et al., this indicates the presence of "*fragments* [underlying] *basalts*" in the mineralized rocks, i.e., presumably, most likely basaltic pyroclastics. A decrease in TM from basalts up the section of the ore-bearing carbonate-silica strata is interpreted as an indication that "*their* [host sediments] *clastic components prevail over deep-sea clays, whose* Al_2O_3/TiO_2 *ratio is about 24*" [355, p. 70], or in TM values – about 0.040.

So, we are dealing with flint volcanic-sedimentary rocks sharply enriched in iron and manganese. This example allows you to indicate the diagnostic signs of such formations.

a) Strong dispersions of the FerM and NKM modules with their reaching extreme values, completely uncharacteristic of normal sedimentary rocks. The FerM anomalies are explained by the supply of hydrothermal Fe and Mn hydroxides to the silica sediment; the NKM anomalies can probably be explained by the presence of non-alumina clay minerals such as Fe-smectites and zeolites. We noted this fact when interpreting the unusual geochemical features of the D_3 silica strata at Pai-Khoi, enriched in Fe, Mn, Ni, and As [206; 295, p. 32; 297].

b) High Mn and Fe contents in combination with TM anomalies indicating the participation of basic material; on the contrary, for exogenous weathering crusts enriched in iron and manganese, high TM values are not necessary; usually, this requires the presence of a high-titanium substrate.

c) Finally, the very paragenesis of manganese silites, Fe-hydrolysates and siferlites (especially the latter) is completely not typical for normal sedimentary rocks.

7.5. Diagnostics of petrogenic volcanoclastics

In most cases, this task turns out to be too difficult for lithochemistry: petrogenic rocks cannot be reliably distinguished from pyrogenic rocks. However, sometimes additional information is available to make a correct diagnosis. An example is the variegated flysch deposits of the Middle Ordovician in NW Altai. As the data processing by I.A. Vyltsan [58] shows, there are many magnesian rocks – pseudosiallites (10 analyzes out of 22), as well as siferlites (4 analyzes). In part, this can be associated with the Mg and Fe presence in the carbonate form (which, however, is also informative); however, in nine analyzes, the Mg and/or Fe is most likely of a silicate nature and is due to the abundance of chlorite. On the module diagram (Na_2O + + K_2O) – FM, carbonate-bearing greywacke-pseudosiferlites are clearly separated from terrigenous rocks. This allows us to think that they

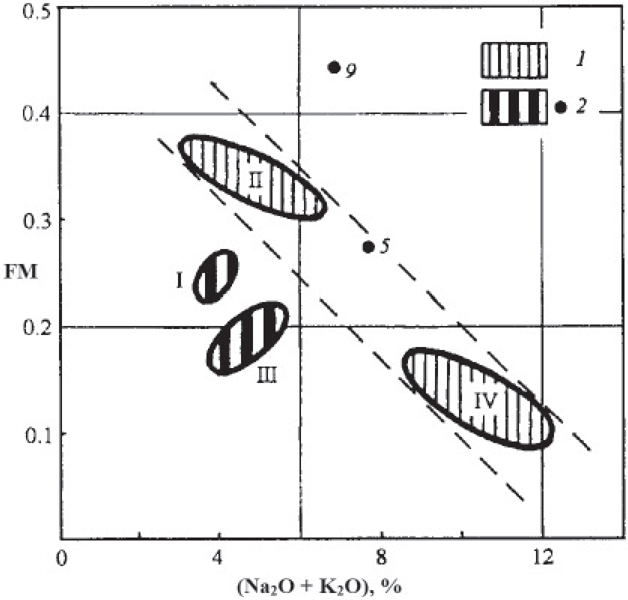

Fig. 77. Module diagram for the Upper Cretaceous volcanogenic-terrigenous rocks of the Small Kurile formation of the Small Kuriles.

Compiled according to V. K. Gavrilov and N. A. Solovieva, 1973 [61, p. 48].

1 – more alkaline, 2 – less alkaline

contain an admixture of volcanic material, and it is volcanoclastic, and not pyroclastic, "*since active volcanism in the considered period of geological time within the Anuisko-Chuya synclinorium and adjacent areas did not appear*" [58, p. 92].

In young island arcs, pyrogenic material is mixed with petrogenic material – a product of volcanic edifices erosion. Table 99 and Fig. 77 show the compositions of the Upper Cretaceous terrigenous rocks of the Small Kuriles: sandstones, siltstones and argillites with an admixture of volcanic material. Part of this material is clearly pyroclastic (crystalloclasts, hyaloclasts and lithoclasts of trachybasaltic and trachydoleritic composition), and part is volcanoclastic (semi-rounded fragments of minerals and rocks),

Table 99

Chemical composition of the Upper Cretaceous volcanogenic-terrigenous rocks of the Small Kurile formation of the Small Kuriles.

Compiled according to V.K.Gavrilov and N.A. Solovieva, 1973 [61, p. 48]

Oxides and modules	I	II	III	IV	5	9
	Pseudo-hydrolisate	Alkaline pseudohydrolisate	Normo-siallite	Alkalite	Alkaline pseudo-siallite	Alkaline pseudo-siferlite
n	2	3	2	2		
SiO_2	50.73	49.10	60.01	50.50	46.39	46.93
TiO_2	0.93	0.89	0.50	0.48	0.48	0.69
Al_2O_3	18.81	14.87	13.11	15.22	14.73	12.43
Fe_2O_3	5.34	7.02	6.23	4.08	6.38	7.05
FeO	3.38	4.37	2.27	0.96	2.61	4.78
MnO	0.20	0.36	0.21	0.19	0.57	0.16
MgO	3.72	5.26	2.78	1.33	3.81	9.08
CaO	8.74	8.10	5.36	8.29	9.05	5.05
Na_2O	3.49	3.96	3.46	6.06	4.62	5.20
K_2O	0.45	1.05	1.17	4.37	3.12	1.73
$S_{general}$	0.16	0.25	0.29	0.22	0.42	0.14
H_2O	0.05	0.08	0.32	0.02	0.24	0.01
CO_2	1.36	1.26	1.30	0.62	1.44	1.80
LOI	2.64	3.78	3.52	8.06	6.52	5.22
Total	100	100.35	100.53	100.40	100.38	100.27
HM	0.56	0.56	0.37	0.41	0.53	0.54
FM	0.25	0.34	0.19	0.13	0.28	0.45
AM	0.37	0.30	0.22	0.30	0.32	0.26
TM	0.049	0.060	0.038	0.032	0.033	0.056
FerM	0.45	0.75	0.64	0.33	0.63	0.91
NKM	0.21	0.34	0.35	0.69	0.53	0.56
AlkM	7.80	3.80	3.00	1.40	1.50	3.00

formed during the erosion of volcanic structures of the Campanian age. As can be seen from the analyzes [61], only 2 compositions out of 11 can be taken as normal sedimentary rocks (siallites), although one of them is superferruginous (FerM 0.65) and therefore partly “suspicious”. Of the remaining nine, two are alkalites, one is siferlite (FerM 0.91, HM 0.54) and six are pseudohydrolysates or pseudosiallites (3.21–5.67 % MgO).

Due to the abundance of magnesian rocks, the module diagram ($Na_2O + K_2O$) – FM is most convenient for clustering, where three or four clusters are well distinguished. It is possible to distinguish, on the one hand, relatively low alkaline rocks of clusters I, III and, on the other hand, a clear rocks series of increasing alkalinity and decreasing femicity: clusters II $\Rightarrow$ IV. Apparently, the former (pseudohydrolysates) are mainly volcanomictic rocks, and the latter are tuffoids (siallites, up to alkalites). The highly femic composition of sample 9 is distinguished by the highest magnesiality and, probably, corresponds to a rock with an olivine-basaltic clastic admixture. Sample 5 is characterized by increased manganese content. We note a characteristic feature of pyrogenic rocks: the positive correlation of femicity and titanium value and a negative correlation of femicity and alkalinity (Fig. 77).

7.6. Diagnostics of tuffoids with different composition (several examples)

Basic tuffoids. Due to the enrichment of the basic igneous rocks with magnesium, iron and titanium, which are part of the dark-colored silicates (olivine, pyroxenes, amphiboles, chlorites) and oxides (magnetite, ilmenite), the increased TM, FerM, FM modules values the inherently "evidence" of the basic composition pyroclastics. In addition, the relatively low contents of SiO_2 at moderate contents of Al_2O_3 and elevated FeO lead to the fact that the HM value often exceeds the limit for siallites (> 0.55), which makes it necessary to qualify the basic rocks and their tuffs as pseudohydrolysates (MgO > 3 %).

For example, among seven analyzes of radiolarites from the ophiolite complex (J–K) of the Lesser Caucasus, published by V.S. Vishnevskaya and M.A. Levitan [54, p. 103], one clearly stands out in titanium and iron content: TM = 0.080 against the background of 0.049–0.055; FerM = 2.67 against a background of 0.29–0.56. In this case, the TiO_2content is ordinary, and the Fe_2O_3 content is anomalous: 7.88 against the background of 0.99–4.45 %. Note that the latter also entails some accumulation of phosphorus: 0.25 % P_2O_5 against 0.01–0.14 %. The combination of these features suggests that this radiolarite contains an admixture of basic pyroclastics.

The likelihood of recognizing tuffoids is increased when characteristic correlations are found on module diagrams, for example, a positive FerM–TM correlation (actually meaning a Fe–Ti correlation) or a negative FM –

NKM correlation, reflecting the antagonism of femic minerals and feldspars. In addition, sometimes the sodium content (AlkM) is diagnostic: for basaltic and andesite-basaltic pyroclastics, the AlkM is, as a rule, greater than unity.

One can see these features in the Upper Cretaceous tuffs of Kamchatka, the rock-forming components of which, according to V.I. Grechin, are effusive rocks fragments (basic, intermediate, less often acidic), crystal clasts (plagioclase, pyroxene, hornblende) and volcanic glass [193, p. 142]. The tuffs of the psammo-aleurite structure are usually crystalline-lithoclastic, while the more dispersed tuffs of the aleuropelitic structure are more often vitro-lithoclastic. Lithochemical certification of rocks shows that only two out of thirteen compositions are siallites; the rest are either pseudosiallites or alkalites. *Thus, only one procedure of lithochemical certification makes it possible to confidently distinguish tuffs from normal sedimentary rocks.*

The module diagram "Alkali – FM" shows clusters that differ mainly in femicity; it is obvious that they correspond to different types of the original tephra – less and more basic; at the same time, for less femic tuffs, there is a clear positive correlation between femicity and TM value. It is interesting that the anomalous-titanium composition (pelitic crystal-vitroclastic tuff, TM 0.107) is also characterized by hyper-ferrous content (FerM 0.67). Obviously, this tuff corresponds to low-alumina basalt – this (and not the increased Fe or Ti contents) is the reason for the high TM and FerM values.

According to the description of A. V. Van and R. G. Matukhin [43, p. 82], in the Devonian sediments of the river Dzhaltul (NW of the Siberian Platform), three lithotypes are distinguished: tuffaceous silicites, tuffaceous microfelsites, and tuffaceous argillites, including ferruginous ones. An examination of the seven analyzes given by them shows that six of them differ in hypertitanium value (TM 0.131–0.648) and hyper-ferrous value (FerM 0.55–0.64). In addition, strong geochemical Mn anomalies can be noted in at least four compositions, allowing them to be classified as manganese (MnO from 0.90 to 2.81%). All this is more than enough to diagnose rocks as volcanogenic-sedimentary with a basic composition of pyroclastics.

Table 100 and in Fig. 78 show the compositions of reliably established volcanic rocks in the Riphean of Podolia, called tuffs and tuff gravelites [210]. Lithochemical diagnostics of these rocks as volcanogenic-sedimentary is not difficult. Indeed, out of 20 analyzed rocks, only 1/5 are certified as silites (which could be mistaken for sedimentary rocks). All others are magnesian or ferrous and are certified as pseudosilites, pseudosiallites, pseudohydrolysates (14 analyzes) or as siferlites (2 analyzes). For diagnosis, lithochemical differences between tuffs (cluster IV) and tuff gravelites (clusters I–III) are very important: there are no normal silites or siallites among tuffs, they are, on average, more ferruginous (FerM 0.71–0.98 versus

0.34–0.87), more femic (FM 0.31–0.47 versus 0.03–0.39) and more titanium (TM 0.074–0.160 versus 0.034–0.107).

In this case, the dispersion of all parameters in tuff gravelites is much higher than in tuffs, since the dispersion caused by the mechanical differentiation of the tuff gravelite material is superimposed on the primary dispersion of the composition. Indeed, as can be seen from the FM – TM plot (Fig. 78), only a part of tuff gravelites form a single correlation field with tuffs; at least 6 analyzes of 15 tuff gravelites have abnormal TM value, which can be attributed to the process of natural heavy concentrating with the heavy titanium minerals accumulation in the gravelites.

Yakutian geologists described variegated silty clay rocks in the Lower Triassic of the Vilyui syneclise and Near-Verkhoyansk trough. They were able to show that these are nothing more than tuffs and tuffites containing autigenic clay matter (Na-montmorillonite, Fe-chlorite, hydromica ± kaolinite) – a product of the transformation of basic effusive rocks fragments and their volcanic glass. Moreover, the overwhelming majority of T_1 clay rocks, upon closer examination, turned out to be tuffaceous argillites. The authors associate such a large participation of pyroclastic material in T_1 deposits with the extremely strong trap volcanism in the neighboring Tungus syneclise [115]. In addition to petrographic observations, the use of the titanium, alumina, and iron contents and characteristic correlations played an

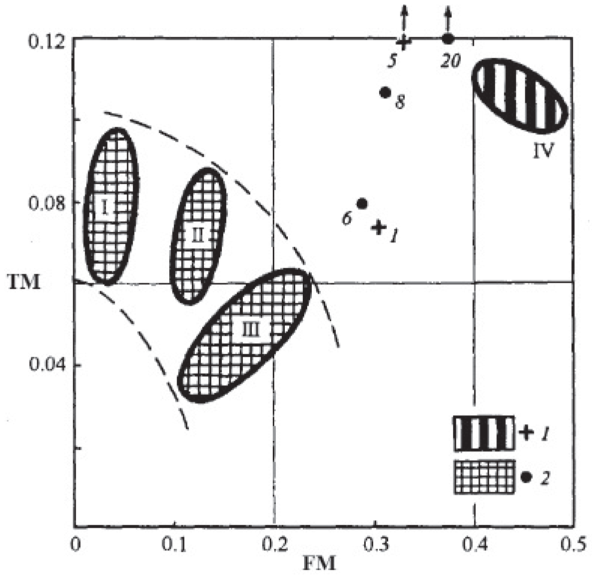

Fig. 78. Module diagram for Riphean basalt tuffs (1) and tuff gravelites (2) of Podolia. *Compiled according to E. Ya. Zhovinsky, 1977 [210]*

Table 100

Chemical composition of the Riphean basalt tuffs and tuff gravelites of Podolia.
Compiled according to E. Ya. Zhovinsky, 1977 [210, p. 90–91]

Oxides and modules	I	II	III	IV	1	5	6	8	20
	Normo-silite	Alkaline myosilite	Alkaline pseudosiallite	Pseudo-siferlite	Pseudo-siallite	Alkaline pseudosiferlite	Pseudo-siferlite	Pseudo-siallite	Ti pseudo-siferlite
n	2	2	8	3					
SiO_2	81.63	67.13	64.25	46.63	48.20	51.74	56.01	50.74	47.20
TiO_2	0.55	0.89	0.57	1.42	0.97	1.79	0.95	1.61	2.88
Al_2O_3	6.77	12.17	12.66	13.45	13.09	11.18	11.78	15.00	13.61
Fe_2O_3	1.64	3.21	3.77	9.85	8.07	10.71	8.00	6.04	9.96
FeO	0.80	2.16	2.66	2.81	1.80	1.87	2.68	4.61	4.24
MnO	0.01	0.08	0.09	0.21	0.18	0.16	0.15	0.17	0.13
MgO	0.69	3.00	4.23	8.31	4.93	5.23	5.59	5.36	4.29
CaO	0.67	1.63	1.44	1.12	4.54	1.46	1.46	1.35	1.12
Na_2O	0.92	2.02	2.43	2.94	2.64	3.07	1.76	2.00	1.21
K_2O	3.01	3.11	2.62	1.46	1.21	2.98	3.15	2.77	3.40
P_2O_5	0.05	0.14	0.08	0.16	0.09	0.12	0.15	0.12	0.09
$S + SO_3$	0.05	0.16	1.64	0.76	0.08	0.54	0.08	1.23	0.09
CO_2	1.44	0.94	1.32	1.45	5.05	0.82	0.88	0.85	0.40
LOI	1.27	3.52	3.47	10.28	9.58	8.97	7.86	8.28	11.90
Total	99.50	100.16	101.23	100.85	100.43	100.64	100.50	100.13	100.52
HM	0.12	0.28	0.31	0.59	0.50	0.50	0.42	0.54	0.65
FM	0.04	0.12	0.17	0.45	0.31	0.34	0.29	0.32	0.39
AM	0.08	0.18	0.20	0.29	0.27	0.22	0.21	0.30	0.29
TM	0.081	0.073	0.045	0.106	0.074	0.160	0.081	0.107	0.212
FerM	0.33	0.42	0.49	0.87	0.71	0.98	0.85	0.65	0.87
NKM	0.58	0.42	0.40	0.33	0.29	0.54	0.42	0.32	0.34
AlkM	0.30	0.60	0.90	2.00	2.20	1.00	0.60	0.70	0.40

important role in this diagnosis. The authors effectively used I.V. Khvorova and A.A. Gavrilov's fruitful idea [265], who for the first time emphasized the significantly different correlation of these elements in magmatic and sedimentary processes.

Let's perform the "thought experiment" so beloved by theoretical physicists. *Is it possible, without petrographic information, to make a correct diagnosis only based on chemical analyzes?* It turns out that we have a difficult case. In analyzes 2 and 3 (Table 101), the HM values (0.66 and 0.61) force us to attribute the rocks to hydrolysates, because the MgO content, unfortunately, does not reach the "three percent barrier", which would allow us to certify the rocks as pseudohydrolysates and thus with light heart to exclude them from the number of normal sedimentary[3]. However, in this difficult case, the

Table 101

Average chemical composition of the Lower Triassic tuffoids of the Lena-Vilyui oil and gas province.
Compiled according to V. Yu. Ivensen and G. V. Ivensen, 1975 [115, p. 77]

Oxides and modules	1	2	3
	Medium and fine-grained tuffs and tuffites (siferlite)	Fine-grained tuffs and tuffites (Ti hypohydrolysate)	Tuff argillites (hypohydrolysate)
п	11	12	19
SiO_2	61.24	49.92	52.62
TiO_2	1.48	2.25	1.88
Al_2O_3	12.00	16.65	17.61
Fe_2O_3	3.41	8.28	8.35
FeO	6.62	5.96	4.34
MnO	0.18	0.12	0.09
MgO	2.79	2.89	2.67
CaO	1.95	1.62	1.15
Na_2O	1.44	1.69	1.25
K_2O	1.27	1.69	2.22
P_2O_5	0.19	0.30	0.25
HM	0.39	0.67	0.61
FM	0.21	0.34	0.29
AM	0.20	0.33	0.33
TM	0.123	0.135	0.107
FerM	0.76	0.76	0.66
NKM	0.23	0.20	0.20
AlkM	1.10	1.00	0.60

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[3] It is in such cases that there is a temptation to lower the "magnesian barrier" for pseudohydrolysates, perhaps to 2.5% MgO. However, our practice has shown that neither a decrease nor an increase in the accepted border of pseudohydrolysates justifies itself.

task of correct diagnosis is by no means hopeless. First, the pelitomorphic clay rocks (analyzes 2 and 3) are hyperferrous (FerM 0.65–0.76) and hypertitanic (TM 0.106–0.135). Even if these were normal hydrolysates, we could confidently assume a basic substrate for them, which already gives a certain "hint". Second, clastic psammite-like rocks (an. 1) are siferlites (FerM 0.76, HM 0.39), moreover, hypertitanic (TM 0.123). Both features are characteristic of basic pyroclastics.

In fact, the difficulty of diagnostics here is quite artificial – we are forced, according to the conditions of the "thought experiment", to operate only with *average* compositions, without having at our disposal the entire primary set of analyzes. There is no doubt that, with unfolded information, we would have found among the individual analyzes a lot of siferlites, as well as pseudohydrolysates, i.e., rocks with HM > 0.55 and MgO > 3 %.

Another material for the “thought experiment” can be six analyzes given by R.A. Mandalyan. These are fairly typical “geosynclinal” limestones of the Lesser Caucasus, containing a volcanic admixture – either pyroclastic or volcanoclastic [166]. In these analyzes, the presence of abnormal HM and FerM values catches the eye, which should be characteristic of a pyrogenic admixture of the basic composition. However, in the case of carbonate rocks, these signs are not in themselves diagnostic, since an increased TM is also characteristic of most platform carbonates, and the FerM anomalies can be explained by the presence of normative or modal $FeCO_3$, which can also occur in normal sedimentary rocks. In this case, the more important can, apparently, be considered the high sodium content values (AlkM up to 4.3) and the dominance of Fe (III) over Fe (II). The first indicates the presence of plagioclase (or the products of its change, for example, paragonite), and the second makes it possible to exclude $FeCO_3$ as a factor in the high value of FerM. Additional evidence in favor of volcanism can be found in the negative correlation between iron content and alkalinity. It may be due to the antagonism between the amounts of plagioclase and dark-colored substances (amphiboles, pyroxenes). This type of correlation is not very typical for normal sedimentary rocks.

A specific type of basic pyroclastics is *alkaline-basaltic*, characteristic, in particular, of rift volcanism.

Table 102 and in Fig. 79 processed 13 analyzes of tuffs and 4 analyzes of argillites of the Ordovician volcanic-sedimentary flysch of the Momsky horst-anticlinorium [35]. Here, sedimentary rocks (argillites, cluster II) are very clearly distinguished from alkaline-basaltic tuffs (clusters I, III, IV): in argillites, the total alkalinity and femicity are much lower.

As for the pyroclastites themselves, they clearly contain psammitic basic tuffs of pyroxene trachybasalts, which are certified as pseudohydrolysates (cluster I), and

Table 102

Chemical rocks composition of the Ordovician flysch volcanogenic-sedimentary formation of the Arga-Tass zone of the Momsky horst-anticlinorium.

Compiled according to M.D. Bulgakova, 1986 [35, p. 119, 126]

Oxides and modules	I	II	III	IVa	IVb	5	13
	Psammitic tuffs (pseudohydrolysate)	Argillites (pseudosiallite)	Tuffs and tuffopelites (alkaline pseudosiallite)	Psammitic tuffs (alkalite)	Tufforhythmites (alkaline pseudosiallite)	Large-silty tuff	Argillite
						Alkaline pseudosiallite	
n	3	4	2	3	3		
SiO_2	47.48	60.42	55.46	55.53	57.48	52.65	57.05
TiO_2	0.68	0.56	0.62	0.59	0.52	0.91	0.51
Al_2O_3	17.43	12.68	16.29	17.34	16.92	17.00	17.33
Fe_2O_3	3.58	1.97	3.29	2.12	2.14	4.99	3.32
FeO	6.11	3.85	4.78	4.91	4.35	5.82	4.39
MnO	0.04	0.05	0.08	0.01	0.08	0.00	0.07
MgO	5.88	5.44	5.00	3.83	3.45	5.31	4.05
CaO	8.83	3.35	2.82	2.23	2.99	1.54	1.79
Na_2O	3.38	1.10	4.76	6.03	5.16	5.50	0.82
K_2O	1.09	3.05	2.01	2.43	2.70	1.10	5.47
H_2O^+	3.15	3.04	3.61	3.10	2.81	4.47	4.79
P_2O_5	0.25	0.14	0.23	0.31	0.23	0.43	0.16
LOI	1.58	4.05	1.16	0.80	1.30	0.25	0.18
Total	99.48	99.70	100.11	99.23	100.13	99.97	99.93
HM	0.59	0.32	0.46	0.45	0.42	0.55	0.45
FM	0.33	0.19	0.24	0.20	0.17	0.31	0.21
AM	0.37	0.21	0.29	0.31	0.29	0.32	0.30
TM	0.039	0.044	0.038	0.034	0.031	0.054	0.029
FerM	0.54	0.44	0.48	0.39	0.38	0.60	0.44
NKM	0.26	0.33	0.42	0.49	0.47	0.39	0.36
AlkM	3.10	0.40	2.40	2.50	1.90	5.00	0.10

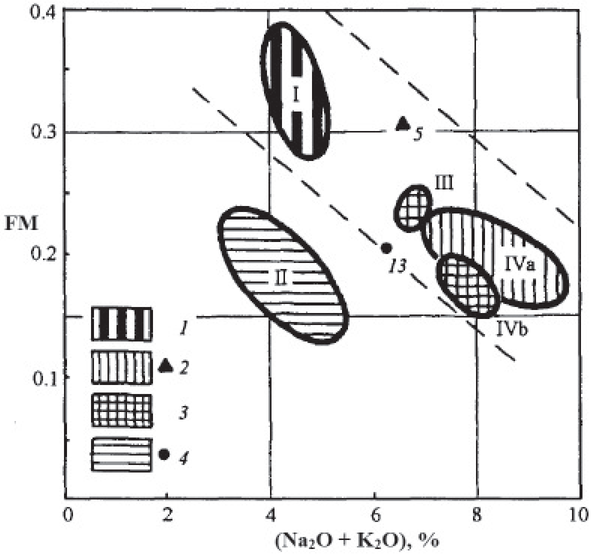

Fig. 79. Module diagram for alkali-basite tuffs, tuffopelites, tufforhythmites and argillites of the Ordovician flysch volcanogenic-sedimentary formation of the Arga-Tass zone of the Momsky horst-anticlinorium.

Compiled according to M.D. Bulgakova, 1986 [35, p. 119, 126].

1, 2 – tuffs: pyroxene trachybasalts (1) and trachyandesite-basalts (2); 3 – tuffs and tuffaceous rocks; 4 – argillites

more acidic tuffs of trachyandesite-basalts (cluster IVa). Two other clusters of tuffs and tuffopelites (III, IVb) are mixed; their heterogeneity indicates this (the presence of pre-polyethylene species is also indicated by the special composition of the large-aleurite tuff – sample 5). Also note that "argillites" of cluster II are magnesian, they are certified as pseudosiallites. Most likely, they contain a pyroclastic admixture and should be treated as tuffoids. This is also indicated by the composition of the "argillite" sample 13 (alkaline pseudosiallite), very close to the trachyandesite-basaltic tuff field.

In N.A. Lizalek's work, five analyzes of unusual Riphean rocks of the Sayan region, described as "tuffs" and "volcanomictic siltstone" [156], are given. In this case, four compositions have a total alkalinity of 9.36–11.30% and are certified as potassium alkalites, and one tuff – as an alkaline pseudosiallite with a high MgO content. Siltstone differs from tuffs not in total, but in normalized alkalinity (NKM 0.64 versus 0.70–0.87 in tuffs) and even more sharply – in terms of reduced FerM 0.18 versus 0.36–0.56 in tuffs. Noteworthy is the combination of potassium and magnesium value, rare for sedimentary rocks, which may be due only to the biotite presence. This mineral is also found in arkoses, in particular in the Mesozoic terrigenous strata of Western Siberia, studied in detail by B.A. Lebedev [153]; however, these rocks are by no means alkalites. *Therefore, we should qualify these Riphean tuffs as derivatives of some alkaline basaltoids, and not as acidic tuffs.* This conjecture seems to be supported by the normal TM value of the rocks (0.042–0.055), while rhyolite or trachyrhyolite tuffs are characterized by a sharply reduced TM value, as a rule, less 0.020, and often even less than 0.005 [315].

Acidic and average tuffoids. The basic diagnostic features of these rocks should be considered increased total and normalized alkalinity and decreased TM value. Thus, the Neogene liparitic-dacite tuffs of Transcaucasia [201] are distinguished by high total alkalinity (6.76–7.42 %) and low TM value (0.022–0.028). Despite the small dispersion of the compositions, there is nevertheless a positive TM – FerM correlation characteristic of petrogenic rocks and a certain tendency of a negative correlation NKM – HM. The famous Lower Ordovician graptolite shales of the Baltics contain orthoclase in the silt fraction; it turned out that these well-studied high-potassium rocks are nothing more than acidic tuffoids [300, p. 83].

Composition of Oligocene tuffs and tuffites of the Ukrainian Carpathians [210] has two distinct features (Table 103, Fig. 80).

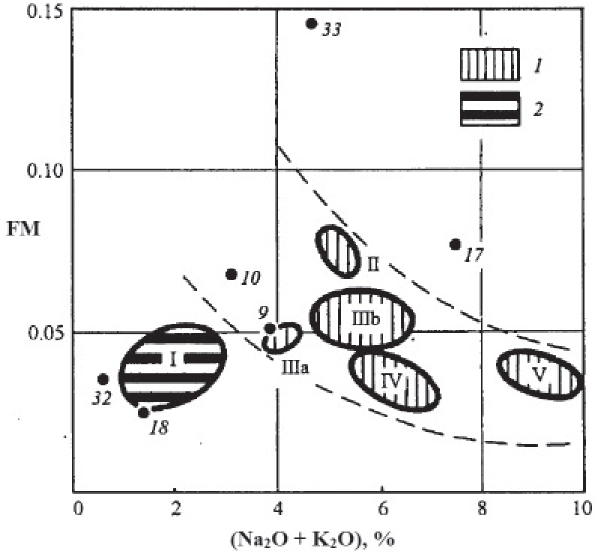

Fig. 80. Module diagram for Oligocene acidic tuffs (1) and tuffites? (2) of the Ukrainian Carpathians.
Compiled according to L.G. Tkachuk et al., 1977 [210, p. 28–29]

Table 103

Chemical composition of Oligocene acid tuffs and tuffites of the Ukrainian Carpathians.

Compiled according to L.G. Tkachuk et al., 1977 [210, p. 28—29]

Oxides and modules	I	II	IIIa	IIIb	IV	V	9	10	17	18	32	33
	Normo-silite	Alkaline myosilite	Myosilite	Alkaline myosilite		Alkalite	Myosilite	Carbonaceous myosilite	Alkaline myosilite	Carbonaceous normosilite	Normosiallite	
n	11	2	2	7	5	2						
SiO_2	75.15	63.65	71.77	68.17	71.44	69.06	73.62	67.70	62.80	77.50	77.40	57.63
TiO_2	0.39	0.36	0.22	0.29	0.21	0.16	0.49	0.39	0.27	0.28	0.35	0.92
Al_2O_3	9.12	13.43	11.26	12.90	12.57	12.38	11.45	9.42	13.61	7.46	7.40	18.07
Fe_2O_3	1.55	1.54	1.82	1.57	1.14	1.04	2.19	3.28	2.04	0.47	1.74	1.73
FeO	0.84	1.86	0.58	1.27	0.63	1.03	0.77	0.72	1.19	0.87	0.36	4.92
MnO	0.00	0.04	0.02	0.03	0.02	0.08	0.00	0.00	0.06	0.02	0.01	0.06
MgO	0.67	1.43	1.11	1.03	0.64	0.45	0.84	0.64	1.67	0.66	0.72	1.72
CaO	0.57	2.13	1.52	1.48	1.15	1.97	0.62	0.53	2.14	0.42	0.44	0.85
Na_2O	0.23	1.15	1.67	2.27	2.94	4.14	0.25	0.26	1.48	0.25	0.21	1.35
K_2O	1.69	4.05	2.39	3.48	3.42	5.05	3.64	2.90	6.05	1.18	0.43	3.37
P_2O_5	0.11	0.06	0.03	0.03	0.02	0.05	0.08	0.07	0.07	0.12	0.06	0.10
S	0.36	0.54	0.00	0.24	0.03	0.12	0.37	0.60	0.37	0.15	0.16	2.56
H_2O^-	3.08	3.36	2.87	2.51	1.67	1.72	2.35	3.10	4.86	1.74	2.79	1.49
LOI	6.72	6.82	4.76	5.24	4.46	2.97	3.16	11.16	3.93	9.43	7.49	5.86
Total	100.48	100.42	100.02	100.51	100.34	100.22	99.83	100.77	100.54	100.55	99.56	100.63
HM	0.16	0.27	0.19	0.24	0.20	0.21	0.20	0.20	0.27	0.12	0.13	0.45
FM	0.04	0.08	0.05	0.06	0.03	0.04	0.05	0.07	0.08	0.03	0.04	0.15
AM	0.12	0.21	0.16	0.19	0.18	0.18	0.16	0.14	0.22	0.10	0.10	0.31
TM	0.043	0.027	0.020	0.022	0.017	0.013	0.043	0.041	0.020	0.038	0.047	0.051
FerM	0.25	0.25	0.21	0.22	0.14	0.17	0.25	0.41	0.24	0.18	0.27	0.35
NKM	0.21	0.39	0.36	0.45	0.51	0.74	0.34	0.34	0.55	0.19	0.09	0.26
AlkM	0.10	0.30	0.70	0.70	0.90	0.80	0.10	0.10	0.20	0.20	0.50	0.40

1. Increased alkalinity, both total and normalized. Out of 35 analyzes, 2 turned out to be alkalites (cluster V) and 15 – alkaline silites (clusters II, IIIb, IV); according to the NKM value, 10 compounds are certified as super-alkaline and 7 – as hyperalkaline.

2. Decreased TM value: out of 35 analyzes, 20 are hypotitanic, others are normotitanic. Meanwhile, 32 analyzes correspond to silites (and only one – to siallite), which can be, in particular, sandstones or siltstones. However, terrigenous clastic rocks are characterized by either normal or slightly increased TM value (the latter is for quartz sandstones and the greywacke series). In addition, we note the characteristic correlations: positive (FM, FerM) – TM and negative (NKM, the sum of alkalis) – FM. Such correlations are usually inherent in petrogenic rather than lithogenic rocks. All this lithochemical information is quite enough to conclude, even in the absence of petrographic data, that the rocks contain a significant admixture of acidic pyroclastics.

Although there is no additional information in the original source, it can be assumed that the most titanium and least alkaline compositions (cluster I) correspond to tuffites.

Unusual silica rocks have been described among the red and grey-colored rocks D_3 – C_1 in the Kempendiais dislocation in the west of the Vilyui depression. In terms of the HM value, these are myosilites (0.20–0.25), which can correspond, for example, to siltstones or arkose sandstones. However, these rocks are hypotitanic, which is not typical even for arkoses (TM is only 0.015–0.020), and, in addition, they are hypoferrous, and the FerM is very low: in three out of four samples, it is only 0.07–0.09. Femicity is also very low: FM is only 0.02–0.05. Two samples contain a lot of alkalis (5.8–6.4%), and the rocks are super-sodium (AlkM 3.4–4.3). Taken together, all this allows to define rocks as acidic tuffs, which in this case has an independent lithological confirmation [273].

According to the descriptions of V.M. Grannik, in the Upper Cretaceous in Sakhalin three lithotypes of tuffites are present: silica, clay, and silica-clay [86]. All of them differ in very low TM value (0.007–0.009), which indicates the acidic composition of pyroclastics. Note also that the first two lithotypes do not have lithochemical differences and correspond to one chemotype – hyperalkaline myosilites (HM 0.19, NKM 0.51).

In the Riphean of the Igarka region, along with basic tuffs, the diagnosis of which is not difficult (magnesian, iron, titanium), curious rocks called “parashales” are also described. These rocks are macroscopically dark grey or even black. Among them, the varieties "quartzite, quartzite-sericite and sericite-quartzite" are distinguished, an abundance of pyrite and leucoxene is noted [77]. However, analyzes show that these are not ordinary metapelitoids or metaaleurolites, as follows from the petrographic description, these are *alkalites* with a total alkalinity 9.4 %. The rocks are hyperalkaline (NKM 0.57–0.58), so it is obvious that they contain a significant amount of feldspars (or Na-K-zeolites), which were missed during microscopic study. So, it is almost certain that we are dealing with acidic metatuffoids that significantly complements the characteristics of the explosive volcanism in this region.

7.7. Difficult cases of diagnosis (a few examples)

Above we gave various examples of pyrogenic impurities diagnostics, which can be considered relatively simple. Indeed, we either had convincing lithological information confirming the tuffoid nature of the analyzed rocks, or we had vivid, irrefutable lithochemical evidence – sufficient for a correct diagnosis even in the complete absence of lithological data.

However, there are situations when lithological information is fragmentary and ambivalent, and petrochemical data can be interpreted differently. In such cases, there is room for doubt, as a result of which the diagnosis becomes probabilistic. For example, the processing given by A.V. Sochava et al. [72] of some ferruginous terrigenous rocks' *average* compositions, as well as proven tuffs and tuffites of the Vendian of the Russian Platform, showed that the tuffites' composition of the Yaryshevskaya Formation does not bear clear petrochemical signs.

This does not allow one to "suspect" the presence of pyroclastic admixtures in the rocks without additional information.

It also happens that the geologist's definition of rocks as tuffs is not at all confirmed by lithochemical indicators. For example, in the northern framing of the Chelyabinsk granodiorite massif, E. A. Belgorodsky and E. V. Shalaginov described stratified deposits of the so-called Dolgoderevenskaya sequence (presumably the Upper Ordovician). The rocks are identified as acidic tuffs of psammitic, aleuropsammitic, and even gravel-psammitic structures [14]. However, this diagnosis raises serious doubts.

First, three analyzes out of four contain only 1.54–2.68 % alkalis, and in two of them the SiO_2 content exceeds 80 %. There are too few alkalis, and there is a lot of silica for acidic tuffs (the clastic structure contradicts the assumption about *silica* tuffs). Second, in two analyzes, the TM value is 0.046 and 0.094; these numbers are unusually high for acidic tuffs, while being quite normal for subarcoses and quartz sandstones.

It seems more plausible that the Dolgoderevenskaya strata is composed of acidic arkoses and subarcoses. In any case, if we plot the points of the compositions of the Dolgoderevenskaya strata on the module diagram (Na_2O + K_2O) – FM, which we used to distinguish between metaarcoses and metaryolites in the Subpolar Urals [315], then all of them will be in the field of metaarcoses.

The tuffs described by G.N. Brovkov [28] in the Devonian and Carboniferous of Tuva are classified as alkaline silites; the Devonian less acidic, and the carbonic more acidic – myo- and normosilites, respectively. In general, the latter are more alkaline – in one analysis the alkalis amount exceeds the alkalite boundary. The Devonian tuffs are characterized by the processes of albitization, adularization, and sometimes also carbonatization. In carbonic tuffs, hydromica, silicification and the appearance of analcime are noted. The widespread development of allochemical processes determines the "looseness" of clusters and a wide spread of points on the module diagrams. At the same time, there is a positive HM and alkalis correlation, in the absence of such a HM correlation with NKM, which can also serve as an argument in favor of allochemical claying of tuffs. And yet, despite a number of diagnostic features, it must be admitted that *rocks with a relatively low total alkalinity*, in the absence of additional information, can hardly be distinguished from arkoses.

Summarizing these and other cases, we can conclude that the greatest diagnostic difficulties arise in three cases.

1. ***Pyroclastics is of andesite composition.*** Such material, in contrast to basalt, may not show increased titanium and iron values, and, unlike rhyolite, may not have increased alkalinity. The only clue is the increased content of non-carbonate (plagioclase) CaO.
2. ***Pyroclastics is buried in greywacke flysch strata.*** The latter differ little from tephra in their chemical composition (for example, sandstones are represented by volcanoclastic greywackes).
3. ***Pyroclastics underwent strong allochemical alteration, but the original (or slightly altered) tuffs have not survived.***

Here are a few more examples with varying degrees of success in the diagnosis.

Table 104 and Fig. 81 processed 19 analyzes of Lower Cretaceous sandstones from the deep well Berge-1 (Yakutia), passed at depths from 1459 to 2190 m. The composition of these rocks is very uniform: all of them are certified as alkaline myosilites, despite the significant dispersion of silica contents – from 57.3 to 70.8 %. The point is that fluctuations in SiO_2 contents are caused by the presence of a significant carbonate impurity in such rocks (up to 20–22 % in cluster I and up to 27 % in sample 4).

High total alkalinity (up to 7.3 % for clusters, and up to 7.95 % for individual samples, i.e., up to the alkalite boundary) and hyperalkaline composition (NKM on average 0.48–0.54, and for individual samples up to 0.58), as well as a positive correlation for the TM – FerM plot (Fig. 81) can mean that we are dealing either with petrogenic arkoses of the first cycle type, or

Table 104

Chemical composition of the Lower Cretaceous sandstones of the Near-Verkhoyansk trough.

Compiled according to G.V. Ivensen, 1991 [114, p. 22–23]

Oxides and modules	I	II	III	IV	V	4	8
	Carbonate alkaline myosilite	Alkaline myosilite				Carbonate alkaline myosilite	Alkaline myosilite
n	2	5	4	4	2		
SiO_2	58.04	70.92	70.37	68.27	68.19	52.25	69.15
TiO_2	0.14	0.20	0.33	0.43	0.62	0.34	0.28
Al_2O_3	11.19	14.61	14.58	14.77	14.34	10.60	15.00
Fe_2O_3	-	0.12	0.68	0.89	0.76	0.70	1.14
FeO	1.22	1.52	1.47	2.08	2.87	0.72	1.29
MnO	0.03	0.03	0.04	0.05	0.06	0.17	0.04
MgO	0.57	0.79	0.87	1.15	1.10	1.08	1.14
CaO	13.20	2.05	2.23	2.53	2.69	16.50	2.49
Na_2O	3.80	4.38	4.61	4.52	4.68	3.36	4.38
K_2O	2.23	2.86	2.67	2.62	2.63	2.09	2.40
P_2O_5	0.04	0.06	0.09	0.14	0.15	0.11	0.08
LOI	9.41	2.29	2.09	2.60	2.27	11.88	2.44
Total	99.87	99.83	100.03	100.05	100.36	99.80	99.83
HM	0.22	0.23	0.24	0.27	0.27	0.24	0.26
FM	0.03	0.03	0.04	0.06	0.07	0.05	0.05
AM	0.19	0.21	0.21	0.22	0.21	0.20	0.22
TM	0.013	0.014	0.022	0.029	0.043	0.032	0.019
FerM	0.11	0.11	0.15	0.20	0.25	0.15	0.16
NKM	0.54	0.50	0.50	0.48	0.51	0.51	0.45
AlkM	1.70	1.50	1.70	1.70	1.80	1.60	1.80

with a pyrogenic admixture in terrigenous rocks. Noteworthy is the very low TM value: except for cluster V, TM on average does not exceed 0.029, and in clusters I and II it is only 0.013–0.014. This suggests that these sandstones may well be acidic tuffoids.

The Yakutian researcher G.V. Ivensen, having petrographic data, came to the unambiguous conclusion that in the Cretaceous time, pyroclastics of acidic (close to dacite) composition entered the sedimentation basin [114]. However, for the sake of fairness, one must admit that, based on only chemical analyzes, the solution of the alternative – petrogenic arkoses or tuffoids – is impossible in this case. ***The reason for the ambiguity of the diagnosis lies***

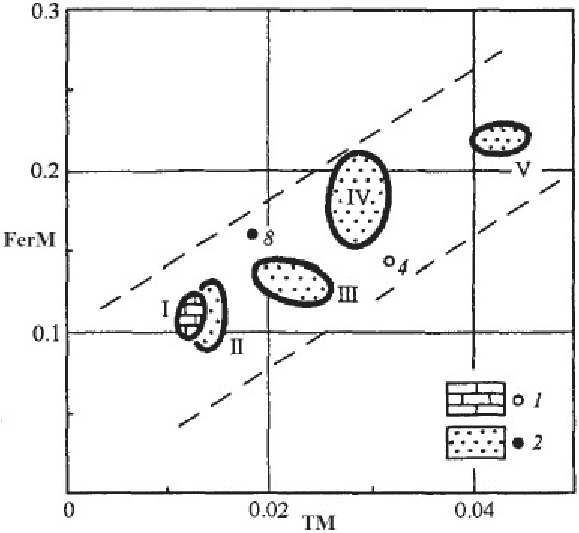

Fig. 81. Module diagram for the Lower Cretaceous sandstones of the Eksenyakh formation from borehole Berge, Near-Verkhoyansk trough.
Compiled according to G.V. Ivensen, 1991 [114, p. 22–23].
1, 2 – alkaline myosilites: carbonate (1) and carbonate-free (2)

precisely in the fact that the pyrogenic material was not so much rhyolitic as much less expressive – dacitic.

Long before G.V. Ivensen's research in the Lena-Vilyui province, A.E. Kiselev described two types of tuffs: aquagenic and ash. Aquagenic tuffs were formed during underwater eruptions in the sedimentation area "*during the formation of myogeosynclinal formations*" ($T_3 – J_1$), while ash tuffs, "*associated with volcanic outbursts in the parent province*," – later, in the "*era of sedimentation of the foredeep formation* ($J_3 – K_1$)" [133, p. 95]. As you can see from the Table 105, the described tuffs have distinct lithochemical differences: the former (clusters Ia, Ib) are high-iron pseudohydrolysates and hydrolysates (apparently already lost some of their magnesium) with high TM value (FerM 0.94–1.71; TM 0.080–0.192), while the latter (cluster II) are normosiallites, including alkaline ones. If the diagnostics of the former is trivial (it is quite obvious that these are basites' derivatives), then the diagnostics of the latter is much more complicated. Nevertheless, here, too, there are two diagnostic features: low SiO_2 contents characteristic of pelitoids (60 ± 2 %) are in contradiction with the high sodium content of rocks (AlkM 1.25–2.74), and TM value is "suspiciously" reduced for normosiallites (0.021–0.027). Such characteristics could correspond to sodium montmorillonite clays – products of the dacite pyroclastics degeneration.

Table 105

Average chemical composition of aquagenic and ash tuffs of the Lena-Vilyui oil and gas province.

Compiled according to A.E. Kiselev, 1970 [133, p. 90–95]

Oxides and modules	Ia	Ib	II
	Aquagenic tuffs		Ash tuffs (normosiallite)
	Ti hypohydrolisate	Carbonate pseudohydrolisate	
n	2	2	2
SiO_2	46.49	43.31	60.63
TiO_2	2.05	1.42	0.44
Al_2O_3	14.03	12.35	18.10
Fe_2O_3	10.56	4.91	3.26
FeO	9.57	8.41	0.72
MnO	0.11	0.44	0.12
MgO	2.96	3.44	1.00
CaO	1.22	10.26	3.15
Na_2O	1.11	1.25	2.53
K_2O	1.42	1.05	1.22
P_2O_5	0.21	0.32	0.14
SO_3	0.07	0.29	0.07
H_2O	3.98	2.13	3.80
LOI	5.84	10.17	6.81
Total	99.58	99.71	101.96
HM	0.78	0.64	0.37
FM	0.50	0.39	0.08
AM	0.30	0.29	0.30
TM	0.146	0.115	0.024
FerM	1.26	1.00	0.22
NKM	0.18	0.19	0.21
AlkM	0.80	1.20	2.10

One should also classify the *Miocene* tuffs of the Ciscarpathian region as difficult to diagnose [210]. In the 32 analyzes which we selected (10 analyzes with bad sums were discarded), two are certified as carbonatolites ("tuff sandstones with lime cement"), and the others are referred to by L.G. Tkachuk and colleagues as "tuffs" (indicating the color), "volcanic glass" and “bentonitized tuffs”. In contrast to the Carpathian *Oligocene* tuffoids, these rocks have much less distinct diagnostic features. The fields on the module diagrams are highly eroded, which may mean both a wide scatter of the initial pyroclastics compositions and its significant allochemical change in lithogenesis.

For example, on the NKM – FM module diagram, seven clusters and ten individual compositions are distinguished; the low degree of information convolution (32/(7 + 10) = 1.88) emphasizes the variability of the rock composition. Alkaline

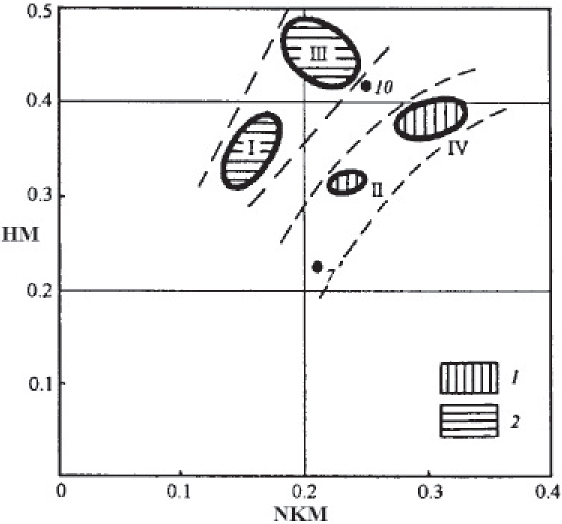

Fig. 82. Module diagram for Jurassic (one analysis is Triassic) shales of the Greater Caucasus, interpreted as primary montmorillonite.
Compiled according to I.V. Kirillova, 1966 [134, p. 87].
1, 2 – two presumed aggregates.

compositions (super- and hyperalkaline silites, less often siallites) here are much less than in the Oligocene – only 7 out of 32. The composition with extreme TM = 0.184 is andesite tuff, which, as noted by Ukrainian geologists, is found as an exception among the dominant rhyolite and rhyolite-dacite tuffs [210, p. 33].

Nevertheless, even in this difficult situation (a relatively low content of alkalis, which is more typical for arkoses than for acidic tuffs), there are still quite informative lithochemical signs. First, it is low TM value: 30 out of 32 compositions are certified as hypotitanic, and in 12 of them TM is less than 0.010. True, silicites or ultraquartz (glass) sandstones could have such TM value, but such rocks should have much more SiO_2, not less than 85–90%. Secondly, it is the presence of characteristic "endogenous" correlations: positive between TM and FerM and negative between FM and NKM.

Genetic diagnosis of bentonites can also be difficult.

For example, among the alkaline Paleocene bentonites from the Nalchik region, one can distinguish two chemotype-clusters: hypertitanic pseudomyosilites and more hydrolysate, normotitanic normosiallites (HM 0.43). Obviously, the latter contain more admixtures of hydromica and, possibly, kaolinite [231, p. 150]. Having no clear diagnostic signs, this type of bentonite turns out to be well "camouflaged". However, here, too, there is a hint – the statistical sample contains anomalous compositions – with minimum HM or with maximum TM values and MgO contents. Obviously, they correspond to either strongly silica bentonites or, conversely, to the purest montmorillonite clays. Such compositions cannot be confused with any normal sedimentary rock.

As is known, the most important process of the clay strata catagenetic alteration is the montmorillonite transformation into hydromica (for example, [153]). This means that when rocks such as bentonites are submerged to a depth of 1–3 km, they can be completely transformed, which will greatly complicate genetic diagnostics. The Jurassic "schists" of the Caucasus are a good example. Having plotted the compositions of clay rocks of a known mineral composition on the $SiO_2 - R_2O_3$ diagram (to which any module diagram with HM can correspond in meaning), I.V. Kirillova came to the conviction that the Caucasian "schists" were originally montmorillonite clays; moreover, they were volcanogenic-sedimentary formations: "*The clays, due to which the "schists" were formed, constituting a significant part of the lower terrigenous formation <...> do not really need to be removed from the land. Middle and basic volcanism may well ensure their formation in large areas*". According to I.V. Kirillova, "*the possibility of a purely terrigenous strata origin with a significant volcanism development raises great doubts*" [134, p. 92].

I.V. Kirillova's diagnosis seems plausible in the light of the Yu.O. Gavrilov's data [60], T.M. Gureshidze et al. [88] on the presence of *silica-chamosite concretions* in the shales of the Greater Caucasus. After we described completely similar concretions in the D_2 and P_1 deposits of the Lemva zone of the North Urals [98, 296], it became clear that they are a sign of "camouflage pyroclastics", as A.G. Kossovskaya puts it [143]. Processing of 14 shales analyzes (Table 106) shows that they included one myosilite (sample 7: apparently, siltstone). Others are assessed as hypo-, normo- and supersiallites with high sodium content (clusters I–III), which may be the distinguishing feature of the former montmorillonite clays, even if montmorillonite has not been preserved today. At the same time, the TM values of the "schists" do not allow us to consider them a product of the basic volcanism, but only the middle one – andesitic.

In addition, the module diagram (Fig. 82) indicates the heterogeneity of the "schists" combination, which clearly falls into two parts: clusters I, III and clusters II, IV plus sample 7. This picture allows two variants of nontrivial interpretation. Either we have two types of initial pyroclastics, respectively, for these two groups, or the the first group rocks are the allochemical alteration (claying) products of the second group rocks according to the scheme cluster II ⇒ cluster I and cluster IV ⇒ cluster III. In this process, feldspars are destroyed (NKM decreases accordingly) and the content of clay matter increases (along with the decrease in the NKM, the HM grows).

Table 106

Chemical composition of “schists” of the Greater Caucasus.
Compiled according to I.V. Kirillova, 1966 [134, p. 87]

Oxides and modules	I	II	III	IV	7	10
	Normo-siallite	Hypo-siallite	Normo-siallite	Alkaline normosiallite	Myosilite	Normo-siallite
n	2	2	6	2		
SiO_2	66.91	67.06	60.47	62.70	73.90	62.42
TiO_2	0.77	0.59	0.83	0.72	0.33	0.54
Al_2O_3	16.05	13.89	19.50	18.51	10.55	17.17
Fe_2O_3	7.00	7.07	6.97	5.03	2.17	8.59
FeO	-	-	-	-	4.09	-
MnO	0.05	0.07	0.06	0.09	0.12	0.09
MgO	1.96	1.85	1.82	1.64	1.00	1.86
CaO	0.94	1.82	1.17	1.52	2.32	0.94
Na_2O	1.06	1.38	1.28	2.38	1.67	1.52
K_2O	1.49	1.86	2.86	3.24	0.58	2.80
H_2O	0.41	0.29	0.35	0.37	0.20	0.63
P_2O_5	0.16	0.13	0.17	0.20	0.09	0.17
LOI	3.49	4.19	4.35	2.47	3.12	3.60
Total	100.29	100.20	99.83	98.87	100.14	100.33
HM	0.36	0.32	0.45	0.39	0.23	0.42
FM	0.13	0.13	0.15	0.11	0.10	0.17
AM	0.24	0.21	0.32	0.30	0.14	0.28
TM	0.048	0.042	0.043	0.039	0.031	0.031
FerM	0.42	0.49	0.35	0.27	0.59	0.49
NKM	0.16	0.23	0.21	0.30	0.21	0.25
AlkM	0.70	0.70	0.40	0.70	2.90	0.50

7.8. Diagnostics of volcanic material in Precambrian metamorphic strata

Attempts at qualitative recognition of tuffaceous rocks among metamorphic rocks have been made several times; the most famous are the methods by A.N. Neyelov and A.A.Predovsky, which we examined in detail in the Introduction. Among other works, the experience of applying the *method of discriminant functions* deserves attention.

G.S. Kurtov, who studied the metamorphites of the Proterozoic Buron Formation in North Ossetia, used a modified Niggli method, bringing to 100% the sum of Al_2O_3, Fe_2O_3 (total), MgO, CaO, Na_2O and K_2O, without recalculating the contents to molecular quantities. Using several training samples, he calculated the discriminant functions equations for igneous rocks of acidic, intermediate and basic composition. The components enter these equations with plus or minus signs and with different coefficients. The value $D > 0$ refers the analysis to tuffs, and $D < 0$ – to igneous rocks. The classification error is 30 %.

Based on his technique, G.S. Kurtov reconstructed the primary pre-metamorphic composition of the Buron Formation and came to a nontrivial conclusion: "*Recognition of the primary nature by chemical composition shows that this sequence is tuffaceous sedimentary. Except for metamorphosed veins of diabases and tuffs, no magmatic rocks were found in the Buron formation*" [152, p. 150]. The overall diagnostic result: out of 23 analyzes, 14 are attributed to sedimentary rocks, 8 – to acidic and one – to average tuffs.

We have verified this diagnosis with module diagrams (Table 107, Fig. 83). A priori, one might think that our diagnosis should not completely coincide with the author's. First, there is SiO_2 in the HM and FM modules – a value not used by G.S. Kurtov. Secondly, he does not consider the TiO_2 (TM) content. Third, our modules, on the contrary, do not use the CaO value.

The most suitable for clustering was the NKM – FM module diagram, on which 5 clusters and 3 separate compositions are distinguished.

Cluster I includes two sedimentary rock analyzes. However, they are certified as magnesian rocks – alkaline normo-titanium pseudosiallites. One may think that these are basic tuffoids, for example, andesitic ones. Cluster II includes seven sedimentary rock analyzes. They are certified as hyposiallites and are most likely quartz-feldspar meta-siltstones. Cluster III includes three "sedimentary rock" analyzes that are classified as alkaline myosilites. Possibly, these are mica metaaleurolites, although the K dominance over Na, the NKM value close to the lower boundary of superal-

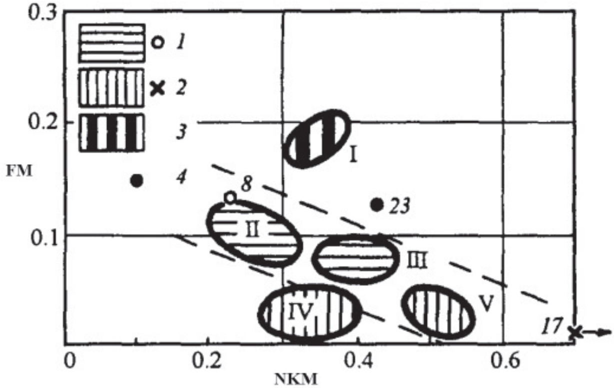

Fig. 83. Module diagram for metamorphic rocks
of the Proterozoic Buron Formation of the North Caucasus.
Compiled according to G. S. Kurtov, 1980 [152, p. 146–147].
Rocks: 1 – metasedimentary, 2 – acidic metatuffs, 3 – basic metatuffs,
4 – intermediate metatuffs (?)

Table 107

Chemical composition of metamorphic rocks of the Proterozoic Buron Formation of the North Caucasus.
Compiled according to G.S. Kurtov, 1980 [152, p. 146–147]

Oxides and modules	I	II	III	IV	V	8	17	23
	Sedimentary rocks			Acidic tuffs		Sedimentary rocks	Acidic tuffs	
	Alkaline pseudosiallite	Myosilite	Alkaline myosilite	Myosilite	Alkaline myosilite	Normosiallite	Alkalite	Alkaline pseudosilite
n	2	7	3	5	3			
SiO_2	58.34	69.11	72.38	75.21	78.00	63.55	76.78	67.70
TiO_2	0.81	0.51	0.25	0.12	0.09	0.70	0.16	0.52
Al_2O_3	18.89	15.17	13.00	13.67	11.87	18.97	11.21	14.01
Fe_2O_3	1.22	0.56	1.07	0.46	0.11	0.81	0.05	0.36
FeO	5.58	4.11	3.06	1.57	1.57	5.89	0.18	4.88
MnO	0.16	0.07	-	0.02	0.02	0.11	-	-
MgO	4.15	2.06	1.76	0.44	0.76	1.90	0.64	3.38
CaO	1.11	1.10	1.38	0.80	0.56	0.34	0.56	0.78
Na_2O	4.03	1.88	1.70	2.75	3.47	0.64	1.88	5.70
K_2O	2.62	2.17	3.37	1.69	2.69	3.76	6.50	0.35
LOI	2.70	3.08	1.99	3.29	0.74	3.52	0.58	1.90
Total	99.61	99.83	99.96	100.02	99.88	100.19	98.54	99.58
HM	0.46	0.30	0.24	0.21	0.18	0.42	0.15	0.29
FM	0.19	0.10	0.08	0.03	0.03	0.14	0.01	0.13
AM	0.32	0.22	0.18	0.18	0.15	0.30	0.15	0.21
TM	0.043	0.033	0.019	0.009	0.008	0.037	0.014	0.037
FerM	0.35	0.30	0.31	0.15	0.14	0.35	0.02	0.36
NKM	0.35	0.27	0.39	0.32	0.52	0.23	0.75	0.43
AlkM	1.50	0.90	0.50	1.60	1.30	0.20	0.30	16.30

kaline siallites, and low TM value may indicate that these are acidic tuffoids. Cluster IV includes 5 analyzes of “acidic tuffs”. They are certified as hypotitanic myosilites and, in contrast to the rocks in cluster III, are more sodium-rich. Cluster V combines three analyzes of “acidic tuffs”: these are alkaline hypotitanic normosilites with a high NKM (0.52), indicating an abundance of feldspars. They are related to the rocks of cluster IV, differing in both higher alkalinity and higher silica content.

Outside the clusters, normosiallites of sample 8 (probably silty shale) and two compositions of tuffs (samples 17 and 23) stay, of which the first is potassium alkalite, and the second is hyper-sodium pseudosilite. It is possible that both compositions are metasomatites.

So, the use of module diagrams yielded obviously not the worst result than with the help of discriminant functions: there were distinguished 5 chemotypes instead of two, in addition to acidic tuffs, the basic ones are also assumed, at least two varieties were identified among sedimentary rocks, indications of the possibility of allochemical metamorphism were obtained, etc.

Let us now consider some examples of diagnostics of tuffaceous metamorphites in strata of different ages.

Archean. In the Iyengra series of the Katarchean, the so-called “basic crystalline shales” are present on the Aldan shield. According to the diagnosis by L.B. Belonozhko and colleagues, these rocks, containing variable amounts of amphibole, pyroxene, biotite and garnet, are parametamorphites: “*The totality of <...> data indicates that according to most of <...> the petrochemical and geochemical parameters, the studied crystalline shales of the Iyengra series differ significantly from magmatic rocks of the gabbro-basalt series and are similar to clay-carbonate sedimentary rocks*” [15, p. 137]. However, lithochemical data (Table 108) raise doubts about this diagnosis.

Of the 9 analyzes (representing already *averaged* compositions), 3 are certified as siferlites, 3 are pseudohydrolysates, 2 are pseudosiallites, and one is pseudosilite. Of course, the high Mg content of the compositions itself is not diagnostic – this may be due to the presence of dolomite in the substrate. However, if it is easy to imagine dolomite marl with siallite (clay) or silite (silt, sandy) silicate admixture, then the presence of *alumina* admixture in it already seems unusual, not to mention *ferrous*. Therefore, assuming without reservation the primary sedimentary nature of the basic shales, it will be necessary to accept that not only magnesium, but also the iron in them was carbonate. Such an assumption, in any case, is not indisputable.

In addition, the module diagrams NKM – FM, FM – TM, TM – FerM show fairly clear correlations, which are more characteristic of petrogenic and pyrogenic than other sedimentary rocks. The TM value of the rocks is also generally increased, four analyzes out of nine are certified as hypertitanic. For the sake of fairness, we note that the increased TM value of carbonate rocks is known, and we have noted it more than once [295, p. 120, 130]. However, the TM values = 0.111–0.117 at TiO_2 contents up to 1.57% are not typical for any carbonate rocks. One can distinguish

Table 108

Chemical composition of the basic crystalline shales of the Iyengra series of the Katarchean on the Aldan Shield.

Compiled according to L.B. Belonozhko et al., 1979 [15, p. 122–123]

Oxides and modules	I	II	III	IV	5
	Pseudosiallite	Pseudohydrolisate			Alkaline pseudosiallite
n	2	2	2	2	
SiO_2	47.08	50.44	51.83	49.69	54.24
TiO_2	0.56	1.19	1.40	1.55	1.03
Al_2O_3	10.39	16.83	15.74	13.55	16.79
Fe_2O_3	2.18	2.22	2.92	4.89	2.73
FeO	3.37	8.07	10.09	7.49	6.50
MnO	0.12	0.12	0.13	0.19	0.10
MgO	14.10	6.87	6.75	9.06	4.69
CaO	18.30	7.68	6.21	8.81	7.07
Na_2O	0.93	2.96	2.40	2.59	3.76
K_2O	0.46	1.78	1.23	0.92	1.48
P_2O_5	0.08	0.27	0.17	0.15	0.24
LOI	2.21	0.36	0.46	0.37	0.23
Total	99.78	98.79	99.33	99.23	98.86
S	-	0.13	0.19	0.20	0.16
HM	0.35	0.56	0.58	0.56	0.50
FM	0.42	0.34	0.38	0.43	0.26
AM	0.22	0.33	0.30	0.27	0.31
TM	0.054	0.071	0.089	0.114	0.061
FerM	0.52	0.58	0.77	0.83	0.52
NKM	0.13	0.28	0.23	0.26	0.31
AlkM	2.00	1.70	2.00	2.80	2.50

4 clusters on the FM – TM module diagram. In the relatively low-titanium rocks of clusters I and II, an admixture of andesitic pyro- or volcanoclastics can be assumed, and in the more titanium rocks of clusters III and IV – basaltic one.

As a result, we believe that if clay-carbonate rocks were the substrate of the Iyengra “basic shales”, then the latter, most likely, were themselves the product of epigenesis of some basic or intermediate tuffoids (or contained a volcanoclastic terrigenous admixture).

The low-calcium Catarchean metamorphites are much easier to interpret. An example is the gneisses and shales of the Amedichin complex on the Aldan shield studied by L.M. Reutov [221], among which he singled out metaaleuropsammites, metatuffoaleurolite and metatuffs (Table 109). These lithotypes are well recognized on the module diagram (Fig. 84), moreover, the "metaaleuropsammites" (clusters Ia, Ib) form a single series with the "metatuffoaleurolites" (cluster II), which suggests the presence of pyrogenic

Table 109

Chemical composition of mica shales and gneiss of the Katarchean Amedichin complex on the Aldan shield.

Compiled according to L.M. Reutov, 1981 [221, p. 68–69]

Oxides and modules	Ia	Ib	II	III	4	7	14
	Metaaleuropsammites		Metatuffosiltstones (alkaline pseudosiallite)	Metatuffs (alkaline myosilite)	Metatuffosiltstone		Metatuff (myosilite)
	Supersilite	Myosilite			Alkaline pseudohydrolisate	Hyposiallite	
n	2	4	5	2			
SiO_2	87.80	74.44	64.40	14.91	55.10	68.10	78.34
TiO_2	0.17	0.54	0.63	0.60	1.97	0.79	0.23
Al_2O_3	6.35	12.31	15.81	11.69	13.75	14.25	6.35
Fe_2O_3	0.18	0.44	1.19	1.50	5.87	7.25	2.99
FeO	1.40	3.67	5.93	2.23	9.36	1.44	6.07
MnO	0.01	0.05	0.10	0.04	0.33	0.01	0.24
MgO	0.35	1.59	3.05	0.05	3.89	1.88	1.62
CaO	0.13	0.86	0.84	0.08	0.58	0.44	1.56
Na_2O	0.14	1.24	1.03	1.45	0.22	0.36	0.93
K_2O	2.30	3.14	4.44	6.24	6.99	3.56	1.36
P_2O_5	0.03	0.09	0.12	-	0.21	0.11	0.04
LOI	0.73	1.32	2.10	0.82	1.24	1.36	0.14
Total	99.59	99.69	99.64	99.66	99.51	99.55	99.87
HM	0.09	0.23	0.37	0.21	0.57	0.35	0.20
FM	0.02	0.08	0.16	0.05	0.35	0.16	0.14
AM	0.07	0.17	0.25	0.16	0.25	0.21	0.08
TM	0.026	0.044	0.040	0.051	0.143	0.055	0.036
FerM	0.24	0.32	0.44	0.31	0.99	0.58	1.41
NKM	0.38	0.35	0.35	0.66	0.52	0.28	0.36
AlkM	0.10	0.40	0.20	0.20	< 0.10	0.10	0.70

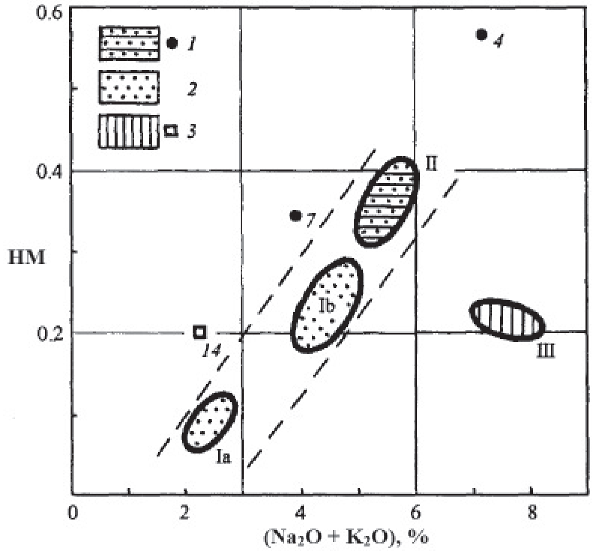

Fig. 84. Module diagram for mica shales and gneisses
of the Katarchean Amedichin complex on the Aldan shield.
Compiled according to L.M. Reutov, 1981 [221, p. 68–69].
1 – metatuffoaleurolites, 2 – metaaleuropsammites, 3 – metatuffs

impurities in them, and the "metatuffs" (cluster III) are sharply distinguished by their high total alkalinity. Abnormal compositions of sample 4 (garnet-biotite-feldspar-quartz shale) and sample 14 (garnet-sillimanite-quartz gneiss) suggest metasomatites in them.

Table 110 processed 29 analyzes of the Upper Archean metamorphic rocks of the Mikhailov KMA series [209]. Recognition of acidic metatuffoids, as well as metabasites, is not difficult here. Diagnostics of the iron-enriched shales substrate is more problematic, as well as diagnostics of individual alkaline and hydrolysate compositions, which can be products of allochemical metamorphism.

We note the following relationships between lithotypes and chemotypes (Fig. 85).

Quartz metaporphyres form cluster I and are certified as hypotitanic normosilites. It is the low TM value of these rocks that can serve as an indication of their nature (metaarcoses should have higher TM values [315]).

Metagreywackes (?) are certified as normo-titanium hyposiallites and form cluster II.

Amphibolites and amphibole shales, i.e., metabasites, form clusters IV, VI, VII and some compositions – samples 1, 2, 5. They are characterized by magnesium content (pseudohydrolysates), femicity (FM up to 0.48) and high TM value (TM up

Table 110

Chemical composition of the Upper Archean metamorphic rocks of the Mikhailov KMA series.
Compiled according to V. D. Polishchuk and V. I. Polishchuk, 1978 [209, p. 136–138]

Oxides and modules	I	II	III	IV	V	VI	VII	VIII
	Quartz porphyres (normosilite)	Gneisses and shales (normosiallite)	Crystalline shales (siferlite)	Amphibolites (pseudohydrolysate)				Crystalline shales (Ti pseudo-hydrolisate)
n	3	2	2	2	2	2	4	2
SiO_2	76.38	66.77	61.98	49.04	53.07	49.71	51.88	46.73
TiO_2	0.31	0.59	0.56	0.91	0.77	1.34	1.92	2.53
Al_2O_3	11.31	14.40	11.70	13.75	18.93	12.74	14.37	19.43
Fe_2O_3	0.97	3.49	7.10	4.08	11.89	4.32	5.36	10.44
FeO	1.85	4.45	9.07	9.30	9.53	10.82	12.73	10.15
MnO	0.06	0.10	0.03	0.12	0.08	0.11	0.12	0.09
MgO	1.38	2.24	2.85	7.72	1.94	6.31	3.94	3.31
CaO	1.61	2.14	1.40	8.43	0.90	9.66	4.69	1.83
Na_2O	0.92	1.43	0.98	2.63	0.23	1.86	0.76	0.89
K_2O	3.90	2.43	2.53	1.45	1.95	0.84	1.41	2.57
P_2O_5	0.05	0.08	0.09	0.07	0.11	0.09	0.31	0.29
SO_3	0.03	0.11	0.17	0.27	0.05	0.41	0.18	0.02
LOI	1.23	1.90	1.26	2.47	0.91	2.23	2.43	1.23
Total	100.00	100.13	99.72	100.24	100.36	100.44	100.10	99.51
HM	0.19	0.34	0.46	0.57	0.78	0.59	0.66	0.91
FM	0.05	0.15	0.31	0.43	0.44	0.43	0.42	0.51
AM	0.15	0.22	0.19	0.28	0.36	0.26	0.28	0.42
TM	0.027	0.041	0.047	0.066	0.041	0.105	0.134	0.130
FerM	0.25	0.54	1.32	0.92	1.09	1.08	1.12	0.94
NKM	0.43	0.27	0.30	0.30	0.11	0.21	0.15	0.18
AlkM	0.20	0.60	0.40	1.80	0.10	2.20	0.50	0.30

Table 110 (continue)

Oxides and modules	1	2	5	12	14	15	16	17	23	29
	Amphibolites			Crystalline shales (Ti hypohydrolisate)	Paragneisses			Crystalline shales		Ferruginous quartzite (pseudosiferlite)
	Ti pseudohydrolisate	Pseudohydrolisate	Pseudosiferlite		Alkalite	Ti alkalite	Alkaline Ti pseudohydrolisate	Normohydrolisate	Alkaline hypohydrolisate	
SiO_2	51.40	46.58	51.92	53.16	61.93	46.75	48.08	49.32	54.49	49.48
TiO_2	2.20	1.55	1.13	0.73	0.71	2.07	2.33	0.88	1.84	0.12
Al_2O_3	13.22	16.85	14.00	18.45	19.12	20.34	19.02	21.76	16.86	4.19
Fe_2O_3	6.18	3.07	2.74	2.49	1.12	3.69	7.21	13.12	2.08	8.86
FeO	10.30	15.36	9.08	10.11	3.88	10.82	10.72	11.08	10.83	13.50
MnO	0.20	0.29	0.08	0.13	0.04	0.13	0.12	0.11	0.05	0.44
MgO	3.92	3.78	6.02	2.60	0.88	1.73	1.76	1.40	2.86	3.75
CaO	7.26	7.48	9.95	0.73	0.57	1.14	2.20	0.80	0.79	7.19
Na_2O	2.40	3.00	1.20	0.55	1.00	0.70	2.40	0.01	0.02	0.66
K_2O	0.31	0.39	0.94	5.25	8.00	8.70	3.50	0.50	6.67	0.86
P_2O_5	0.27	0.17	0.06	0.06	0.06	0.30	0.34	0.03	0.32	0.30
SO_3	0.07	0.00	0.04	0.15	0.13	0.96	0.16	0.24	-	-
LOI	0.60	2.24	2.65	4.98	2.46	3.08	1.87	1.14	3.11	8.04
Total	98.33	100.76	99.81	99.39	99.90	100.41	99.71	100.39	99.92	97.39
HM	0.62	0.80	0.52	0.60	0.40	0.79	0.82	0.95	0.58	0.55
FM	0.40	0.48	0.34	0.29	0.09	0.35	0.41	0.52	0.29	0.53
AM	0.26	0.36	0.27	0.35	0.31	0.44	0.40	0.44	0.31	0.08
TM	0.166	0.092	0.081	0.040	0.037	0.102	0.123	0.040	0.109	0.029
FerM	1.08	1.02	0.79	0.66	0.25	0.65	0.85	1.07	0.69	5.29
NKM	0.20	0.20	0.15	0.31	0.47	0.46	0.31	0.02	0.40	0.36
AlkM	7.70	7.70	1.30	0.10	0.10	0.10	0.70	< 0.10	< 0.10	0.80

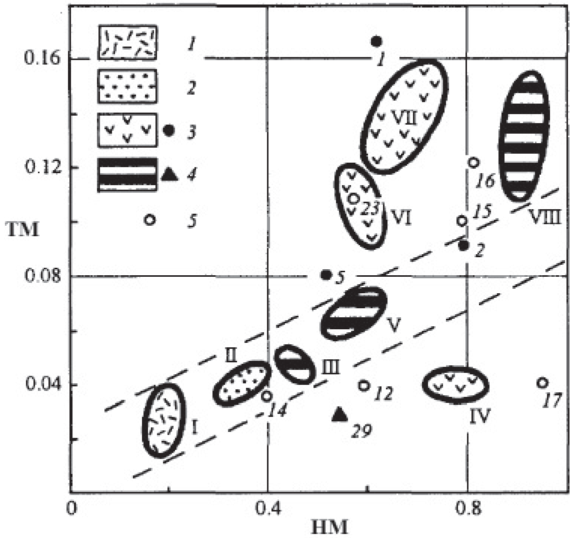

Fig. 85. Module diagram for the Upper Archean metamorphic rocks of the Mikhailov KMA series.
Compiled according to V.D. Polishchuk and V.I. Polishchuk, 1978 [209, p. 136–138].
1 – metaporphyres, 2 – metagreywackes (?), 3 – metabasites, 4 – ferruginous rocks, 5 – probably apopelitic rocks

to 0.166, TiO_2 up to 2.20 %). At least two groups of metabasites can be distinguished: relatively low-titanic (cluster IV) and high-titanic (clusters VI, VII). Possibly, this division corresponds to intrusive and effusive mafic rocks.

Clusters III, V and VIII represent ferruginous crystalline shales. This group is heterogeneous. Some rocks (clusters III, V) have low TM value and are apparently related to ferruginous quartzite, sample 29, while others (cluster VIII) are high-titanic, magnesian and clearly tend to the metabasites of cluster VII. They can be either some kind of "ore" differentiates of metabasites, or products of their metasomatic alteration.

Among individual compositions, hydrolysates and alkaline hydrolysates (samples 17, 23), including titanic ones (samples 16), and, apparently, related alkalites and titanium alkalites (samples 14, 15), are distinguished. Probably, these are the products of weathering crusts metamorphism with respect to acidic (relatively low-titanic) and basic (high-titanic) substrates.

Karelian. Of the seven analyzes of the Taimyr green shales of the Karelian age given by M.G. Ravich [219], one is certified as siferlite, and the other magnesian ones – pseudohydrolysates or pseudosiallites. The processing of these data on the TM – FerM plot shows a positive correlation, and on the FM – TM plot one can distinguish relatively titanium compositions (two clusters) and three separate low-titanium compositions with a strong FM dispersion. Thus, firstly, it is clear that we are dealing with metabasites. Secondly, since a strong dispersion of compositions is completely not characteristic of normal magmatic series, one can assume that here we have both meta-effusive and metapyroclastic rocks.

As one can see from our experience in studying the volcanogenic metabasite sequence of the Riphean-Vendian of the Polar Urals (Bedamel Group), high TM values are characteristic of pyroclastites. M.G. Ravich came to the same conclusion (using other means): compositions characterized by an increased SiO_2content and strong scatter of other parameters (for example, MgO), he interpreted as metatuffites and metatuffs of andesite-basalts [219, p. 134].

Among the deposits of the Udokan Group of Karelids in the west of the Vitimo-Aldan Shield, the metapsammites of the Upper Chitkanda formation of the Chinea subseries are noteworthy. They are distinguished by increased sodium content (on average 4.88 % Na_2O according to 34 analyzes). This allowed A.V. Sochava to assume that the primary sediments were formed "*due to the redeposition of acidic effusives of the sodium series*" [246, p. 28]. Indeed, the rocks are certified as super alkaline, hypofemic and hypotitanic normosilites. However, this diagnosis can be strengthened if the *metapelites* of this formation are also considered. The average values of the modules HM, FM, TM and NKM for 26 analyzes are obtained, respectively, 0.41, 0.16, 0.043, and 0.44. Thus, these are superalkaline normosiallites, and their total alkalinity is so high (7.67 %) that it approaches the alkalite boundary. *It is obvious that such feldspar rocks cannot in any way be ordinary sedimentary metapelites and, most likely, are metatuffoids.*

Table 111 gives the compositions of metasedimentary and metavolcanic rocks of the Toming series on the Kola Peninsula, consisting of five strata (lower sedimentary, subsequent volcanic-sedimentary and volcanic) [117]. The module diagram shows a wide variety of compositions, which are grouped into clear clusters. The anomalous compositions outside the clusters are also quite informative (Fig. 86).

Cluster I is the least homogeneous; responds to hypertitanic and hyperfemic pseudohydrolysates. It includes four compositions of metasedimentary and two of metavolcanic rocks[4]. In this case, such averaging cannot raise objections because the high-titanium and magnesium contents of the "metasedimentary" rocks clearly indicate that we are dealing with basic metatuffoids. The same cluster also includes a composition with increased carbonate content (in the original – “greywacke metapsam-

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[4] Both here and in the examples on p. 342—344, the data for which are taken from the book of Kola geologists [117], most of the figures represent *the average* of several analyzes.

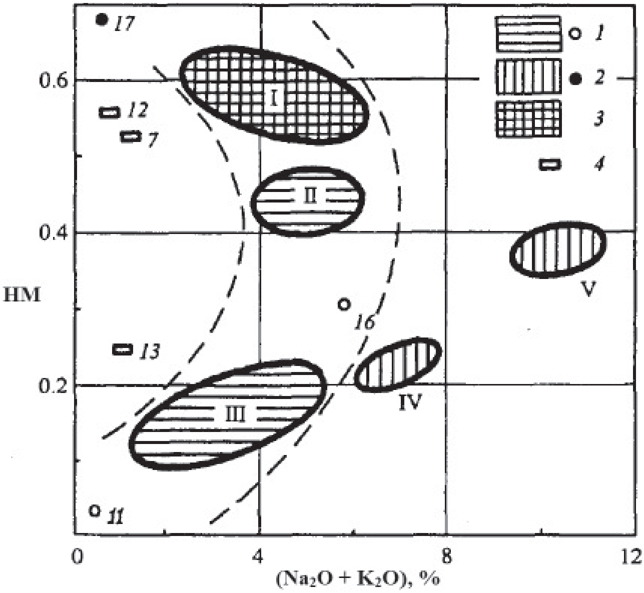

Fig. 86. Module diagram for metamorphic rocks of the Toming series of Karelids on the Kola Peninsula.
Compiled according to the data of V.G. Zagorodny et al., 1982 [117].
1 – metasedimentary rocks, 2 – acidic and alkaline metavolcanics, 3 – mixture of lithotypes, 4 – metacarbonate rocks

mites with a carbonate admixture," $CO_2 = 7.28$ %). Dolomite compositions are also located nearby (samples 7, 12). All this shows the proximity of carbonate-free rocks and dolomite, which is due to their genetic relationship with basic source material rich in Ca and Mg. Cluster II corresponds to normofemic and normoalkaline hypertitanic pseudosiallites. Obviously, these are also metatuffoids, but they contain less volcanogenic material than in the rocks of cluster I. Cluster III is normal alkaline normosilites, among which there are sulfidized black shales (S = 3.52 %). Obviously, these are silica and clay-silica sedimentary rocks (phtanites, etc.). Cluster IV is represented by metarhyolites – these are hyperalkaline normosilites. In this case, a high amount of alkalis (6.98 %) is diagnostic, which makes it possible to distinguish these rocks from similar in metaarcoses composition in the absence of reliable petrographic signs [315]. Cluster V is represented by trachytic metaporphyres – these are alkalites, $Na_2O + K_2O = 10.47$ %. Compared to metarhyolites, they have significantly higher alumina content (AM = 0.28 versus 0.16) and femicity (FM = 0.12 versus 0.07), which is obviously a simple consequence of the lower SiO_2 content.

Outside the clusters, there are essentially carbonate rocks (samples 7, 12, 13), silicites with a small clay admixture (sample 11), and a highly specific hypertitanium pseudohydrolysate (sample 17) – "picrite metaporphyrite". The composition of the "greywacke metapsammites", sample 16, is also separated on the plot. They differ

Table 111

Average chemical composition of metamorphic rocks of the Toming Group of Karelids on the Kola Peninsula.

Compiled according to the data of V.G. Zagorodny et al., 1982 [117]

Oxides and modules	I	II	III	IV	V	7	11	12	13	16	17
	Pseudo-hydrolisate	Alkaline pseudosiallite	Normo-silite	Alkalite-myosilite	Alkalite	Carbo-natolite	Hypersilite	Carbonatolite		Alkaline hyposiallite	Pseudo-hydrolisate
	63	12	11	8	4	4	7	3	1	2	1
	6	4	3	2	2						
SiO_2	49.14	58.84	79.58	72.46	60.93	19.95	96.48	8.16	29.98	66.77	42.41
TiO_2	1.84	1.37	0.39	0.48	0.27	0.03	0.05	0.24	0.58	0.56	2.35
Al_2O_3	14.50	14.77	7.93	11.34	16.80	4.02	0.27	1.62	4.04	13.18	9.34
Fe_2O_3	3.05	2.97	1.99	1.32	3.14	1.13	0.68	0.33	0.45	1.22	1.99
FeO	8.57	6.26	2.00	3.24	2.92	4.83	1.94	2.26	2.13	5.45	14.98
MnO	0.14	0.31	0.02	0.06	0.11	0.46	0.01	0.11	0.21	0.08	0.22
MgO	6.20	3.43	0.80	0.75	1.25	13.21	0.06	16.60	2.25	2.61	14.80
CaO	5.55	1.57	0.45	1.19	1.30	21.86	0.10	28.00	31.70	2.22	8.29
Na_2O	2.71	3.20	1.93	3.05	5.99	0.49	0,01	0.45	0.06	3.90	0.47
K_2O	1.29	1.96	1.50	3.93	4.48	0.74	0,02	0.26	0.95	1.90	0.17
P_2O_5	0.19	0.20	0.07	0.07	-	0.25	0,01	0.07	0.02	0.14	0.21
H_2O	4.36	3.80	1.74	1.10	1.44	1.44	0.30	0.81	2.04	1.54	4.38
CO_2	1.93	0.60	0.17	0.71	1.22	31.66	0.14	40.45	25.48	0.86	0.15
Total	99.47	99.28	98.57	99.70	99.85	100.07	100.07	99.36	99.89	100.43	99.76
HM	0.57	0.44	0.15	0.23	0.38	0.52	0.03	0.56	0.25	0.31	0.68
FM	0.36	0.22	0.06	0.07	0.12	0.96	0.03	2.35	0.16	0.14	0.75
AM	0.30	0.25	0.10	0.16	0.28	0.20	0.00	0.20	0.13	0.20	0.22
TM	0.127	0.092	0.049	0.042	0.016	0.007	0.174	0.148	0.144	0.042	0.252
FerM	0.72	0.59	0.48	0.39	0.36	1.59	8.30	1.45	0.60	0.49	1.47
NKM	0.28	0.35	0.43	0.61	0.62	0.31	0.11	0.44	0.25	0.44	0.07
AlkM	2.10	1.60	1.30	0.80	1.30	0.70	0.50	1.70	0.10	2.10	2.80

from the tuffoids of cluster II by the absence of volcanogenic admixtures (therefore, they are normal-titanium and normal-iron), and from the clay silicites of cluster III, apparently, by a lower content of quartz. They are characterized by alkalinity (5.8 %) and sodium content (AlkM = 2.05), which is quite typical for average greywackes.

Table 112 and in Fig. 87 shows the compositions of the metasedimentary rocks of the Strelna series of the Karelians of the Kola Peninsula, in Purnach, Kukshin, and Seydorechensk formations (from bottom to top) [117]. These data make it possible to distinguish five "lithostratigraphic" clusters (within the formations) and one mixed.

Cluster I corresponds to normal alkaline hypersilites of the Seydorechensk formation. These are quartz metapsammites – quartzites. Cluster II – Seydorechensk myosilites-metagreywackes. The rocks are normal alkaline, hyperferrous, and hypersodium, which is generally quite typical for many greywackes. Cluster III corresponds to magnesian rocks – hypersodium and hyperferrous pseudosiallites (HM 0.41, FerM 0.98, MgO 11.6 %). These are Seydorechensk metatuffs. Due to their high magnesiality, they also turn out to be hyperfemic (FM = 0.43). Cluster IV corresponds to the Seydorechensk alkaline supersiallites, which are called metapelites by the authors of the primary materials. However, the hyper-iron content of these rocks shows that they can also be metatuffoids. Cluster V is mixed; it contains one compo-

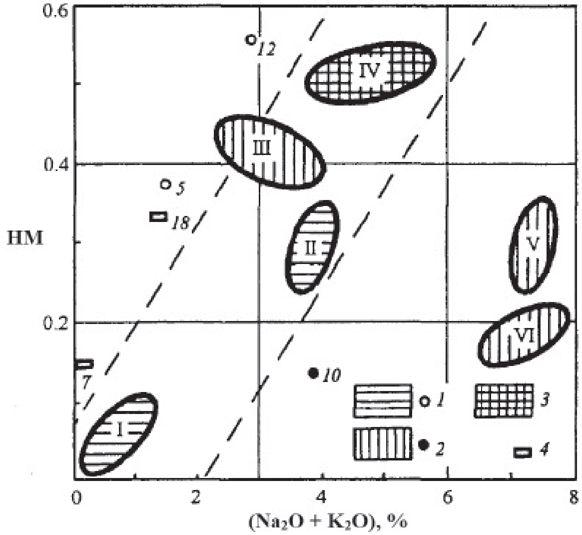

Fig. 87. Module diagram for metamorphic rocks of the Strelna series of Karelids, Kola Peninsula.

Compiled according to V. G. Zagorodny et al., 1982 [117].

1 – normal metasedimentary rocks, 2 – metatuffoids, 3 – mixture of lithotypes, 4 – carbonatolites

Table 112

Average chemical composition of metamorphic rocks of the Strelna series of the Karelians of the Kola Peninsula.

Compiled according to V. G. Zagorodny et al., 1982 [117, p. 36–38].

Oxides and modules	I	II	III	IV	V	VI	5	7	10	12	18
	Hypersilite	Myosilite	Pseudo-siferlite	Super-siallite	Myosilite	Alkaline normosilite	Pseudo-siallite	Carbo-natolite	Normo-silite	Hypohydro-lisate	Carbo-natolite
m	11	8	6	12	14	8	2	1	4	2	3
n	3	2	2	3	3	3					
SiO_2	89.88	70.63	52.09	58.65	66.97	72.54	59.07	27.42	82.03	57.23	22.35
TiO_2	0.11	0.54	0.62	0.87	0.48	0.18	0.55	0.04	0.21	0.85	0.17
Al_2O_3	2.34	11.51	10.34	16.65	13.30	11.00	13.45	2.25	8.58	16.93	3.09
Fe_2O_3	0.58	3.15	2.82	3.60	1.85	0.75	4.01	0.30	0.71	1.60	0.78
FeO	1.51	5.08	7.62	8.39	3.44	2.14	4.10	1.24	1.67	12.50	3.04
MnO	0.06	0.10	0.18	0.12	0.05	0.05	0.13	0.23	0.01	0.12	0.36
MgO	0.53	1.95	11.58	2.16	1.57	0.89	6.31	1.48	0.43	2.62	6.57
CaO	1.86	0.86	7.02	0.55	2.12	2.55	4.30	36.99	0.49	1.61	30.42
Na_2O	0.38	2.94	2.55	1.95	4.90	3.89	1.41	0.08	1.86	1.02	0.34
K_2O	0.37	0.94	0.63	2.80	2.40	3.35	0.08	0.03	2.01	1.85	1.00
P_2O_5	0.03	0.10	0.09	0.12	0.09	0.07	0.08	0.03	0.04	0.10	0.06
H_2O^+	0.80	2.22	3.31	3.46	1.01	0.33	4.42	0.85	1.06	3.16	0.56
CO_2	1.35	0.09	0.68	0.05	1.18	1.58	0.57	28.78	0.02	0.01	29.98
LOI	0.79	0.44	0.21	3.79	0.29	0.73	0.58	0.15	0.72	0.15	0.85
Total	100.59	100.55	99.74	103.16	99.65	100.05	99.06	99.87	99.84	99.75	99.57
HM	0.05	0.29	0.41	0.51	0.29	0.19	0.38	0.15	0.14	0.56	0.33
FM	0.03	0.14	0.42	0.24	0.10	0.05	0.24	0.11	0.03	0.29	0.46
AM	0.03	0.16	0.20	0.28	0.20	0.15	0.23	0.08	0.10	0.30	0.14
TM	0.049	0.046	0.060	0.052	0.036	0.016	0.041	0.018	0.024	0.050	0.055
FerM	0.88	0.69	0.97	0.69	0.39	0.26	0.59	0.77	0.27	0.80	1.28
NKM	0.32	0.34	0.31	0.29	0.55	0.66	0.11	0.05	0.45	0.17	0.43
AlkM	1.00	3.10	4.00	0.70	2.00	1.20	17.60	2.70	0.90	0.60	0.30

sition from each formation. Nevertheless, the rocks are of the same type and, on average, are certified as hyperalkaline supersodium supersilites with high total alkalinity (7.30 %), approaching the alkalite boundary. The authors of the materials interpret them as "greywacke and subgreywacke metapsammites", but, rather, they are still metatuffoids of albitophyres. Cluster VI is in many ways similar to cluster V, but its compositions are noticeably more acidic – these are hyperalkaline normosilites of the Kukshin formation. The version about the possible presence of acidic metatuffoids among them is even more probable, especially since at least one composition out of three is certified by the authors themselves as “metatuffites; Monchegorsk region". In any case, low TM value (0.016) is a feature more characteristic of acidic metatuffs than “arkose metapsammites and metaaleurolites”. However, there is still no complete confidence in our diagnosis (see [315]).

Outside the clusters are, firstly, carbonate rocks (samples 7, 18, of which the first is low-alkaline), secondly, high-Mg metagreywackes of the Kukshin formation (sample 5) and, thirdly, “arkose metapsammites” (sample 10), which have a much lower alkalinity than rocks in clusters V and VI. Thus, the version about the essentially acidic metatuffoid nature of the latter is even more strengthened. Finally, the anomalous composition of “metapelite” (sample 12) is also isolated – it is Fe-hypohydrolysate (HM 0.56, FerM 0.80). It can be assumed that this is a metamorphosed product of the ancient weathering crust.

Thus, the materials on the Karelians of the Kola Peninsula show that, in the absence of clear signs of allochemical metamorphism, the diagnosis of various compositional metatuffoids is no more difficult than that of unmetamorphosed rocks. However, as for the latter, there is a problem of distinguishing pyrogenic (metatuffoid) from petrogenic (metagreywacke) rocks, which usually requires additional petrographic data.

Riphean. The Riphean shales of the Mama series are interpreted by D.A. Velikoslavinsky as “metapelites” [47]. However, an examination of the analytical data (29 analyzes) shows the heterogeneity of these rocks, allowing the original population to be broken down into nine clusters and seven separate compositions. The basic metatuffoids are likely to include magnesian rocks, which are characterized by increased TM value, femicity, or both together – in total, almost half of all compositions.

Only 11 compositions can be attributed to normal metapelites-siallites, the remaining 18 are certified as alkalites (2), hydrolysates (4) and pseudosiallites, pseudohydrolysates (12). This means that, in addition to normal aluminosilicate sedimentary rocks, among the “metapelites” of the Mama series, there are undoubtedly rocks of increased hydrolysability – weathering crusts’ derivatives, as well as, very likely, rocks of volcanogenic-sedimentary. In particular, attention is drawn to the correlation between increased TM and magnesiality: of the 7 super- and hypertitanium compositions (TM > 0.065), 6 are pseudosiallites. This combination is not accidental – it indicates an admixture of basic pyro- or volcanoclastics. In other words, there may well be major metatuffoids among these "metapelites". As for the hydrolysates, their totality is also heterogeneous: among them there are ferruginous (with staurolite), alumina (with kyanite), and alkaline (with abundant muscovite). One of the alkalites, which is distinguished by a contrasting potassium composition, clearly is close to the latter.

Table 113 shows the two lithotypes' *average* compositions of the Riphean shales, the Anangra formation, the Patom Upland: "metapelites" (cluster I) and "tuff siltstones" (cluster II) [158][5]. In terms of iron content, alkalinity and femicity, these rocks almost do not differ, however, there are still differences in composition: a) metapelites are more hydrolysate (HM 0.37–0.43 versus 0.33–0.37 in tuffaceous siltstones); b) metapelites are distinguished by characteristic potassium content (AlkM value in them is less than one – 0.17–0.63); in all tuffaceous siltstones, on the contrary, AlkM > 1, with two average com-

Table 113

Chemical composition of the Riphean shales
of the Anangrian formation of the Patom Upland.
Compiled according to B.V. Petrov, 1974 [158, p. 142–143]

Oxides and modules	I	II	1
	Metapelites (normosiallite)	Tuff siltstones	Metapelite
		Pseudosiallites	
n	3	4	
SiO_2	63.99	62.00	62.89
TiO_2	1.13	0.93	0.88
Al_2O_3	17.39	13.85	17.54
$FeO + Fe_2O_3$	8.36	6.96	4.60
MnO	0.10	0.16	0.07
MgO	1.59	4.19	3.24
CaO	0.46	5.66	0.40
Na_2O	0.67	2.27	1.60
K_2O	3.43	0.77	2.52
LOI	3.10	3.07	6.14
Total	100.22	99.86	99.88
HM	0.42	0.35	0.37
FM	0.16	0.18	0.12
AM	0.27	0.22	0.28
TM	0.065	0.067	0.050
FerM	0.46	0.48	0.25
NKM	0.24	0.22	0.23
AlkM	0.20	2.90	0.60

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[5] The characteristic feature of average compositions is observed in the module diagrams: very compact, small clusters. The fact is that the natural variance was greatly reduced during the first averaging.

positions hypersodium, AlkM equal to 8 and 17; c) tuffaceous siltstones are distinctly more magnesian, as a result of which they are all certified as pseudosiallites. A notable feature of both rocks is their low alkali content; it is possible that this is a sign of the primary montmorillonite composition of clay matter.

According to the B. Butler's description [323], the Riphean mica shales of the Moines series in Scotland consist of micas, quartz and feldspars with an admixture of epidote, ore, carbonate, garnet, and accessory apatite. He distinguishes three petrotypes among them: 1) mica shales associated with metapsammites; 2) mica shales in banded rocks composition (similar to injection gneisses), which are interpreted as alternation of thin sedimentation layers of metapsammitic and metapelite material, as well as interlayers in garnet bearing shales of the third type; 3) garnet-bearing mica shales, thin-banded; some of them are associated with metapsammites, others containing 0.20–0.30 % dispersed graphite, – with metapelites. Both are treated as metagreywacke. As one can see, this typification uses two features: the petrographic association of mica shales and the presence or absence of garnet.

If we plot the points of 19 analyzes on the module diagram (Fig. 88, Table 114) and neglect a small "noise" (hitting a cluster of one "extraneous" point), then the mica shale types indicated by B. Butler form distinct clusters and, therefore, admit meaningful lithological interpretation.

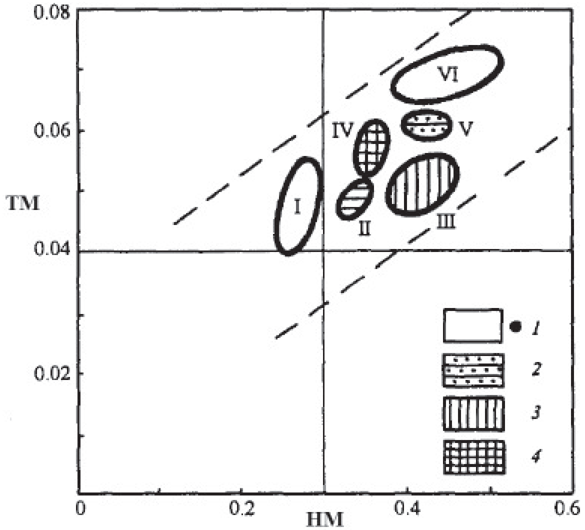

Fig. 88. Module diagram for Riphean mica shales of the Moines Series, Scotland.
Compiled according to B. Butler [323, p. 172].
1 – metasedimentary rocks, 2 – metatufoaleurolites, 3 – metatuffoids, 4 – a mixture of lithotypes

Table 114

Average chemical composition of the Riphean mica shales
of the Moines series, Scotland.
Compiled according to B. Butler, 1965 [323, p. 172]

Oxides and modules	I	II	III	IV	V	VI
	Alkaline myosilite	Alkaline normosiallite				
n	2	2	5	2	2	6
SiO_2	70.13	65.68	60.72	64.84	60.69	59.89
TiO_2	0.70	0.77	0.95	0.94	1.09	1.25
Al_2O_3	14.49	15.58	18.36	16.23	17.64	18.02
Fe_2O_3	2.39	1.99	1.18	1.03	1.04	1.39
FeO	1.59	3.63	5.40	5.05	5.89	5.51
MnO	0.02	0.06	0.09	0.08	0.09	0.12
MgO	0.85	2.12	2.04	1.79	2.19	2.02
CaO	0.70	1.10	2.86	2.12	3.04	1.73
Na_2O	0.79	1.85	2.88	2.30	2.65	2.25
K_2O	5.79	5.04	3.67	3.93	3.91	5.13
P_2O_5	0.10	0.25	0.30	0.17	0.28	0.19
H_2O^+	2.14	2.03	1.64	1.54	1.74	2.24
CO_2	0.38	0.03	0.06	0.07	0.12	0.54
LOI	0.06	0.15	0.28	0.06	0.05	0.07
Total	100.13	100.28	100.43	100.15	100.42	100.35
HM	0.27	0.34	0.43	0.36	0.42	0.44
FM	0.07	0.12	0.14	0.12	0.15	0.15
AM	0.21	0.24	0.30	0.25	0.29	0.30
TM	0.048	0.049	0.052	0.058	0.062	0.069
FerM	0.26	0.35	0.35	0.36	0.37	0.36
NKM	0.45	0.44	0.36	0.38	0.37	0.41
AlkM	0.10	0.40	0.80	0.60	0.70	0.40

Clusters I–II and VI correspond to the first petrotype; cluster V – to the second one and cluster III – to the third one. And only cluster IV turns out to be mixed (first + third petrotypes).

The compositions of the first shale type are characterized by high alkalinity: NKM > 0.40 (which means that the ratio of "feldspars/mica" is increased in them). Leaving aside the well-individualized shales of the cluster V, one can see that the garnet-bearing shales are the least alkaline, which allows us to agree with their author's interpretation as metagreywacke. Let us pay attention to the rocks composition in cluster VI: the strange combination of increased TM and NKM has no simple explanation in terms of sedimentogenesis. For example, it can be assumed that these are metapsammites, for which increased TM value and the presence of feldspar are natural. But this is contradicted by a rather high HM – such values do not exist in psammites. Is it possible to admit the presence of an *alkaline titanium pyroclastics* admixture in the rocks? In particular, the most titanium composition (TiO_2 1.40%, TM 0.071) turns out to be alkalite (8% alkalis). We have already seen (see Section 6.6) that, as a rule, alkalites do not belong to the number of normal sedimentary rocks.

Brief conclusions

1. Tuffoids, i.e., sedimentary rocks with a noticeable pyrogenic admixture, constitute a significant portion of the sedimentary shell, but due to the diagnostics difficulties, this portion is still underestimated. This situation should change with the widespread use of tuffoids' lithochemical diagnostics.

2. The eolian and water differentiation processes of volcanic ash before their burial in sediments can strongly change the pyroclastics composition in comparison with the corresponding effusive rocks composition. However, knowledge of such differentiation patterns (for example, selective accumulation of alkalis) helps a successful diagnosis.

3. During burial of ashes in sediments, and especially in diagenesis, pyroclastics can undergo strong allochemical changes – claying, silicification, zeolitization, carbonatization. Despite this, the very nature of such changes can serve as a diagnostic sign if it is possible to build a genetic series from the original (least altered) to more altered rocks.

4. In addition to pyroclastic rocks, sedimentary rocks (most often in silica and carbonate rocks) may contain an exhalative impurity. Its best indicators are geochemical anomalies of manganese, as well as abnormally high FerM and TM modules values.

5. Tuffoids of basic composition are easily and reliably diagnosed by signs of increased magnesium content (MgO), iron content (FerM), titanium value (TM and TiO_2) and femicity (FM), which are often correlated with each other. An additional sign can be an increased sodium content (AlkM).

6. Acid tuffoids are recognized by their increased total alkalinity (often up to alkalites), by a sharply reduced TM value, and also sometimes by contrasting AlkM value (very low or, on the contrary, very high).

7. Recognition of tuffoids with andesitic pyroclastics is one of the most difficult cases of diagnostics, especially if it is buried in thick terrigenous formations of the flysch type. Here, the problem of distinguishing pyrogenic rocks from petrogenic ones (volcanoclastic greywackes and first cycle rock arkoses) is urgent. Usually, lithochemical signs alone are not enough, and additional lithological information is required for a successful diagnosis.

8. Diagnostics of metatuffoids in metamorphic strata prior to the Cambrian is in principle not more difficult than diagnostics of unmetamorphosed tuffoids, but it can be complicated by the processes of allochemical metamorphism.

CHAPTER 8

GEOLOGICAL EVOLUTION OF HYDROLYSATES

In the last two decades, researchers have sharply increased their interest in reconstructing the ancient hypergenesis conditions based on the "material evidence" of this process – ancient metamorphosed weathering crusts; and the problem of recognizing such objects, i.e., distinguishing them from metasomatites is very acute (we will consider it in the next chapter). But if certain metahydrolysates are indeed products of ancient WCrs, then this makes it possible to reconstruct the compositional features of the ancient atmosphere and hydrosphere of the Earth.

Studies of Siberian lithologists [112, 171, 172, 242] were devoted to this problem, and later –numerous works of Ukrainian geologists who studied Late Archean and Karelian ferrous quartzites [99, 148, 175] and the most ancient weathering crusts on the Ukrainian crystalline shield and in the basement East European platform [95–97,149, 232, 233]. The appearance of large generalizations by Yu.P. Kazansky [121], V.K. Golovenok [82], A.I. Pak [200], E.T. Bobrov and I.G. Shchipakina [21] was of great importance.

According to V.D. Matz et al. [171], on the territory of the Russian and Siberian platforms, five main, well-comparable interregional horizons of Precambrian weathering crusts have been distinguished[1].

1. Epiontarian – pre-early Karelian 2.8–2.7 billion years.
2. Epidominion-reefian – pre-Witwatersrand 2.6–2.5 billion years.
3. **Epikarelian – pre-Akitcanian** 2.0–1.9 billion years.
4. Epiburzianian – pre-Urmatinian 1.4–1.3 billion years.
5. **Late Riphean-Vendian** 0.70–0.66 billion years.

The first and second horizons are substantially sericite everywhere, the third and fourth are sericite and hydromica-kaolinite, and the fifth horizon is dominated by clay minerals. At the same time, "*the most ancient, accurately diagnosed kaolin and hydromica were found in the third horizon of the*

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[1] We gave the name and geochronological binding of the horizons in accordance with the terminology of L.I. Salop [234], and not as in the original source.

Anabar massif <...> and the Near-Sayan area. The primary nature of sericite products has not been precisely established; however, most researchers associate their formation with the metamorphism of hydromica-kaolinite matters <... >" [171, p. 169].

The third and fifth horizons recording geological events of a global scale, are best traced; they "*are confined to critical epochs in tectonic development. The beginning of their formation coincides with the beginning of the orogenic epochs. But only at the end of geotectonic cycles, at the moment of a change in the sign of tectonic movements, the most favorable conditions are created for the development of strong crust. This is facilitated by the general leveling of the territories <...> The weathering crusts formed on the boundary of geotectonic cycles are the most widespread, are distinguished by the greatest thickness and deep transformation of the substrate rocks <...> Weathering crusts of the final (orogenic) stage of the previous cycle and are overlapped by the volcanogenic-terrigenous (in mobile zones) or terrigenous strata of the initial stage of the next cycle*" [171, p. 166–169].

Despite significant advances in the understanding of ancient weathering crusts, we consider that the use of the lithochemistry arsenal may serve to better understand the evolution of weathering crusts in the history of the Earth.

8.1. Toward a discussion of ancient weathering crusts: uniformitarianism versus evolutionism

This discussion developed based on practical needs – forecasting the bauxite content of ancient strata. It is known that all the main bauxite deposits, firstly, are relatively young – post-Silurian, and secondly, they are formations genetically associated with weathering crusts of the laterite type. Modern and Quaternary laterites of Africa or India are a visual model of such crusts [236]. The absence of older bauxites can have two explanations.

1. Bauxites (and, consequently, laterite weathering crusts) were also formed in the deep Precambrian but were destroyed by the processes of erosion and/or subsequent allochemical metamorphism; the extreme uniformitarians of the Acad. A. V. Sidorenko's school took such a position.

2. There were no pre-Devonian bauxites (and, consequently, laterite WCr) due to a fundamentally different style of ancient weathering, radically different from the post-Silurian one. The finds of high-alumina formations in ancient metamorphic strata (formally even corresponding to bauxites) should be associated not with the processes of ancient hypergenesis, but with hydrothermal-metasomatic processes.

Thus, in the discussion of the ancient WCr, the struggle between two currents in Russian geology was clearly reflected: uniformitarianism (which was bashfully called *actualism*) and evolutionism. Uniformitarian evidences were based on *similarities* between ancient and young sedimentary rocks, and evolutionist evidences were based on their *differences*. One should note that finding differences in seemingly similar objects is usually much more difficult than simple analogies[2].

The most complete narrative of the ideological search's history of Soviet geologists in the ancient WCr problem is given in the book by A.D. Savko and A.D. Dodatko [233]. They note that many geologists, including A.D. Dodatko, B.M. Mikhailov (1975), Yu.P. Kazansky [121], S.A. Karpov and I.K. Kashik [127, 128], V.I. Sirotin (1977), in their works indicated a clear change in the weathering products in the geological column or focused on the data obtained by other methods on changes in hypergenesis environments. For example, the estimates of the composition of the Earth's ancient atmospheres made by Yu. P. Kazansky by analyzing gas-liquid inclusions in ancient silica rocks are widely known.

At the same time, other major researchers were close to uniformism, which is especially characteristic of Acad. A. V. Sidorenko's school. Thus, V.A. Tenyakov (1980) argued that both the weathering processes themselves and the weathering crust generated by them throughout the history of the Earth were basically of the same type. More cautious are the conclusions by D.G. Sapozhnikov et al. (1981), who also believed that the weathering nature did not change significantly in different epochs but limited their conclusion only to the Fanerosoan piece of the Earth's history.

The uniformitarian concept asserted that the upper (bauxite-bearing) horizons of the Precambrian weathering crusts fully corresponded to the Phanerozoic laterites, but were cut off by subsequent erosion, so that only the roots remained – the lower hydromica horizons of the ancient WCr. B.M. Mikhailov wittily criticized this idea: "*It must be admitted that a remarkable feature of the Precambrian was the presence in those days of some processes that arose during the formation of a strong weathering crust, composed of intensively processed rocks (kaolins, laterites, ocher, etc.) and immediately led to cutting off its upper part strictly to the hydromica zone. It is strange that these processes disappeared precisely at the beginning of the Devonian, that is, just at the time when the accumulation of industrially ore-bearing hypergenic formations that arose under conditions of surface hypergenesis, began in the geological section <...>*" [181, p. 63].

There were also attempts to identify the sericite shales zone with the former *kaolinite* zones of the ancient WCr. Siberian geologists V.D. Mats and Yu.G. Popov noted two features of the sericite shale zone: a) primary dark-colored minerals, plagioclases and potassium feldspar are absent in the sericite shales of metamorphosed WCr (*not all – Ya. Yu., M. K.*); in the

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[2] This idea was expressed in V. I. Vernadsky's letters.

Phanerozoic WCr, such a depth of weathering is characteristic only for the kaolinite zone; b) a significant loss of primary quartz and corrosion of the remaining grains in these shales, which, in young WCrs, is again typical of hydromica-kaolinite and kaolinite zones. As a result, they concluded: "*All this gives us the right to compare the sericite shales zone of Precambrian weathering crusts with the kaolinite zone of Phanerozoic crust*" [172, p. 106].

However, the tension of this conclusion is obvious. If there was kaolinite in the sericite shales, then under the conditions of isochemical metamorphism we should have direct evidence of its former presence – high-alumina minerals such as pyrophyllite, kyanite (andalusite, sillimanite), chloritoid, staurolite. Otherwise, we need to admit the obligatory addition of potassium, which has transformed kaolinite into mica.

Based on their data on the weathering crusts by the basement of the East European Platform, A.D. Savko and A.D. Dodatko distinguish three stages of geological history with specific features of weathering: Archean–Early Proterozoic, Late Proterozoic–Early Devonian, Middle Devonian–Holocenian [233, p. 206]. This periodization is not the only possible one. For example, Yu. P. Kazansky has not three periods, but four, and their boundaries are somewhat different: 1) Archean–Early Proterozoic, 2) Middle and Late Proterozoic; 3) early Paleozoic; 4) Devonian–modern [121, p. 57].

Regarding the Katarchean, A.D. Savko and A.D. Dodatko emphasize the absence of documented weathering crusts: "*In the Early Archean, no residual metamorphosed crusts have been found, and weathering can only be judged by correlative sediments (Savko, Shchegolev, 1979).*" Concerning Karelian, then "*the early Proterozoic crust, currently metamorphosed and transformed into shales of different composition, arose in the absence of oxygen in the atmosphere. The acidic medium of hypergenesis caused an unusual (for modern conditions) migration of the main petrogenic elements and ensured an intense removal of iron outside the eluvium*". In general, at the Archean–Karelian stage, weathering had the character of acid leaching with the removal of all components from the substrate: "*The lower part of the crust, into which less aggressive waters penetrated, that is, those that consumed most of the reagents, were represented by clay minerals. The intensive removal of the least mobile aluminum and ferric iron is evidenced by the presence of metasedimentary ferrous and high-alumina rocks in the Archean sections*" [233, p. 206–210].

At the Riphean–Early Devonian stage, the same type, predominantly hydromica-kaolinite, WCrs were formed everywhere. "*A characteristic feature of these weathering crusts formation was the removal of silica, alumina, alkalis and alkaline earths*"; however, it "*took place in a more delayed form than in the early Precambrian, which is associated with a change in the composition of the atmosphere caused by the carbon dioxide absorption and free oxy-*

gen release. All this weakened the aggressiveness of the weathering agents and made possible the formation of rather thick clay weathering crusts <...> In the unmetamorphosed crusts of the Late Precambrian (pre-Ovruchian and younger epochs), no intensive iron removal is noted; tendencies of changes in the migration abilities of silica and alumina are distinguished; several other features are observed in the residual products of weathering. This period coincides with the transition of living organisms to oxygen respiration and free oxygen appearance in the atmosphere, in the presence of which migration-capable ferrous forms of iron were converted into oxide forms and were able to accumulate in eluvium. For the weathering crusts of this period, only a partial iron movement along the profile, an increase in the silica migration and a decrease in the alumina removal are noted" [ibid, p. 206; 210–211].

At the Middle Devonian–Holocene stage, in connection with the vegetation emergence on land, such a strong weathering factor as soil humic acids was added, and as a result, a lateritic process appeared. "*However, its implementation was performed under certain tectonoclimatic conditions and the source rocks presence, relatively rich in alumina.*" According to A.D. Savko and A.D. Dodatko, "*during the entire last stage, the weathering geochemistry remained practically unchanged*" [233, p. 207].

A.I. Pak came to very similar conclusions, summarizing the published materials on the Precambrian weathering crusts. He also concluded that there was no bauxite in them, and kaolinite appeared only in the Riphean:

"*The most complete profiles of weathering crusts have a three-zonal structure <...> the zone of oxidolites (lateritic bauxites) is absent <...> The main rock-forming minerals are clay ones; iron oxides and hydroxides are widespread, forming significant accumulations in places. In the weathering crusts of the Early and Middle Riphean, plagioclase sericitization is noted; kaolinite, iron hydroxides, and other clay minerals appear in the lower part of the profiles. In the Late Riphean (Pre-Vendian) and Early Vendian crusts, sericitization is absent; clay minerals (kaolinite, hydromica, montmorillonite, mixed layer formations), zeolites, hydroxides, and iron oxides are widely developed. As a result of the iron accumulation, ferrous kaolinite rocks were formed. In most sections of the weathering crust, aluminum is still removed. In this regard, minerals of free alumina in the weathering crust still could not form*" [200, p. 60].

Having made a simple typification of the ancient weathering crusts, A.I. Pak put all the collected data on a geographical map of the world and came to the conclusion that in early Karelian on the Earth the rudiments of climatic zoning appeared [200, p. 91], which already becomes quite distinct in the Late Karelian zones: "*According to the climate indicators, one can unambiguously distinguish the myohumid and myoarid (by evaporites and carbonate red-colored deposits) zones. The first ran along the south of the East European* *platform and south of the Great Lakes of the North American continent, the second was located in the north of the North American continent and in Greenland <...> The southern arid belt is recorded by the red-colored rocks development, magnesite dolomites in southern Africa, the Pamirs, etc. Despite the existence of climatic zoning, the differences in landscapes and climatic zones at the end of the Early Proterozoic on ancient continents are not as contrasting as in the Phanerozoic*" [200, p. 90–91].

In the Riphean, the climatic zoning became more contrasting; not two, but three climatic zones appeared: subarid, subhumid and subboreal (moderately humid). "*Apparently, the sub-humid climatic zones, in contrast to the myohumid ones of the early Proterozoic, were more humid. Preconditions arose for the development <...> of qualitatively new weathering crusts of a polyzonal structure <...> Due to the absence in landscapes of sharply acidic environments which are formed <...> due to the decomposition of plant and animal organic matter <...> the processes of crust formation in the late Proterozoic were not so intense, as in the humid tropics of the Cenozoic. Therefore, in the landscapes of the sub-humid tropical climate of the Late Proterozoic, conditions existed, at best, for weathering crusts formation with a three-zonal structure <...> mainly of a clay composition with iron oxides and hydroxides*" [200, p. 96–97].

8.2. On the question of the Catarchean weathering crusts

The question of the very existence of Catarchean sedimentary rocks is still being debated, despite the presence of carbonates and flints of seemingly indisputable sedimentary nature. The possibility of detecting Catarchean weathering crusts is considered even more problematic.

A.I. Pak, A.D. Savko, and A.D. Dodatko insist that no reliable Archean WCrs have survived, but only correlative sediments – in particular, quartz, high-alumina and ferrous sediments. Leading evolutionary geologist L.I. Salop, fully not admitting the existence of Archean WCrs, considered Catarchean quartzites not as clastic rocks, but as a chemogenic sediment arising from the extraction of silica from the weathering crust, both subaqual and subaerial [234].

A.I. Pak believes that since it has not been reliably established whether there are actually Catarchean continental deposits, it is impossible to talk about subaerial WCr in the Catarchean: "*The meta-sedimentary Catarchean rocks, known all over the world, are deposits associated with sedimentation water basins. No signs of the land denudation areas existence were found*" [200, p. 34]. A.I. Pak interprets the explicit differentiation of the metasedimentary rocks composition as a result of material dynamic sorting in underwater conditions. This explanation seems to us very doubtful; in any case, nothing of the kind is observed in Phanerozoic subaqual sediments.

According to A.I. Pak, the first subaerial WCr appeared on our planet only in the late Archean; this is the metamorphosed weathering crust on metabasites of the Kontok Group (Kostomuksha iron ore deposit in Karelia) described by V. Ya. Gorkovets and M.B. Raevskaya [85]. This most ancient WCr is still quite peculiar: it shows the removal of Mg, Na, Ca, Mn, Fe and some accumulation of Si, K, S, P with a practically unchanged Al content.

Aldan quartzites and corundites. According to uniformitarian geologists (A.V. Sidorenko and his followers), deeply differentiated formations – Katarchean quartzites and corundites – are an indisputable *residual product* of the Early Archean WCr. One should also recognize that the association of high-alumina gneisses with quartzites, which is widespread in the Katarchean, is very reminiscent of the same association of unmetamorphosed rocks in the Phanerozoic. In addition, there is a strong argument in favor of the fact that the Aldan quartzites are not chemogenic, but terrigenous-detrital rocks [149, 221].

L.I. Salop points to the contradictory geological and lithological features of the Aldan quartzites [234, p. 59].

1) Despite the complete recrystallization of these quartzites and the absence of clastic structures, they often exhibit distinct layering, contain rounded fine zircon and accessory sillimanite, sometimes magnetite, and in the section there is an alternation of quartzites with sillimanite and corundum-bearing gneisses. All of this is undoubted evidence of the quartzites' sedimentary nature.

2) Aldan quartzites are often associated with metavolcanics, which creates a temptation to consider them as metamorphosed analogs of the Phanerozoic siliceous-volcanogenic formations. However, this is contradicted by the features of p.1 and the huge thickness of quartzites (up to 2800 m in the Iyengra complex).

3) There are no conglomerates anywhere in the strata of quartzites and no signs of facies changes are seen, so no one can indicate for them the source areas of clastic material.

"*We see the elimination of these and other contradictions in the assumption acceptance that the Catarchean quartz sediments were formed mainly as a result of sedimentation from silica solutions extracted from the chemical decomposition crusts of sialytic rocks*" [234, p. 60]. At the same time, L.I. Salop admits that the Catarchean WCr could be both subaqual and subaerial.

The second important point in the discussion about the Catarchean WCrs is high-alumina metamorphic rocks – corundites, known in some Archean metamorphic complexes on shields: in India, Africa, Russia, Ukraine, Kazakhstan. There have been attempts to interpret corundites as products of hydrothermal-metasomatic acid leaching processes. However, according to E.A. Kulish, Aldan corundites are metamorphic analogs of ancient bauxites formed by deep chemical weathering of basic rocks, which can be judged, in particular, by the increased content of Cr_2O_3 in corundites. These rocks are also distinguished by a strong boron accumulation in the form of tourmaline (up to 1.2 % B_2O_3). At the same time, E.A. Kulish admits that these ancient formations could undergo subsequent granitization and regressive allochemical metamorphism (diaphthoresis): "*The relatively intense transformation of corundum rocks by these processes is primarily due to their specific ultra-alumina composition, which makes them subject to various changes in chemical and mineralogical composition under significant mobility conditions of* SiO_2, CaO, K_2O, Na_2O, H_2O*, etc.*" [149, p. 79].

E.A. Kulish's arguments against the allochemically-metamorphogenic primary nature of corundites are particularly interesting for our topic: "*N. A. Korenev [1947] <...> believes that corundum bodies arose in the process of metamorphic processing by fluids of Precambrian rocks during Proterozoic diaphthoresis <...> He points out that the fluids affected only feldspars at first with the disthene formation, which was then transformed into corundum; at the same time,* K, Na, Ca *and* Si *were removed from the rock strata. Such colossal scales of traceless removal of almost all elements, except for alumina, in narrow-localized areas during the regional development of diaphthoresis processes from the petrological point are difficult to explain. Corundum in diaphthorites, in addition to the host rocks containing corundites, is unknown; on the contrary, during diaphthoresis it is actively replaced by disthene, micas, pyrophyllite, etc. Corundum rocks, in equal measure with the rocks of the Aldan Archean complex, are subject to the effects of granitization and diaphthoresis, and are dislocated in the same way, which indicates their genetic relationship <...> There is completely no genetic confinement of corundum deposits to faults, diaphthoresis zones or any magmatic rocks*" [149, p. 91–92].

Based on 19 analyzes of corundum rocks given by E.A. Kulish, we calculated the average compositions for three groups with different silica contents (Table 115).

As one can see, the rocks belong to super- and hyperhydrolysates with two characteristic features: they are hypotitanic and hypoferrous. If these are isochemically metamorphosed residual weathering crusts, then it must be assumed that they were formed not on the basic, but on the acidic substrate. Another idea is also possible: the substrate of these rocks was more basic (for example, of "grey gneiss" type that have a granodiorite composition), but weathering took place in an acidic reducing environment, which caused the titanium removal in the form of Ti^{3+} and iron in the form of Fe^{2+} (gley process). Nevertheless, neither the granites nor the granodiorites should contain any noticeable admixtures of chromium.

Table 115

Some characteristics of Al-hydrolysates of the Aldan shield.
Compiled according to E. A. Kulish, 1983 [149, p. 79]

Oxides and modules	Average compositions		
n	4	10	5
SiO_2	5–10	10–20	20–30
Al_2O_3	88.15	73.16	62.54
HM	12.4	5.8	2.2
AM	11.9	5.5	2.2
TM	0.009	0.012	0.025
FerM	0.03	0.05	0.03

Therefore, it is quite possible that corundites were originally not eluvium, but a chemical sediment of $Al(OH)_3$, which sedimented during alkalinization of an acidic solution (pH sedimentation 4.1–4.3). Iron and titanium were previously removed from the solution, hydrolyzing at lower pH ($Fe (OH)_3$ – 2.5–2.7, $Ti(OH)_3$ – 4.0). With further solution alkalization, the alumina sediment could adsorb Cr^{3+} ions from it (the sedimentation pH of $Cr(OH)_3$ is 5.1).

Are the shales of the Pilbara block a product of the oldest weathering crust? Table 116 processed twelve analyzes of Catarchean shales of the Pilbara block in Western Australia [340], which are probably the oldest relatively low-metamorphosed terrigenous (?) clay rocks on Earth. These rocks turned out to be supersiallites and hypohydrolysates, with an MgO content > 3% in eight analyzes. Some analyzes from the George Creek region can be grouped into two clusters, while others (Wick Creek) are more diverse and cannot be averaged. They are certified as Fe- and Al-pseudohydrolysates (samples 8 and 9), pseudosiallite (samples 9) and supersiallite (sample 11). The increased hydrolysability of these rocks most likely indicates their connection with weathering crusts. The substantial potassium shales of the George Creek region were probably based on granodiorites, and, in general, for the more soda and titanium shales of the Wick Creek region, it appears to be basic rocks. The retention of appreciable MgO amounts in WCr indicates that magnesium was less mobile than calcium.

Another indirect evidence of strong Archean weathering is the presence of yellow-brown shales enriched with goethite, rutile, and anatase among the silica rocks of the Pilbara block, with very high TM values exceeding unity. According to K. Sugitani et al. [340], this indicates a strong titanium removal during the chemical weathering of the Archean substrate in an acidic medium, which existed due to the high CO_2 content in the atmosphere and the additional influx of volcanogenic H_2S and HCl into the waters.

Table 116

Chemical composition of the Catarchean shales of the Pilbara block, Western Australia.
Compiled according to S. McLennan et al. 1983 [341]

Oxides and modules	I	II	8	9	11	12
	Alkaline pseudosiallite		Alkaline pseudo-hydrolisate	Pseudo-siallite	Super-siallite	Pseudo-hydrolisate
n	2	6				
SiO_2	56.02	58.42	47.11	67.15	58.91	48.07
TiO_2	0.54	0.67	1.06	0.55	0.72	0.66
Al_2O_3	25.54	22.74	27.15	13.83	23.91	15.57
FeO	4.50	4.68	7.69	7.51	4.84	20.91
MnO	0.012	0.021	0.054	0.055	0.065	0.102
MgO	3.02	3.00	4.98	4.37	2.68	4.78
CaO	0.01	0.01	0.03	0.01	0.52	1.69
Na_2O	0.39	0.62	0.88	0.19	1.60	0.66
K_2O	4.88	4.89	4.76	1.91	2.26	0.99
LOI	5.12	4.90	6.08	4.27	4.42	6.36
Total	100.03	99.95	99.79	99.85	99.93	99.79
HM	0.55	0.48	0.76	0.33	0.50	0.77
FM	0.13	0.13	0.27	0.18	0.13	0.53
AM	0.46	0.39	0.58	0.21	0.41	0.32
TM	0.021	0.029	0.039	0.040	0.030	0.042
FerM	0.17	0.20	0.27	0.53	0.20	1.29
NKM	0.21	0.24	0.21	0.15	0.16	0.11
AlkM	0.10	0.10	0.20	0.10	0.70	0.70

8.3. The oldest weathering crust of the Late Archean and Karelian age

Late Archean WCr in the Krivoy Rog superdeep well. S.N. Suslova et al. [251] described the following section in the Krivoy Rog superdeep well:

2076–2276.3 m – basic metavolcanics.

2276.3–2351 m – white muscovite quartzite, andalusite-kyanite- and staurolite-bearing shales.

2351.4–2384.2 m – quartz-two-mica shales connected by gradual transitions with underlying granites.

2384.2–3550 m – porphyroblastic plagiogranites and gneiss granites (Dnipropetrovsk complex).

The interval of a well with a thickness of more than 100 m (2276–2384 m) is interpreted as a metamorphosed weathering crust, partly redeposited (a member of white muscovite quartzites and quartz muscovite shales with andalusite, kyanite, staurolite), and partly in situ (a member of quartz-mica-quartz and plagioclase – two-mica shale). In the latter, two zones are distinguished: "*the upper one, composed of quartz-two-mica shales, and the lower one, represented by plagioclase-quartz-two-mica shales, in which the structural and textural features of the parent rocks are preserved in places, which indicates their weak weathering*" [251, p. 109–110].

For our topic, it is especially important that here one can distinguish the Archean hypergenic process from allochemical metamorphism: "*In contrast to the metasomatic processes in which granitoids are depleted in alumina, total iron and magnesium, and are enriched in silica, during weathering there is a slight decrease in the silica content, an increase in the alumina, total iron, slightly magnesium content. These processes also differ in the behavior of impurity elements, rubidium and strontium are especially indicative. With weathering, there is a clear decrease in the* Sr *content, an increase in the* Rb *content, less distinct* – Mn, V, Sn*, with quartz-alkaline metasomatism, the opposite tendency is observed – an increase in* Sr, Rb, Mn, Sn" [251, p. 110]. Lithochemical processing of the analyzes given by the Petersburg authors did not reveal any hydrolysates among them – all rocks are certified, on average, as hypotitanic myosilites. The shales' HM with andalusite, kyanite, and staurolite is even lower (0.24) than in the original plagiogranites (0.26). In the series "original plagiogranites" ⇒ weathered plagiogranites ⇒ plagioclase-quartz-two-mica shales ⇒ quartz-two-mica shales ⇒ muscovite quartzites shales with andalusite, kyanite, staurolite clearly decrease the total alkalinity (6.44 – 4.55 – 4.50 – 4.42 – 1.57 – 1.94) and NKM (0.43 – 0.30 – 0.29 – 0.27 – 0.22 – 0.12); a less clear tendency is shown by AlkM (2.39 – 0.96 – 0.90 – 0.11 – 0.14 – 0.14) and TM (0.020 – 0.020 – 0.021 – 0.017 – 0.017 – 0.014). Thus, the process of feldspars decomposition is evident (in this case, sodium is quickly removed at first). Titanium is removed, alumina accumulates very weakly (from 14.82 % in plagiogranites to 16.19 % in shales with kyanite and andalusite).

Late Archean eluvium of Ukrainian crystal shield and KMA (Kursk Magnetic Anomaly). Table 117 and in Fig. 89 processed 11 analyzes of Late Archean (?) metamorphosed eluvium on the substrate of Archean metagranites and metabasites occurring in the basement of the Krivoy Rog-Kremenchug zone of the Ukrainian shield and the Voronezh crystalline massif (KMA). In its present form, the ancient WCr is represented by metamorphic rocks – various crystalline shales of acidic, intermediate and basic composition, belonging to the green shale and, less often, to the amphibolite facies [21, p. 52–88].

A paradoxical WCr feature for an acidic substrate (cluster I ⇒ cluster II ⇒ sample 6) is an increase in alkalinity – both total (up to alkalite)[3], and

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[3] However, sample 6 may also be alkaline metasomatite.

Table 117

Chemical composition of Late Archean residual rocks on acidic and basic substrates, Krivoy Rog and KMA.

Compiled according to E.T. Bobrov and I.G. Shchipakina, 1991 [21, p. 78, 80]

Oxides and modules	I	II	III	2	6	11
	Alkaline myosilite	Myosilite	Normo-hydrolisate	Carbonate myosilite	Alkalite	Pseudosiallite
n	4	2	2			
SiO_2	71.17	69.90	50.35	42.64	67.86	51.55
TiO_2	0.33	0.22	0.87	0.24	0.34	0.56
Al_2O_3	16.67	13.99	21.30	9.33	18.84	17.81
Fe_2O_3	0.53	0.75	12.35	0.36	-	2.66
FeO	1.15	1.91	9.64	1.66	0.80	6.75
MnO	0.02	0.05	0.11	0.12	0.01	0.03
MgO	0.79	1.15	1.81	2.03	0.68	6.67
CaO	0.60	3.58	1.00	21.43	0.80	5.84
Na_2O	1.40	0.21	0.18	0.30	2.74	1.23
K_2O	5.54	4.49	1.35	3.40	6.66	3.38
P_2O_5	0.07	0.17	0.12	0.30	0.03	0.08
SO_3	0.03	0.14	0.33	0.20	0.04	0.15
LOI	2.10	3.53	1.11	17.45	1.71	3.15
Total	100.40	100.09	100.52	99.46	100.51	99.86
CO_2	-	4.20	-	16.04	-	-
HM	0.26	0.24	0.88	0.27	0.29	0.54
FM	0.03	0.05	0.47	0.09	0.02	0.31
AM	0.23	0.20	0.42	0.22	0.28	0.35
TM	0.020	0.015	0.041	0.026	0.018	0.031
FerM	0.10	0.19	1.00	0.22	0.04	0.51
NKM	0.42	0.34	0.07	0.40	0.50	0.26
AlkM	1.00	< 0.10	0.10	0.10	0.40	0.40

normalized (NKM). As for the main substrate, it can be assumed that the quartz-carbonate-chlorite-biotite shale is relatively less altered (sample 11). From it, in the process of ancient (?) alteration, on the one hand, carbonated rocks[4] (sample 2) are obtained, and on the other hand, hydrolysate quartz-biotite shales of cluster III.

Another feature of this ancient WCr is that, regardless of fluctuations in the hydrolysate module HM, some silica accumulation is noted in the supposed weathering products. According to E.T. Bobrov, I.G. Shchipakina [21, p. 82], this phenomenon can be associated with three processes: a) silica redistribution in the WCr profile, namely, its removal from the upper zones and fixation in the lower ones; b) the silica release during the clay minerals

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[4] Again, if this is not the result of allochemical carbonate metasomatism.

metamorphism (*but this is an isochemical process and cannot lead to additional acidification of rocks. – Ya.Yu., M.K.*); c) the silica introduction "*during later metasomatic processes, which is accompanied by an increase in the* SiO_2 *amount up to 73.50–75.8 %*" [21, p. 82]. However, if the latter process is real, then this greatly depreciates the reliability of judgements about ancient weathering.

However, there is another possible (non-uniform) mechanism: residual silica accumulation in the WCr due to the removal of other components, including alumina. This is exactly the interpretation of the same picture (late Archean WCr on Saksagan granites) by Ukrainian scientists [233]. As for the potassium accumulation in WCr in acidic substrate, E.T. Bobrov and I.G. Shchipakina associate this with the alkaline weathering environment and the absence of vegetation on the continents in the Precambrian.

Metamorphosed WCr up to 25 m thick, developed on the Lower Karelian (Saksagan) plagiogranites, was previously described by A.D. Dodatko et al. [97]. The lower horizons of the WCr are represented by sericitized granite with carbonate, the middle horizons are quartz-biotite-sericite shales (also with the carbonate presence), and the upper horizons are sericite-quartz shales with a high carbonate content. Judging by the HM values calculated by us in these zones, HM fluctuates from the substrate (0.020) to the lower and middle zones, but generally increases slightly (up to 0.033), and in the upper zones it clearly increases (0.065–0.067). Noteworthy is the strong WCr carbonatization (up to 38.5 % of the normative $CaCO_3$ in sericitized granite at the contact with shale [121, p. 59]) – a phenomenon that is completely uncharacteristic of humid WCr of the Phanerozoic.

Discussing the chemical composition of this crust, Ukrainian scientists note some unusual features of the ancient weathering process: "*a) there were no stable (" immobile ") oxides in the weathering crust; 6) the alumina removal significantly outstripped the silica removal, because of which the quartz accumulation occurred in the eluvium; c) hypergenic mobility of potassium and sodium, as well as calcium and magnesium <…> was different. This contradicts the geochemical properties of these pairs in hypergenesis and is most likely due to their introduction during epigenesis and metamorphism of the crust*" [233, p. 18].

However, the danger of the latter explanation is that it undermines the very possibility of judging the primary composition of the ancient WCr. *After all, if the primacy of the observed picture is denied in relation to alkalis and alkaline earths, then why should it be recognized in relation to silica and alumina?* It seems to us more likely that the process of metamorphism here mainly remained isochemical, and the potassium accumulation (noted in many ancient crusts) was syngenetic to crust formation. We discuss this issue in more

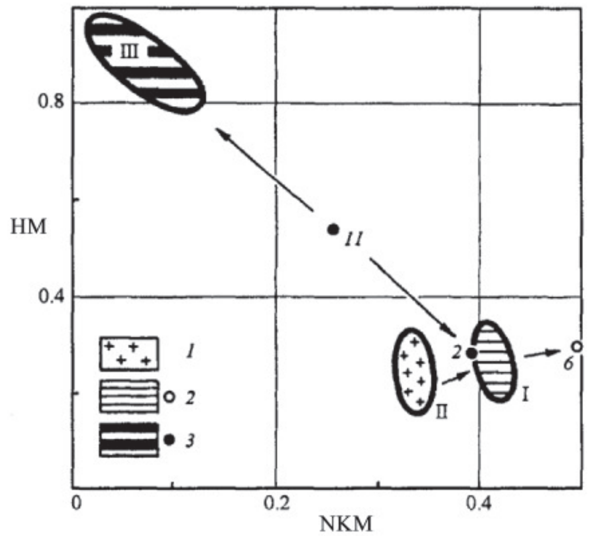

Fig. 89. Module diagram for the Upper Archean residual rocks on acidic and basic substrates, Krivoy Rog and KMA. Compiled according to the data of E. T. Bobrov, I. G. Shchipakina, 1991 [21, p. 78, 80].
1 – metagranites, 2 – quartz-sericite shales, 3 – quartz-biotite shales and metavolcanites

detail below (see Section 8.6). The WCr carbonatization phenomenon here can hardly be completely attributed to allochemical processes: weathering in an atmosphere rich in CO_2 can lead to the formation of syngenetic carbonates of the caliche type, which was described by A.V. Sochava on the Baltic Shield [245] and confirmed by S.A Kashik and I.K. Karpov's thermodynamic calculations [127].

Are Javanahalli metaarcoses products of the ancient weathering crust? In the Upper Archean shale belt of Javanahalli, India [345], a strata of high- potassium gneisses-metaarkoses is developed, which are interbedded with epidote quartzites and lime-silicate gneisses (Table 118). There are no high-potassium rocks among the most likely parent rocks around the source area. The idea of the superimposed K-metasomatism of arkoses is also not confirmed, they are interpreted as rocks of the first cycle of weathering – *first cycle sediments*. As a result, Indian geologists concluded that high-K arkoses are a product of ancient weathering of Archean tonalites, and a certain amount of basic and even ultrabasic rocks were also present in the substrate.

On the module diagram, it is possible to separate metaarcoses and their "transitional" varieties from more basic and less alkaline rocks (Fig. 90).

Table 118

Chemical composition of the Upper Archean metamorphic rocks of the Yavanahalli belt (India).

Compiled according to S. Naqvi et al., 1980 [345]

	I	II	III	1	2	3	11	12	13	14	16
	Pseudo-siferlite	Alkaline normosilite	Alkalite	Alkalite	Pseudo-silite	Alkaline normosilite	Alkaline pseudosilite	Normosilite			Pseudo-hydrolisate
n	2	4	3								
SiO_2	53.63	74.39	73.04	74.15	76.28	71.66	65.79	78.69	80.66	72.11	46.59
TiO_2	0.73	0.37	0.39	0.01	0.01	0.01	0.52	0.23	0.22	0.21	0.90
Al_2O_3	10.80	11.50	10.77	12.77	7.72	10.15	11.69	12.49	6.93	9.89	15.29
Fe_2O_3	4.18	0.81	0.79	0.37	0.50	0.98	1.56	0.25	2.56	3.66	4.23
FeO	4.78	1.52	1.40	0.76	4.16	1.84	4.92	1.36	1.38	0.74	5.54
MnO	0.33	0.12	0.09	0.07	0.17	0.26	0.19	0.14	0.15	0.21	0.38
MgO	4.96	2.17	2.30	2.22	3.46	2.78	3.67	0.66	2.22	0.66	3.81
CaO	17.78	2.61	2.29	1.01	4.37	6.17	6.11	2.30	5.94	9.53	20.16
Na_2O	0.48	2.09	1.92	1.63	1.03	2.07	4.79	3.77	0.30	1.82	1.13
K_2O	0.32	4.63	6.61	7.17	2.84	3.82	0.30	0.06	0.07	0.89	0.01
H_2O	0.89	0.22	0.34	0.22	0.18	0.78	0.37	0.24	0.08	0.11	0.56
P_2O_5	0.10	0.09	0.19	0.28	0.02	0.14	0.25	0.02	0.04	0.25	0.22
CO_2	1.32	-	-	-	-	-	-	-	-	0.45	1.58
Total	100.30	100.52	100.15	100.66	100.74	100.66	100.16	100.21	100.55	100.53	100.40
HM	0.39	0.19	0.18	0.19	0.16	0.18	0.29	0.18	0.14	0.20	0.57
FM	0.26	0.06	0.06	0.05	0.11	0.08	0.15	0.03	0.08	0.07	0.29
AM	0.20	0.15	0.15	0.17	0.10	0.14	0.18	0.16	0.09	0.14	0.33
TM	0.068	0.032	0.036	0.001	0.001	0.001	0.044	0.018	0.032	0.021	0.059
FerM	0.81	0.21	0.20	0.09	0.62	0.30	0.55	0.14	0.57	0.46	0.63
NKM	0.07	0.58	0.79	0.69	0.50	0.58	0.44	0.31	0.05	0.27	0.07
AlkM	1.50	0.50	0.30	0.20	0.40	0.50	16.00	62.80	4.30	2.00	113.00

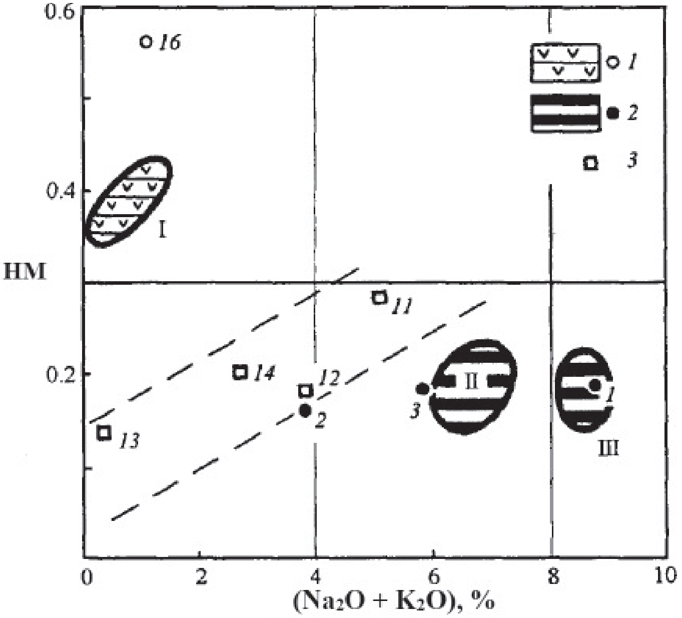

Fig. 90. Module diagram for the Upper Archean metamorphic rocks of the Yavanahalli belt (India).
Compiled according to S. Naqvi et al., 1980 [345].
1 – calcareous-silicate gneisses, 2 – metaarcoses, 3 – epidote quartzites

Clusters II–III are represented by metaarcoses, sample no. 11–14 are represented by epidote quartzites – rocks, less alkaline, more titanium and ferrous. Sample no. 13 is characterized by minimal alkalinity, and sample no. 11, on the contrary, is close in NKM to metaarcoses, to their "transitional" varieties. The low K_2O contents with significant Na_2O contents suggest that these could be some greywackes, for example, andesite volcanoclasts with an admixture of quartz. Cluster I includes magnesian rocks, super- and hyper-ferrous. *Ferrous pseudohydrolysate* is also close to them (sample 16). Obviously, these are metabasites.

Thus, it can be assumed that high-potassium terrigenous material from the weathering crust of Archean tonalites entered the Late Archean sedimentation basin, forming layers of high- potassium arkoses. However, most likely, this process was accompanied by rather strong synchronous volcanism (andesite and basaltic), which determined a significant admixture of basic material in the rocks. As a result, mixed rocks of the "greywacke-arkoses" type (or, perhaps, "tuff-arkoses") were obtained, and covers (or sills?) of basaltoids were periodically formed. Note that this whole picture (including the rocks composition) is surprisingly similar to that described for the Middle Riphean (?) Shchekurya Formation, which we studied in the Subpolar Urals [178].

Late Karelian weathering crust over the basalts of Canada. Table 119 shows 16 analyzes' data of the pre-Riphean "fossil soil" (ancient weathering crust) developed over the substrate of the Upper Karelian basalts in Canada and sampled in two profiles [334].

Data clustering on a module diagram (Fig. 91) makes it possible to distinguish six clusters along profile 1, one along profile 2, and one mixed. These formations are certified as normal and alkaline hypohydrolysates (clusters Ia, b, IIa), as magnesian rocks – pseudohydrolysates, including alkaline (clusters IIb, III and samples 15, 20, 21, 24) and pseudosiferlites (cluster VI) , and, finally, as ferrous rocks – siferlites (clusters IV, V and sample 23). And only one composition out of 16 (sample 17) turned out to be normal siallites.

These data allow us to note at least two features in the Late Karelian crust formation. First, the abundance of magnesian rocks. Obviously, during the weathering of basalts, a significant part of the magnesia was retained in the weathering crust (in hydrochlorite or montmorillonite). Secondly, both in the WCr itself and in the original "unweathered green shale" (samples 15,

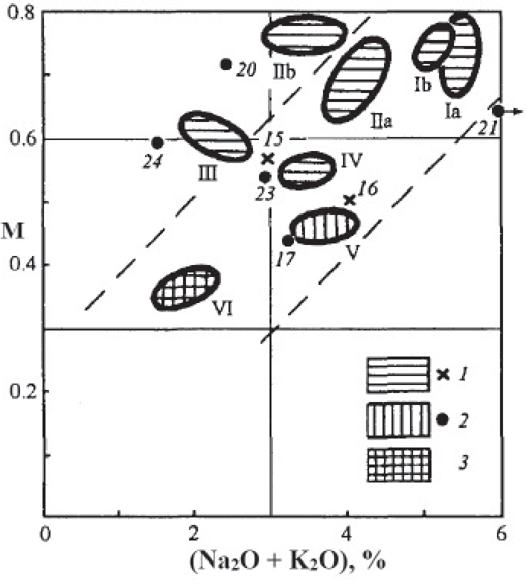

Fig. 91. Module diagram for two profiles from the pre-Riphean metamorphosed "fossil soil" on the Upper Karelian basalt substrata, Canada.
Compiled according to H. Holland et al., 1989 [334, p. 376–377].
1 and 2 – respectively rocks in profiles 1 and 2; 3 – rocks from both profiles

Table 119

Chemical composition of pre-Riphean “fossil soil” in Canada.
Compiled according to H. Holland et al., 1989 [334, p. 376–377]

Oxides and modules	Ia	Ib	IIa	IIb	III	IV	V	VI
	Alkaline hypohydrolisate		Hypohydro-lisate	Pseudohydrolisate		Siferlite		Pseudosiferlite
n	3	2	2	2	2	2	2	2
SiO_2	53.58	53.86	55.02	51.73	54.08	60.07	64.31	66.37
TiO_2	0.84	0.53	0.79	0.74	0.73	0.74	0.75	0.54
Al_2O_3	21.04	20.83	19.52	20.09	16.96	17.57	15.83	12.72
Fe_2O_3	15.35	16.87	13.o7	8.91	5.24	8.40	11.54	4.78
FeO	2.62	1.91	4.66	9.57	9.52	6.23	1.90	6.24
MnO	0.05	0.04	0.04	0.13	0.18	0.10	0.06	0.13
MgO	0.58	0.46	1.90	4.31	6.74	2.45	0.87	4.33
CaO	0.09	0.39	0.18	0.26	3.12	0.31	0.51	2.18
Na_2O	1.97	2.07	1.60	1.64	0.78	1.40	1.52	0.68
K_2O	3.51	3.07	2.59	1.80	1.54	2.02	2.15	1.23
P_2O_5	0.07	0.05	0.13	0.11	0.10	0.05	0.34	0.14
SO_3	0.01	0.00	0.01	0.00	0.01	0.02	0.04	0.00
Total	99.71	100.08	99.51	99.90	99.00	99.36	99.82	99.34
HM	0.74	0.75	0.69	0.76	0.60	0.55	0.47	0.37
FM	0.35	0.36	0.36	0.44	0.40	0.28	0.22	0.23
AM	0.39	0.39	0.35	0.39	0.31	0.29	0.25	0.19
TM	0.040	0.025	0.040	0.037	0.043	0.042	0.047	0.042
FerM	0.82	0.88	0.88	0.89	0.84	0.80	0.81	0.84
NKM	0.26	0.25	0.21	0.17	0.14	0.19	0.23	0.15
AlkM	0.60	0.70	0.60	0.90	0.50	0.70	0.70	0.60

Table 119 (continuation)

Oxides and modules	15	16	17	20	21	23	24
	Pseudo-hydrolisate	Pseudo-siferlite	Normo-siallite	Pseudo-hydrolisate	Alkaline pseudohydrolisate	Siferlite	Pseudo-hydrolisate
SiO_2	48.57	54.97	64.91	51.59	51.41	59.67	53.84
TiO_2	0.54	0.59	0.88	0.92	0.66	1.04	0.91
Al_2O_3	16.68	15.16	17.39	18.92	17.65	16.42	15.72
Fe_2O_3	3.05	3.23	8.58	6.76	7.05	9.19	2.89
FeO	7.23	8.63	1.93	10.36	7.83	5.73	12.41
MnO	0.29	0.24	0.00	0.20	0.15	0.15	0.11
MgO	4.25	7.21	1.26	5.85	5.47	2.92	7.31
CaO	14.99	4.78	0.94	1.64	2.55	0.94	3.64
Na_2O	0.57	2.71	1.65	1.12	5.03	1.17	0.20
K_2O	2.40	1.34	1.59	1.33	1.21	1.78	1.35
P_2O_5	0.38	0.19	0.66	0.17	0.12	0.35	0.21
SO_3	0.02	0.01	0.00	0.01	0.01	0.02	0.03
Total	98.97	99.06	99.79	98.87	99.14	99.38	98.62
HM	0.57	0.51	0.44	0.72	0.65	0.55	0.60
FM	0.30	0.35	0.18	0.45	0.40	0.30	0.42
AM	0.34	0.28	0.27	0.37	0.34	0.28	0.29
TM	0.032	0.039	0.051	0.049	0.037	0.063	0.058
FerM	0.61	0.77	0.58	0.87	0.82	0.86	0.93
NKM	0.18	0.27	0.19	0.13	0.35	0.18	0.10
AlkM	0.20	2.00	1.00	0.80	4.20	0.70	0.10

16, 24), the titanium module is surprisingly low. In any case, we do not know any Precambrian or Paleozoic basalts with such a low TM (on average, no higher than 0.047, and for some samples – up to 0.032). So, according to the average data of A.B. Ronov et al. [228], the TM for the main effusive rocks of the Katarchean, Upper Archean, Karelian, and Riphean is 0.073, 0.070, 0.092, 0.115, respectively. This gives reason to believe that "unweathered green shales" are by no means metabasalts, but metamorphosed products of some more ancient weathering, in which titanium was more mobile than alumina. Possibly, it was being restored and removed from the ancient WCr in the form of $Ti^{3+.}$

Ferrous quartzites as evidence of ancient weathering. Remarkable indirect evidence of the strong Late Archean and Karelian carbon dioxide-reducing (gley) weathering are *ferrous quartzites* – chemogenic sediments formed during removing weathering products of the Upper Archean granite-greenstone regions into the ocean [99, 175].

D.A. Kulik and V.V. Pokalyuk [148] constructed a model of Karelian iron accumulation in the Krivoy Rog iron ore basin, where the Saksagan formation is ore-bearing, numbering in the most complete section 7 iron ore horizons and 7 shale horizons with a total thickness up to 1400 m. It is called "iron-silica-shale formation" (ISSF); the formation consists of 70–80 % ferrous-silica rocks (containing 25–40 % Fe and 40–60 % SiO_2) and 30–20 % of shale-metapelitoids. The average thickness of the ferrous rocks of the Saksagan formation is 1 km with an average Fe content 30 % and SiO_2 46 %. The authors suggested that the weathering crusts on the Upper Archean plagiogranite-greenstone substrate served as the Fe and Si source during the ore sediment accumulation of the Saksagan formation. Preliminary estimates (using an inert witness element Al) showed that 90 % $FeO + Fe_2O_3$ and 25 % SiO_2 are removed from the upper WCr horizons along Archean plagiogranites. In absolute terms, this is 73.12 and 472.50 kg, respectively, from each cubic meter of substrate. Estimates for basic rocks give: 30 % $FeO + Fe_2O_3$ (99.78 kg/m^3) and 30 % SiO_2 (431.11 kg/m^3).

The redeposition model in the Krivoy Rog basin of chemogenic weathering products is written in the form of a material balance equation: $S_{rem} \cdot d \cdot p_i = S_{bas} \cdot v_i$, where S_{rem} is the area of the source space; d is the linear weathering rate, which is, on the average for continents, 100 m per 1 million years; p_i – the mass of the component removed from a unit volume of weathered rocks (its estimates are given above); S_{bas} – the area of the Pra-Kryvoy Rog basin, amounting to 5 thousand km^2; v_i is the rate of the dissolved component sedimentation from the waters of the basin. For Fe and SiO_2, the v_i estimates give 20 and 30 mg/cm^2 per year. Thus, only S_{rem}, that is, the area of the weathering region, remains an unknown quantity in the material balance equation. Substitution of the known estimates gives about 1.8·10^5 km^2 for it (if it were entirely composed of plagiogranites) or 1.3·10^5 km^2 (if it were composed only of metabasites), and on average 1.5·10^5 km^2.

"*This value is quite comparable with the area of the Near-Dnieper block (1.2 · 10^5 km^2) and significantly less than such granite greenstone areas as the Yilgarn block (Western Australia, > 1 · 10^6 km^2) or the Archean Ungava craton on the Canadian shield <...> At the same time, the ratio of the drift regions to the sedimentation region (in the case under consideration, 30) is close to the present-day: ratios of this kind for humid regions (on the order of 20–40 ...) <...> Therefore, it seems that the humid weathering of plagiogranite-greenstone regions under the conditions of a reducing nitrogen-carbon dioxide atmosphere (but devoid of hydrogen sulfide) could have ensured the synchronous iron sedimentation <...> in the Krivoy Rog and other similar basins*" [148, p. 45].

However, the mass of chemogenic sedimentary material is only 1/4–1/5 of the total mass of the eroded substrate. Consequently, the remainder must have been deposited somewhere in the form of clastic material. Since there is too little such material in the Saksagan formation (no more than 30 %), we have to assume that the clastogenic derivatives of the eroded pre-Saksagan WCr settled in another zone of the ancient basin: "*With regard to the Krivoy Rog basin, this could mean that beyond its boundaries one should look for relics of thick (10 km or more) terrigenous (shale, gneiss) strata, spread over an area not less than the iron ore basin area, and of the same age with* [iron ore strata]". As such (as if correlative with respect to the iron ore strata), the authors consider the thick (10 km) metaterrigenous strata of the Ingulo-Ingulets series developed to the west of the Kryvoy Rog-Kremenchug ISSF development band: "*Due to its significant thickness and distribution area, the deposits of the Ingulo-Ingulets series could correspond to terrigenous avalanche sedimentation areas, synchronous with iron accumulation in the Krivoy Rog basin. This formulation of the question <...> allows us to explain where the huge mass of terrigenous material removed from the land during the granite-greenstone areas weathering during the Saksagan formation sedimentation of the Krivoy Rog series, disappeared*" [148, p. 47].

Note that the cited Ukrainian geologists considered alumina to be an inert component during weathering. However, they expressed the idea the alumina removal from the WCr. Thus, while studying the Ukrainian crystal shield ancient weathering crusts, A. D. Dodatko drew attention to the ubiquitous process of plagioclases silicification and hornblende replacement with actinolite in ancient metamorphic eluvium. In his opinion, these phenomena definitely indicate not the SiO_2 input (which suggests itself), but the *Al removal* (together with the Fe and Si removal from the ancient weathering crusts recognized by all researchers). However, if the transported Fe and Si are present (this is the iron ore strata of the Saksagan group), then *where was the transported alumina deposited*? If it were really performed, then, according to V. K. Golovenok, “*we should have had complementary alumina accumulations in even more significant amounts than iron among the deposits of the Krivoy Rog series. However, we do not observe anything of the kind in the deposits of the Krivoy Rog group*” [81, p. 137]. In the opinion of A. D. Dodatko, V. K. Golovenko's argument is not valid, because in the Saksagan group, the removed alumina was recorded in seven shale horizons with a total thickness of 400–450 m. “*These horizons are composed of quartz-bearing sericite, biotite, chlorite, phyllite and other shale, the alumina content of which varies from 12 to 28 %. In addition, the upper formation of the Krivoy Rog series (according to the modern classification, the Gdantsevskaya and Gleyevatskaya formations) also includes horizons of quartz-carbonaceous-sericite, quartz-biotite-chlorite and other shales up to 200–400 m thick and with similar alumina contents. With the accumulation of these metasedimentary rocks' strata, all alumina performed from eluvium could be consumed without any special “complementary” accumulations*” [95, p. 140].

In this interpretation, we have to consider the Saksagan shales not as metaterrigenous (which seems to have not been disputed earlier), but as metachemogenic formations (of the ferrous quartzites type, but of a different composition). This idea seems too radical. In addition, the aluminum removal, as V. K. Golovenok rightly pointed out, should be reflected in the TM value of eluvial products. Although A.D. Dodatko does not consider such an objection to be serious, it seems nevertheless that the removal of aluminum from the Late Archean and Karelian WCrs could not have been significant. In addition, at low total titanium contents, the TM of ferrous quartzites is increased, which may indicate some titanium removal together with iron from the initial substrate with a relatively inert behavior of aluminum.

Another argument by A. D. Dodatko (accumulation of quartz due to the alumina removal) is refuted by the experiments of E. T. Bobrov and T. G. Shchipakina, who found that under conditions simulating the green-shale metamorphism of clay products of the weathering crust, an isochemical process of secondary silicification is observed: “*The metamorphism of clay minerals was accompanied by the excess silica release in the composition of α-crystobalite and quartz, which may explain the presence of numerous quartz veins in the profiles of metamorphosed residual rocks and their redeposited products, usually considered as a manifestation of quartz metasomatism*” [21, p. 25].

Thus, based on the totality of the available data, previously well summarized in the monographs by Yu. P. Melnik [175], Yu. P. Kazansky [121], V. K. Golovenok [82], A. I. Pak [200], A. D. Savko and A. D. Dodatko [233], E. T. Bobrov and I. G. Shchipakina [21], it should be admitted that in the Late Archean and Karelian WCrs there was no noticeable aluminum removal (maybe the removal was very weak and manifested itself only locally), but more often there was its accumulation (for example, from 14–15 % of alumina in the original granites to 20–23 % in mica shales in terms of carbonate-free matter [121, p. 59]).

8.4. Riphean and Vendian weathering crusts

Ontario Grenville shales. The two-mica garnet-staurolite Grenville shales of Ontario, Canada, were apparently formed from clay rocks – derivatives of the ancient weathering crust [335]. Shales have a rather high TM value: only one composition out of 11 is normo-titanium, and the rest are all super- and hyper-titanium. The absolute TiO_2 content is noticeably higher than the clarke content for the Riphean shales: 1.3–2.7 versus 0.94 % [228]. Since the increased TM is not accompanied by increased iron content, there is no evidence to assert that basites were the substrate for the ancient WCr. But if the substrate was acidic or medium, then why is TM so high? Therefore, it cannot be ruled out that the Riphean[5] weathering took place at a more vigorous removal of Al and Fe than Ti.

This assumption is partly confirmed by the analysis of E. T. Bobrov and I. G. Shchipakina's data of for the Riphean WCr for acidic and basic substrates [21, p. 41–47]. For the gneisses and granites substrate, there is a negative correlation of alkalinity with HM and FerM and a tendency towards a positive correlation FerM – TM, while for the basic rocks the picture is different – a positive correlation HM – TM and negative correlations of total and normalized alkalinity with HM and FerM. The tendency of negative correlation between TM and iron content is also curious, while the opposite was observed in the ancient WCr for granites. This could mean that Al and Fe were removed from the ancient WCr profile over the main substrate more intensively than Ti.

Riphean eluvium on different substrates. Table 120 processed 12 analyzes of Riphean (?) weakly metamorphosed eluvium on the gneisses, granites, amphibolites, diabases and gabbros substrate of the Archean basement of the Russian platform (Middle Near-Dniester, Volga region, Belorussky massif) [21, p. 29–51]. Basically, these are the middle and upper zones of the ancient WCr profile over the acidic substrate, or only the middle ones, essentially chlorite of hydromica composition – over the basic sub-

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[5] The age of the pre-metamorphic substrate of these shales is unclear. As L.I. Salop points out, the Grenville geosynclinal belt in the southeast of the North American Platform "*is composed mainly of basement rocks (in age from the Catarchean to the Mesoprotozoic, inclusive), intensively reworked during the Grenville diastrophism*" [234, pp. 256–257].

strate. According to E.T. Bobrov and I.G. Shchipakina, the primary (pre-metamorphic) “*composition <...> of the middle zones rocks was not chlorite-hydromica (illite), but chlorite-montmorillonite with an admixture of mixed layer minerals of the montmorillonite-hydromica type, and also kaolinite and goethite <...> The mixed-layer formations present in the residual rocks profile, containing up to 40 % of swelling layers, should be considered as relict*”. As a result, they divided the minerals of weakly metamorphosed ancient eluvium into two associations: primary hypergenic (chlorite-montmorillonite-mixed-layer-hydromica-kaolinite) and metamorphogenic (illite-dickite-hematite) [21, p. 44–45].

Table 120

Chemical composition of the Riphean residual rocks of the Middle Near-Dniester, the Volga region and the Belorussian massif.

Compiled according to E.T. Bobrov and I.G. Shchipakina, 1991 [21, p. 46–48]

Oxides and modules	I	II	III	IV	V	6
	Metagneisses and granites		Metabasites			Metagneiss (hypohydrolisate)
	Alkaline myosilite	Alkalite hypohydrolisate	Pseudo-hydrolisate	Alkaline supersiallite	Ti pseudo-hydrolisate	
n	3	2	2	2	2	
SiO_2	67.89	53.78	39.81	53.98	41.77	54.60
TiO_2	0.34	1.05	1.42	1.84	2.26	0.72
Al_2O_3	17.18	19.53	20.22	15.78	14.11	19.33
Fe_2O_3	1.93	4.84	11.84	7.44	10.51	14.21
FeO	0.76	5.91	7.45	3.23	4.32	1.61
MnO	0.01	0.03	0.12	0.07	0.22	0.02
MgO	0.47	2.50	3.70	2.88	4.87	0.48
CaO	1.02	1.36	2.03	5.49	8.19	1.08
Na_2O	1.80	1.59	0.19	2.28	0.77	1.61
K_2O	5.78	4.65	3.95	2.94	3.70	2.78
P_2O_5	0.16	0.29	0.25	0.48	0.50	0.20
LOI	2.98	4.83	9.54	2.97	8.57	2.77
Total	100.32	100.36	100.52	99.38	99.79	99.41
HM	0.30	0.58	1.03	0.53	0.75	0.66
FM	0.05	0.25	0.58	0.25	0.47	0.30
AM	0.25	0.36	0.51	0.29	0.34	0.35
TM	0.020	0.054	0.070	0.116	0.160	0.037
FerM	0.15	0.52	0.90	0.61	0.92	0.79
NKM	0.44	0.32	0.20	0.33	0.32	0.23
AlkM	0.30	0.30	0.10	0.80	0.20	0.60

The module diagram (Fig. 92) clearly shows two fields of positive correlation HM – TM: one for the acidic substrate (clusters I, II, and sample 6) and the other for the main one (clusters IV, V). The rocks of cluster III (Middle Near-Dniester) occupy a separate position, which, probably, should be associated with the basic substrate composition peculiarities, which is represented here by gabbro and gabbronorites, markedly altered in the zones of contact with granites and migmatites.

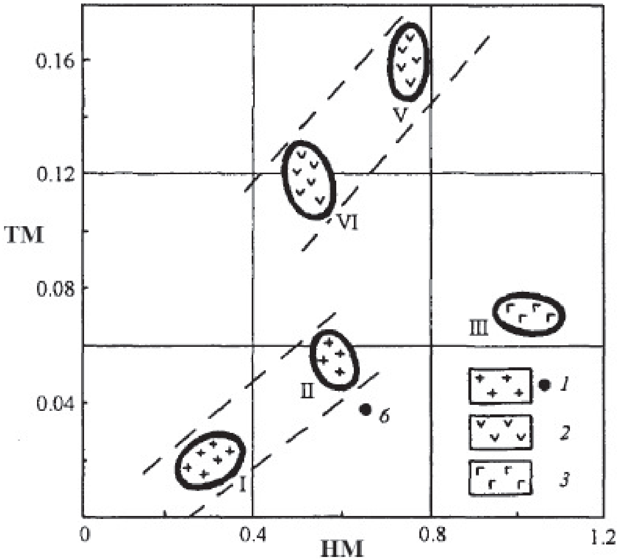

Fig. 92. Module diagram for the Riphean residual rocks of the Middle Near-Dniester, the Volga region and the Belorussian massif.
Compiled according to E.T. Bobrov and I.G. Shchipakina, 1991 [21, p. 46, 48].
1–3 – eluvium on the substrate: granites and gneisses (1), metabasites (2), gabbro (3)

8.5. Kaolinite and its derivatives – evidence of humid weathering

According to the data compiled by A. I. Pak (200], reliable kaolinite appears in *unmetamorphosed* weathering crusts only starting from Riphean. This is a clear mistake. In fact, kaolinite in weathering crusts undoubtedly appeared long before the Riphean; this is evidenced by indications of the kaolinite presence in weakly metamorphosed WCrs of the Karelian time in Finland [285] and on the Anabar shield [112, 242]. If we also consider the *metamorphosed WCrs*, then we will have to admit that kaolinite was formed in weathering crusts much earlier – not only in Karelian, but and in the Archean.

It can be argued that all low-alkaline metamorphic hydrolysates originally contained kaolinite.

These formations include the following: Upper Archean Keivskian shales on the Kola Peninsula [82, p. 126–133], aluminous shales of the Witwatersrand (lower Karelian) [349], Lower Karelian gneisses of the Teterevbug formation in the west of the Ukrainian crystal shield [82, p. 161], aluminous shales developed over the substrate of Archean gneisses and conglomerates in Finland [285], ancient weathering crusts on the Anabar shield over the substrate of biotite-garnet [112] and pyroxene gneisses [242], the Akitkania formation [234] and Purpol formation R_2 in the Baikal mountainous region [82, p. 50–57]; Riphean diaspores bauxites and corundites of Mongolia [98]; Zigalga formation R_3 in the Southern Urals [82, p. 114–118], the Riphean strata of the Yenisei ridge (the Potoskui, Shuntar and Kirgitei formations in the Tungusik series R_2, and especially the Upper Angara formation at the base of the Oslyan series R_3 [82, pp. 98–103]). Among the Lower Paleozoic metamorphic rocks, in the substrate of which kaolinite was undoubtedly present, let us call the “*sparkling shales*” D_2 in the Northern Urals [295, p. 192] and the Tanamys S–D strata of the Northern Pamir [33].

There can hardly be any doubt that aluminous and ferrous minerals such as pyrophyllite, kyanite, staurolite, and chloritoid have their genetic lineage from kaolinite.

They can be obtained either by the simplest reaction of kaolinite with quartz and magnetite, or in reactions of exchange decomposition (kaolinite + potassium feldspar, kaolinite + montmorillonite, etc.):

$$\underset{\text{kaolinite}}{Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O} + \underset{\text{quartz}}{2SiO_2} \Rightarrow \underset{\text{pyrophyllite}}{Al_2O_3{\cdot}4SiO_2{\cdot}H_2O} + H_2O$$

$$\underset{\text{kaolinite}}{Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O} \Rightarrow \underset{\text{kyanite}}{Al_2O_3{\cdot}SiO_2} + \underset{\text{quartz}}{SiO_2} + 2H_2O$$

$$\underset{\text{kaolinite}}{2(Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O)} + \underset{\text{(magnetite)}}{FeO} \Rightarrow \underset{\text{staurolite}}{FeO{\cdot}2Al_2O_3{\cdot}SiO_2{\cdot}H_2O} + \underset{\text{quartz}}{3SiO_2} + 3H_2O$$

$$\underset{\text{kaolinite}}{2(Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O)} + \underset{\text{(montmorillonite)}}{FeO, MgO} \Rightarrow \underset{\text{chloritoid}}{(Fe, Mg)O_2{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}H_2O} + \underset{\text{quartz}}{SiO_2} + 3H_2O$$

It is known that kaolinite formation requires an acidic environment. In the absence of real soils and terrestrial vegetation (which did not appear earlier than the late Silurian), the acidic environment on the Earth's surface was provided almost exclusively by atmospheric CO_2[6]. Fluctuations in atmospheric CO_2 content, as proved by A. B. Ronov, were controlled by fluctuations in the volcanism intensity. In turn, the epochs of strong vol-

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[6] If we neglect local foci of sulfuric acid weathering or hydrothermal leaching associated with volcanoes.

canism were thalassocratic epochs: at this time there was a subsidence of the continents' earth crust. Since in the Phanerozoic history of the Earth the epochs of mass development and subsequent erosion of the weathering crusts were also thalassocratic (for example, O_2, D_3, C_1, J_3, etc., it became clear long ago that the thalassocratic epochs were characterized by the dominance of a humid climate. In these epochs polar caps decreased in size, and climatic zoning became less contrasting. On the contrary, the geocratic epochs (D_1, P_2–T, Pleistocene) are associated with global climate aridization, continental glaciations, and a very sharp climatic zoning.

Thus, there is every reason to believe that the intervals of the Precambrian section, enriched in rock-forming elements-hydrolysis (Al_2O_3, Fe_2O_3, TiO_2), corresponded to thalassocratic epochs with the humid climate dominance. However, the Phanerozoic history of the Earth shows that the ratio of the oceans and continents areas was controlled by global tectonics. It has already become clear that the predominance of arid environments in Karelian and the Early-Middle Riphean is associated with the formation of the first Pangei, the Precambrian supercontinent [263]. The split of the supercontinent at the boundary between the Middle and Late Riphean, as evidenced by, inter alia, strong Sr isotope anomalies in carbonates [357], should have been accompanied by climate humidization. Is this not evidenced by an increase in the frequency of kaolinite occurrence (or its metamorphic derivatives) in the Upper Riphean deposits?

8.6. Potassium accumulation in red-colored strata – evidence of arid weathering

High-potassium shales, containing 5–6, and often up to 10–12 % K_2O, are known in the Upper Archean shale belt of Javanahalli (India) [345], in the Huronian superseries of Canada (Karelian) [82, p. 207], in the Segozero series of Central Karelia (Lower Karelian) [298, p. 691], in the Udokan series of the Olekmo-Vitim mountainous country (Karelian) [298, p. 693], in the lower reaches of the Kursk KMA series [82, p. 182–183], at the base of the Burzyania (Bolsheinzerskaya formation R_1) and Karatavia (Biryanskaya subformation of the Zilmerdak formation R_3) in the South Urals [298, p. 693], in the Novobobrovskaya and Anyugskaya formations R_3 on Timan, in the Dzhalagunskaya formation R_1 of the Srednevitimskaya mountain country [82, p. 77], in the series R_3– $€_1$ Dalred in Scotland and Connemara in Ireland [82, p. 190–191], in the copper-bearing Katanga Formation R_3 of Central Africa [246], in the Khoidyshor volcanogenic-sedimentary sequence $€_3$–O_1hd in the Polar Urals [298].

The phenomenon of potassium accumulation in ancient WCr has long been discussed in the literature but has not received a satisfactory explanation. For example, Siberian geologists, noting the “unusual behavior” of potassium, which, in contrast to the post-Cambrian crust, accumulates in the ancient WCr’s upper profile, tried to interpret this phenomenon in the spirit of uniformitarianism, attributing it to superimposed metamorphism: “*Assuming the hydromica-kaolinite primary crust composition, potassium input should be allowed. It is performed, probably, in two ways: with potassium metasomatism in the metamorphism process and due to the potassium input leached from the upper horizons of the weathering crust by groundwater*” [171, p. 169]. In fact, the first model is a typical *ad hoc* hypothesis that itself requires proof, while the second contradicts the authors' assertion that potassium-rich formations are precisely the *upper* horizons of the weathering crust.

In 1991, we proposed a radically different interpretation of potassium accumulation in ancient weathering crusts. It is based on three provisions.

1. In agreement with B.M. Mikhailov [181] and many other geologists, we believe that the ancient micaceous shales are by no means the lower horizons of normal (lateritic) weathering crusts, in which the upper horizons are cut off by erosion: these are in most cases the *upper* horizons of primitive ancient WCr. As a rule, they are not products of allochemical metamorphism (with the potassium input) of the former kaolinite or kaolinite-hydromica zones of full-profile weathering crusts. Although such a process is not excluded, it cannot be accepted a priori, without solid evidence.

2. Ancient micaceous shales are often red-colored and are in significant paragenesis with red-colored high-potassium arkoses.

3. Ancient micaceous shales, as V.K. Golovenok clearly showed for the first time [82], often contain potassium feldspar.

Taken together, all this means that the ancient (Upper Archean, Karelian and Riphean, and partly also the Early Paleozoic-Pre-Devonian) red-colored high-potassium clay shales are nothing more than derivatives of the weathering crust of the alkaline arid type. The unusualness of this interpretation lies in the fact that most researchers of the Phanerozoic weathering crusts seriously considered only the epochs of a humid climate: it was tacitly assumed or openly declared [233, p. 186], ***that the weathering crust was not formed during the epoch of arid climate.***

However, *in relation to the Precambrian*, we must reckon with three important circumstances:

– the epochs of the arid climate could be very long, so even relatively weak alkaline weathering could eventually lead to significant geological results.

– low humidity could be partially compensated by the increased CO_2 content in the atmosphere and the increased temperature of the Earth's surface, which made the processes of rock-forming minerals decomposition more intense.

– arid landscapes of the Precambrian should not be mechanically identified with the modern deserts of Asia or Africa; it is highly probable, in agreement with A.I. Pak [200], that the climatic conditions were *subarid*, that is, with greater moisture than, for example, in the modern inland deserts Sahara or Gobi. In such a climate, periodic removal of soluble weathering products is possible, which ensures the substrate development to a great depth from the surface.

A retrospective study of the geological literature shows that the arid weathering importance has long been pointed out by very authoritative researchers; however, their voice was drowned out by the prevailing "laterite paradigm", according to which "weathering" was implicitly understood only as an acidic humid process that generates WCr with bauxite or, at least, with kaolinite. The "laterite paradigm" made it difficult to appreciate the widest manifestation of arid weathering processes in the Precambrian.

Among the few geologists who paid due attention to arid weathering in the Precambrian, A.I. Pak [200] should be named, according to whom the weathering crusts along the Archean gneisses of the southeastern slope of the Anabar shield (data by E.A. Shamshina, L.V. Nikishova, 1971), most of the described Riphean crusts of Siberia (Angara-Pitsky region, Near-Sayan region, south of the Aldan shield). He notes evaporates, direct indicators of an arid climate, in the Riphean sections of the North American Platform and Greenland, as well as in the Riphean and Vendian in most of Hindustan. In the pre-Vendian epoch and in the early Vendian on the Siberian platform and in its folded frame, according to A.I. Pak, based on the data of Siberian geologists, arid environments also prevailed [200, p. 51–57]. According to V.A. Sokolov and K.I. Heiskanen [244], who described several horizons of metamorphosed WCr within the Karelian complex in Karelia, they were formed in a warm, but dry climate and in the atmosphere, although with the presence of free oxygen, but with an increased CO_2 content. According to A.I. Pak, "*in similar climatic conditions, apparently, formed and early Proterozoic weathering crust of the region of lake Huron on the Canadian shield.*" However, this conclusion is contradicted by his next phrase: "*The weathering crust of both regions* (i.e., the Baltic and Canadian shields – *Ya.Yu., M.K.*) *are represented by quartz-carbonate-biotite types of profiles with single segregations of andalusite, cordierite and other products of kaolinite metamorphism*" [200, p. 44]. It seems, however, that kaolinite cannot be formed during arid weathering. Likely, in these regions, kaolinite was formed in humid weathering episodes, which took place against the background of longer arid epochs. As for cordierite, as shown by E.T. Bobrov and I.G. Shchipakina's experiments [21], it is formed of chlorite.

However, 12 years before A.I. Pak's generalizing summary, back in 1975, N.N. Verzilin energetically emphasized the specificity of arid weathering, based on his experience in studying arid Cretaceous strata of the Fergana depression: "*With the same level of relief in a hot humid climate, weathering crusts are formed that are qualitatively different from those arising in the arid climate zone. Naturally, sedimentation of the same age with weathering crusts will also differ significantly in both climates <…> It seems appropriate to emphasize that in arid conditions the processes themselves proceed significantly differently than in humid ones, and that the development of kaolinite weathering crusts under such conditions is out of the question*" [50, p. 22].

The main reason for the specificity of arid weathering is the alkaline environment: "*As you know, weathering in an arid environment is usually characterized by an alkaline or neutral environment <…> in contrast to the predominantly acidic environment of the kaolinite weathering crusts formation <…> We should expect that <…> not only the direction of clay minerals formation <…> will be different, but also the stability of many other components of weathered rocks. A similar conclusion follows from the data obtained by A.S. Zaporozhtseva (1968) in an experimental study of the dissolution of several detrital minerals, and from the I.I. Ginzburg's instructions that potassium-sodium feldspars in a neutral, and even more so an alkaline environment do not release free energy during decomposition and therefore are stable. According to this researcher, in an alkaline environment and weak water exchange <…> the formation of mica and even feldspars from kaolinite + silicic acid + potassium is more likely than the decomposition of mica into kaolinite*" [50, p. 22].

In 1972, in the book Fundamentals of Geochemistry, the prominent Soviet geochemist V.V. Shcherbina devoted much space to the problem of arid weathering. "*Depending on the average annual temperature and humidity, two types of weathering are distinguished: arid (anhydrous), characteristic of a hot dry climate, and humid (damp, moisture), characteristic of a temperate climate with high humidity.*

The arid type is characterized by an alkaline weathering process, because during the decomposition of an ordinary deep-seated rock, weak silica acid is not able to neutralize the K_2O, Na_2O, CaO, MgO *liberated during the silicates' decomposition. The dryness of hot air does not favor the vegetation development, scarce plant residues quickly oxidize (decay) without forming soil acids. Decomposition products remain in place, and only soluble alkaline salts are removed to some extent by the water. They carry with them silica acid (in the form of soluble silicates) and partially alumina (in the form of aluminates) <…> Under arid weathering, oxidative processes predominate, intensified by the fact that in an alkaline environment the redox potentials strongly decrease, favoring the oxidation of lower oxides to higher ones by oxygen (for example,*

$Mn^{2+} \rightarrow Mn^{4+}$), *which is impossible under acidic conditions, because the potential of this reaction (+ 1.35 V) is higher than the decomposition potential of water with the oxygen release (+1.23 V)*" [282, pp. 199–200].

One of the predicted consequences of such weathering should be an increase in TM in the weathering products, since alumina, according to V.V. Shcherbina, is partly removed, and titanium in an oxidizing environment should be immobile. It is possible that this is the reason for the rather noticeable (and higher than in the original granites) TM values in some red-colored arkoses and shales of the first cycle type. In the diagenesis of red-colored sediments, characteristic changes in the mineralogical and, accordingly, chemical composition can occur. Indeed, according to microscopic observations of N.N. Verzilin, in arid Cretaceous sandstones and siltstones of Northern Fergana, the content of quartz grains and especially fragments of silica rocks decreases in the direction from the source area into the depths of the sedimentary basin; it noticeably decreases in the sections located relative to the source of drift further only by 10–20 kilometers. Since the source area in the compared sections was clearly the same, N.N. Verzilin explains the observed picture by diagenetic dissolution and silica removal in the alkaline environment of the arid basin. A paradoxical result is obtained: the detrital rock is enriched with feldspars that are relatively unstable in hypergenesis. Obviously, a similar effect should be expected in the arid weathering crust.

It is curious that the relative concentration of feldspars occurs more intensively in siltstones than in sandstones, which, "*perhaps, sometimes should be explained by the greater ease of dissolution during diagenesis of relatively small grains composed of silica than larger grains*" [49, p. 1184]. Consequently, we can assume that arid arkose siltstones (due to both weathering and diagenesis) should differ from the arkose sandstones associated with them not only by a higher HM (which is characteristic of any siltstones), but also by a higher NKN value, that is not inherent to humid siltstones, of course (the presence of a clay fraction in siltstones always decreases the NKM but does not increase). This means that an increase in NKM in the series sandstone coarse-grained → sandstone fine-grained → siltstone → argillite (?) is a diagnostic sign of arid deposits.

If arid weathering develops over an acidic substrate, then high-potassium products are formed – shales and arkoses. If ultrabasic rocks are the substrate, then *an unusual paragenesis of hydrolysates and silites* may be evidence of arid weathering. This picture is due to the epigenetic *silicification* process, manifested, for example, in Precambrian serpentinites in the basement of the Russian Platform. A.D. Savko and A.D. Dodatko describe this process as follows: "*The formation of silification zones, in our opinion, proceeded as follows. As a result of the impact on the serpentinites of atmospheric waters, alkaline earths were performed. At the same time, calcium and magnesium in the* *form of bicarbonates migrated downward. Slightly lower along the profile, calcite sedimented in the form of* $CaCO_3$, $MgHCO_3$ *was discharged from the profile <...> In dry periods, water moved upward along the capillaries, and their alkalinity was increased (a small amount of water and a large amount of alkaline earth elements). In this environment, silica became mobile <...> and migrated up the profile, falling out during evaporation*" [233, p. 200].

The process of silicification developed even more vigorously during the weathering of serpentinite with sulfide dissemination: "*When acidic solutions acted on serpentine, magnesium ions were released, which, being strong electrolytes, caused the coagulation of silicic acid. In addition, the silicification of rocks in the mineralization zone could be performed as a result of the silica sedimentation from the true solutions carrying silicon ions. Alkaline solutions, getting into the oxidation zone, where the pH of water as a result of the sulfides decomposition was less than 7, were neutralized, which led to the* SiO_2 *sedimentation*" [233, p. 200–201].

8.7. Gley process – the leading type of pre-Riphean weathering

We have seen that, with respect to at least the pre-Riphean weathering crusts, all researchers' data are in good agreement with each other and indicate the predominance of rock-forming elements removal from the WCr – not only sodium and calcium, but also silicon and aluminum, although their mobility was, of course, not the same. Such a process is possible with weathering in an atmosphere rich in carbon dioxide; researchers of ancient weathering crusts came to this conclusion long ago. By analogy with the modern process described in soil science and introduced into the geochemistry of hypergenesis by A.I. Perelman, ***we will call carbon dioxide weathering in a reducing (but not hydrogen sulfide) environment a gley process.*** The most obvious modern gley process is the rocks clarification due to the removal of trivalent iron compounds from them.

However, the modern gley process develops at relatively low CO_2 contents in ground and groundwater, amounting to 0.n% CO_2 or HCO_3. Although this is by an order higher than the CO_2 concentration in the modern atmosphere (about 0.03 % or $P_{CO2} = 3 \cdot 10^{-4}$ atm), it is significantly lower than the CO_2concentration in the early Precambrian atmosphere. Therefore, the only pore-forming element capable of migration in the modern gley process is iron, which is reduced to Fe^{2+} and migrates in the form of $FeHCO_3$. In the atmosphere (and hydrosphere) of the Early Precambrian, the CO_2 content is believed to be by three orders higher than the current one, and the pressure was several tens of atmospheres and contributed to the CO_2dissolution even in hot waters. For example, presumably syngenetic gas bubbles from quartzites of the Iyengra complex on the Aldan Shield (collection of L.I. Salop) contained about 61% CO_2, and about 35 % was the sum of H_2S, SO_2, NH_3, HCI, and HF; 44 % CO_2 and 31 % of the sum of H_2S, HF, NH_3 were found in bubbles from pebbles of Karelian Upper Archean quartzites, and 32 % CO_2 from Karelian phtanites [121, p. 8]. If we resort to an actualistic assessment of the Catarchean atmosphere composition according to the modern volcanic exhalations composition, the CO_2 content in it should be at least 10% [234, p. 56], which is also by three orders higher than the present day.

Thus, it is possible to outline in general terms the specifics of the ancient gley process.

First, it was stronger than the modern one due to much higher (300—1000 times) CO_2 content in the atmosphere and, accordingly, in meteoric waters.

Second, the absence of such strong complexing agents as humic acids (without which the laterite process is inconceivable) could be partly compensated by the presence of volcanogenic acid gases in the atmosphere and, respectively, strong acids (HCI, HF, H_2SO_4) in waters.

Third, the increased average temperatures on the Earth's surface, reducing the solubility of acid gases in water, greatly accelerated the course of dissolution and hydrolysis reactions. The increased atmospheric pressure also acted in the same direction, which, according to some estimates for the Catarchean, was 50—60 bar. If in the modern ocean only 3 cm^3/l of CO_2 is in equilibrium with the atmosphere, then at $P_{CO2} = 20$ bar and $T = 1200$ °C this content will be 5000 cm^3/l [234, p. 56].

All this means that deep decomposition of magmatic rocks to their constituent components: Al_2O_3, Fe_2O_3, SiO_2 with the formation of corresponding chemogenic sediments in the form of corundites, iron ores, and ferrous quartzites, as well as products of authigenic resynthesis, was quite possible in the Catharchean weathering crusts from solutions in the form of ferrous chlorites and other silicates.

In the Karelian eon, all the parameters of the gley process became lower (temperature, pressure, and concentration of CO2 and acid gases in the atmosphere) and, apparently, the alumina removal and silica from the weathering crust apparently stopped. The most important event was the appearance of free oxygen in the atmosphere about 2.2 billion years ago at a level of about 0.01 of the present, which should have prevented the mass removal of iron from the weathering crust into the ocean. It is to this milestone that the appearance of the most ancient red-colored strata on Earth is timed [300, p. 234—235].

It can be assumed that in the Late Archean and up to the middle of Karelian, at the first stages of gley weathering, there was an effective removal of bases in the form of soluble carbonates and bicarbonates (Ca, Na, Fe^{2+}, and partly, apparently, Al in davsonite-type compounds). As alkalis accumulated in pore solutions due to hydrolysis, first of all, K_2CO_3 and Na_2CO_3, the pH of these solutions should have become alkaline, which led to the sedimentation of sparingly soluble carbonates: calcite and dolomite. This is how carbonates could have formed in the middle and lower horizons of the ancient WCr. In this very general, rough scheme, significant adjustments were made by the climate: the process, apparently, was significantly different in arid and humid conditions. It can be assumed that if there was no noticeable accumulation of potassium feldspar in the ancient WCr, then the process was predominantly humid (weakly acidic). However, such humid (sub-humid or myo-humid, in A.I. Pak's terminology) weathering was not an analogue of the post-Silurian laterite process.

So, the foregoing shows the impossibility of a uniformitarian (actualistic) comparison of the Meso-Cenozoic weathering with the Precambrian one, at least with the Archean and Karelian. In this situation, for the reconstruction of the process, in addition to direct observation of its products (which, unfortunately, are subject to transformations when superimposed by allochemical metamorphism), experiment and thermodynamic modeling are of decisive importance.

S.A. Kashik and I.K. Karpov performed a computer simulation of the granodiorite weathering at different CO_2 partial pressures and at different Eh (P_{gen} = 1 atm, 25 °C). The open-closeness condition of the fluid-rock metasomatic system was also varied. Modeling has shown that under reducing conditions (Eh, close to zero or less), "*there is a clear tendency of an increase in the aggressiveness of the geochemical environment of hypergenesis with an increase in the* CO_2 *content in the atmosphere. First of all, this manifests itself in a sharp increase in the rocks solubility, starting from the value* $P_{CO2} = 10^{-2}$ *atm. Dissolution and removal of matter from weathering crusts seem to become the dominant processes of hypergenic rocks transformation, if* P_{CO2} *is within 0.1–1 atm., as newly formed phases, in this case kaolinite, appear at relatively late stages of hydrolysis. In such physicochemical environment conducive to the mass migration of all elements without exception, the differentiation of aluminum and silicon could not occur or occur on a very insignificant scale. In an acidic environment of hydrolytic decomposition of granodiorites (pH 4.0–4.4),* Al *and* Si *pass into an aquagenic solution in comparable amounts. In the field of solutions for pressures of* $CO_2 > 0.1$ *atm, the* Al/Si *ratio becomes constant and equals 0.5. This leads to the fact that gibbsite (or diaspore) disappears in the rear zone of the metasomatic column of the weathering profile. Kaolinite becomes the predominant mineral in the upper zone of the weathering crust, and when* P_{CO2} *approaches the upper limit (*10^{-66} *atm), pure kaolin clays are formed, devoid of any admixture of iron-bearing minerals.*

High content of carbon dioxide in the atmosphere ($P_{CO2} > 1.0–1.5$ *atm) leads to the disappearance of the mixed-layer silicates zone – montmorillonites* *and chlorites – in the hypergenic metasomatic column, and its place is occupied by a silica-carbonate zone, which contains kaolinite in varying amounts. This composition is well comparable with the metamorphosed Precambrian weathering crusts. For example, sericite-carbonate-quartz shales on plagiogranites of the Krivoy Rog basin can be considered as a metamorphosed analogue of the kaolinite-silica-carbonate horizon <...>"* [127, p. 56–57].

The same calculations showed why, with a high carbon dioxide content in the ancient atmosphere, one should not expect free alumina minerals to weather in the crusts – the latter begin to form only at P_{CO2} values from $10^{-1.5}$ atm and below. At the same time, the filtration mode is of great importance:

"*The emergence of all theoretically predicted zones is possible only in those cases when continuous filtration of water through the rocks is ensured at a rate sufficient to establish partial equilibrium between the percolating solution and newly formed minerals along the entire length of the metasomatic column. Extremely strong drainage and a high rate of water filtration lead to the formation of predominantly one upper zone, since, due to the short term contact of circulating solutions with the original rocks, the concentrations of dissolved components are maintained at a level close to the initial process stages. On the contrary, in a stagnant hydrodynamic regime in the weathering zone, mineral associations mainly develop, corresponding to high degrees of the rainwater interaction with rocks*" [127, p. 57–58].

If the metasomatic system "rainwater-rock" is open with respect to atmospheric CO_2 (i.e., P_{CO2} is always at the atmospheric level), then its evolution under the conditions of a flushed (but not too rapid) regime can lead to the formation of a complete metasomatic columns (gibbsite + goethite → kaolinite + goethite → montmorillonite + carbonates). If the system is isolated from the atmosphere, then the seeping water quickly alkalizes and "*the process practically ends in the kaolinite-goethite zone with* pH 9" [127, p. 58].

Note on our own that these remarkable results clearly explain the "gingerbread" phenomenon in Indian and African laterites when the gibbsite (or gibbsite-goethite) crust lies directly on fresh dolerite – in the absence of intermediate weathering crust zones. The point is that such "gingerbread" is observed *on the slopes* of hills, while full laterite profiles develop on their tops. Obviously, rainwater quickly rolled down the slopes (and not slowly filtered, as on flat tops) and therefore only the WCr rear zone had time to form.

Brief conclusions

1. The study of ancient (usually metamorphosed) weathering crusts is of key importance for understanding the evolution of the Earth's atmosphere and hydrosphere. Two approaches stand out here: uniformitarian (actualistic) and evolutionary. Adherents of uniformitarianism consider the main

similarities between ancient (Precambrian) and Phanerozoic lithogenesis, while evolutionists emphasize the features of their differences. Judging by the largest modern generalizations by Yu.P. Kazansky, L.I. Salop, A.I. Pak, A.D. Savko and A.D. Dodatko, E.T. Bobrov and I.G. Shchipakina, the ideas of evolutionism are now clearly dominant in literature. Most researchers have already agreed that in the Precambrian (especially in the Early Precambrian) there could not be a full-profile lateritic weathering crust on the Earth.

2. In our opinion, the question of the existence of terrestrial weathering crusts in Catharchean is no longer relevant. Hydrolysate shales of the Pilbara block (Western Australia), as well as chemically differentiated products, clastogenic quartzite-metasandstones and corundites, are indirect evidence of such crusts. The question of whether the latter can be considered eluvial and terrigenous-clastic formations is still not clear, although it seems to us that the data in favor of their chemogenic-sedimentary nature are weightier.

3. Throughout the Late Archean, Karelian and Riphean, during the existence of the supercontinent – ancient Pangei – epochs of arid and subarid climates prevailed on Earth. In these epochs, high-potassium weathering crusts were formed on the acidic substrate, and on the basic and middle substrates – more hydrolysate WCrs, but with the retention of a significant magnesium amount in them. The migration of calcium and magnesium along the WCr profile led to the formation of epigenetic carbonates (caliche). Geological evidence of the alkaline arid WCrs' wide development is the thick red-colored strata of Karelian and Riphean, in which high-potassium arkoses are associated with high-potassium clay shales containing orthoclase, – residual or authigenic.

4. The periods of the Pangei split were distinguished by the humidization of the climate. At this time, in the ancient weathering crusts, despite the absence of soil acids, kaolinite could form, as evidenced by the presence of alumina minerals, obvious derivatives of kaolinite, and sometimes kaolinite itself, – and in more ancient WCr, up to the Upper Archean.

5. Both humid and arid weathering in the Early and Middle Precambrian had the character of a reducing gley process. One can consider this proven based on the study of ancient weathering crusts, the profiles of which are very different from the Meso-Cenozoic, as well as based on numerical computer simulations performed by S.A. Kashik and I.K. Karpov.

6. At the same time, it is undoubted that all our judgments about the ancient and most ancient WCrs, represented by deeply metamorphosed rocks, are very complicated by the phenomenon of allochemical metamorphism, which can also generate chemically differentiated (in particular, alumina) rocks. The next chapter is devoted to a detailed analysis of the *metahydrolysates composition convergence*.

CHAPTER 9

GEOCHEMICAL CONVERGENCE OF HYDROLYSATES

9.1. On the convergence of the endo- and exogenous hydrolysates composition

According to the Geological Dictionary [70, vol. 1, p. 350], convergence is understood as “The formation of products of a similar type from different sources and in different ways.” According to D.I. Tsarev [267], a clear formulation of the convergence idea (“heterogenesis”) in petrology goes back to F.Yu. Levinson-Lessing, and the philosophical analysis of this idea in modern geology is given in the works of G.L. Pospelov. A.A. Sidorov, who devoted a problematic article to convergence with the expressive title “The Depths and Damnations of Convergence,”[1] argues that no convergence can create identical objects; it is only necessary to find alternative diagnostic signs of convergent objects.

Within our topic, we will be interested in the convergence of the material composition of metamorphic and metasomatic[2] rocks belonging to the hydrolysates type.

Fluid moving through the rock porous medium reacts with minerals, leaching some of them and precipitating others (newly formed). D.S. Korzhinsky discovered the mechanism of these processes by in the 1950s. He showed that there is “the formation of several simultaneous sharp replacement fronts, on each of which one of the minerals of the rock undergoes complete replacement. During infiltration metasomatism between these sharp replacement fronts, no changes in the rock occur” [142, p. 10–11]. As a result, a metasomatic column is formed, consisting of separate well-distinguishable zones of different mineral composition. As we can see, neither

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[1] Bulletin of the Russian Academy of Sciences, 1996. Vol. 66, No. 9. P. 836--840

[2] Following A.A. Marakushev [204], we consider metasomatism as *allochemical metamorphism*. In this sense, near-ore hydrothermal argillisites are also metamorphic rocks.

the temperature nor the composition of the fluid is specified – these factors, although important, do not determine the process itself. In particular, the eluvial weathering crust (WCr) is nothing but a low-temperature (hypergenic) infiltration metasomatic column [128]. This circumstance is the objective reason for the surprising similarity of the chemical and mineral composition of metamorphosed weathering crusts with endogenous high-temperature metasomatites.

The seriousness of this dilemma (ancient hypergenesis or thermal metasomatism?) is confirmed by the evidence of prominent metamorphic geologists: "In relatively low-temperature zones and at high chemical potentials of potassium, characteristic quartz-muscovite shales arise (quartz-muscovite facies of acid leaching – Korikovsky, 1967), which often develop in granitoid shearing zones. When these zones appear at the boundary between supracrustal strata and granites, they become similar to metamorphosed chemical weathering crusts both in their geological position and composition. Only with careful lithological and petrological studies can these formations be distinguished from each other <...>" [257, p. 22].

It may seem that a significant difference in the geological settings of formation of metahydrolysates of different types should provide a criterion for their recognition. Unfortunately, the structural and tectonic features also turn out to be convergent, since the same structural factors are equally favorable for the formation of both endogenous and hypergenic metasomatites, primarily the increased substrate permeability. For example, such a striking structural-tectonic feature as the metahydrolysates localization near the surface of large structural unconformities is by no means a decisive proof of their eluvial-crustal nature. As V.N. Razumova emphasizes, "the surface of the ancient peneplain, as the boundary line of two structural floors, is a zone of increased permeability, and the sedimentary platform cover acts as a screen, which in turn contributes to the localization of the metasomatic leaching and cementation processes near the boundary with the platform foundation – supplier deep solutions and gases that activate groundwater" [220, p. 84].

In particular, in the Subpolar Urals, on the ridge Maldynyrd, the interformation contact of the Uralides (Cambrian–Carboniferous) sequencees with the Pre-Uralides (Riphean–Vendian) strangely coincides with the zone of the large Maldin fault, where aluminous and ferruginous metahydrolysates are developed [111, 304]. It can be assumed that the very location of the Maldin fault was predetermined by the position of the interformational contact. If ancient pyrophyllite and sericite slates existed at this contact, they inevitably created a weakened zone along which tectonic stresses were relieved. Moreover, these slates were an ideal natural "lubricant" along which large blocks of massive conglomerates (the Uralides bottom) or rhyolites (the Pre-Uralides top) could slip. Such an idea is quite consistent with the now fashionable concept of "tectonic layering of the lithosphere."

Usually, the morphological criterion also turns out to be insufficiently informative: neither the stratiformity nor the linear orientation of bodies of problematic genesis, composed of hydrolyzed rocks, can in themselves serve as a reliable diagnostic feature.

Finally, the problem of recognizing convergent hydrolysates becomes especially difficult when it comes to ancient polymethomorphic sequencees, during the formation of which (by definition!) overlapping thermal processes of different ages took place. Here the problem comes down to the old discussion: was metamorphism isochemical or allochemical?

In the most clear and detailed form, the convergence ideas of metahydrolysates features of different genesis were formulated by V.N. Razumova in her remarkable book [220].

In 1977, V.N. Razumova, a well-known expert on weathering crusts, published a sensational book in which, based on a large amount of factual material, she seemed to "break with her eluvial past" and sharply criticized the concept of ancient metamorphosed weathering crust. Most of these objects, in her opinion, are products of hydrothermal-metasomatic processes, and not metamorphosed ancient eluvium. The views of V.N. Razumova seemed so radical to her colleagues at the Geological Institute of the USSR Academy of Sciences that the book was even preceded by a special preface by E.V. Shantser, designed to warn the orthodox reader from rejecting such heretical ideas at the very beginning.

However, the significance of V.N. Razumova's book lies not in the fact that she overthrew the old dogmas and approved new views – in our opinion, she failed to do either. ***The book by V.N. Razumova is remarkable in that in it the very problem of convergence of leaching and hydrolysis metamorphosed products was posed with extreme sharpness.***

V. N. Razumova emphasizes that the eluvial-soil nature of hydrolysates (products of "metasomatic leaching") cannot by any means be accepted without evidence, although this style of thinking has become customary: "Having stamped "weathering crust" on this or that deposit, the researcher calms down and stops analyzing the geological material, thus considering all issues of genesis resolved" [220, p. 11]. Hydrolysate products that develop in the folded basement roof of ancient platforms require special attention – they are usually identified with ancient weathering crusts: "The doctrine of ancient weathering crusts has become extremely fashionable in recent years, therefore, along with the recognition of the endogenous factors participation in the formation of some weathering crust deposits many formations began to be attributed eluvial origin without sufficient grounds for this <...>

Thus, if weathering crusts were originally understood as products of surface leaching, then historically it turned out that the sequence of ancient weathering crusts also included products of hydrothermal-vadose leaching – clay metasomatites of fault zones, and sometimes even hydrothermal formations proper, with which one cannot agree < ...> At present, a serious revision of the materials on ancient weathering crusts is needed in order to clearly distinguish the products of hydrothermal-vadose leaching from hydrothermal proper, as well as soil-eluvial formations" [220, p. 9–10].

Having cited several convincing examples proving, firstly, the development of hydrolysate products on the basement blocks uplifted along faults, and secondly, the strongest development of linear-type WCr precisely in the fracture zones associated with faults, V.N. Razumova argues that in all such cases, the formation of hydrolysis products was the result of an endogenous ("hydrothermal-vadose") process. If eluvial WCrs could form later on, then, in her opinion, they must certainly have been superimposed on older, high-temperature metasomatites. Thus, V.N. Razumova does not allow the development of ancient eluvial WCrs directly over the primary substrate of fresh basement rocks.

In order to develop methods for recognizing convergent metahydrolysates of different genesis, we first consider the lithochemical features of such objects, the genesis of which is considered to be more or less established, and then we study some objects of disputed genesis. In concluding this chapter, we will attempt to formulate several empirical criteria for the genetic diagnosis of hydrolysate products.

9.2. Hydrolysate formations of endogenous nature

Among these objects one can distinguish: a) postmagmatic, closely associated with volcanics, b) associated with areas of regional progressive granulite and retrograde metamorphism – amphibolite and lower grade one.

Metasomatic formation of secondary quartzites. According to A.D. Rakcheev, the term "secondary quartzites" was introduced at the beginning of the 20th century by E.S. Fedorov to designate a special type of near-ore changes in rocks. As a result of extensive geological research, among which the fundamental works of N.I. Nakovnik stand out, it has now been established that secondary quartzites are naturally associated with the stages of development of mobile ("geosynclinal") zones [204, p. 262].

The bodies of secondary quartzites form the so-called "massifs", i.e., zones of areal hydrothermal alteration and clarification of rocks with up to tens of square kilometers area. They are either isometric in plan (if formed at the apical part of intrusions or around volcanic centers) or linear if they are controlled by fault zones or the strike of permeable rocks such as tuffs. "*Massifs of secondary quartzites are formed on the site of acidic and medium volcanic rocks: lavas, lava breccias, tuffs, tuff breccias, tuff agglomerate-breccias, as well as porphy-*

ritic granitoids. Metasomatites of identical mineral composition are formed in all these rocks, only the quantitative ratios of minerals vary somewhat depending on differences in the contents of such low-mobile components as alumina and titanium oxide in the original rocks" [204, p. 262].

A characteristic feature of the secondary quartzites formation is a rough mineral zoning: from the propylitization zone on the periphery, through the weak change zone, to the strong change zone in the central part. As the mineral parageneses change, they gradually become depleted and, in the limit, approach the monomineral one. This zonation is also observed in the vertical section, but the roughly symmetrical arrangement of the zones is very important, i.e., the location of the most altered rocks in the center with decreasing alteration degree both upwards and downwards (which never happens in the eluvial WCr profile).

The typomorphic minerals of the secondary quartzite formation are:

1) quartz, and in near-surface subvolcanic facies also opal, chalcedony, cristobalite, and tridymite.

2) sericite-muscovite, and in low-temperature near-surface facies – light hydromica, sometimes sodic (on the substrate of andesites).

3) high-alumina minerals: andalusite, diaspore, pyrophyllite, alunite.

4) halide silicates: zuniite $Al_{12}(OH, F)_{18}\cdot[AlO_4Si_5O_{20}]Cl$ and topaz $Al_2\cdot[SiO_4]\cdot(F,OH)_2$.

5) borosilicate dumortierite $(Al, Fe)_7\cdot[BSi_3O_{18}]$ and much less frequently – boratosilicate tourmaline.

Let us give several examples of hydrolysate formations, which can be attributed to the formation of secondary quartzites by the totality of features.

Pyrophyllite and diaspore metasomatites over the volcanic substrate. These formations include: metasomatites after Riphean volcanic rocks described in the zone of the Ovruch rift; pyrophyllite rocks on an acidic substrate in pyrite deposits, described in the book by V.V. Zaikov et al. [107], acid apovolcanites studied by A.V. Govorova in the South Urals [79], and by B.A. Goldin et al. in the Northern Urals [8], diaspore apovolcanites among carboniferous tuffs of Kazakhstan [146], Jurassic apovolcanites of Armenia [205], as well as specific formations – dumortierite concretions.

Ovruch rift zone. Pyrophyllite rocks are described here, which are considered metasomatites based on the substrate of Riphean volcanic rocks of intermediate and felsic composition [107]. Judging by the ratio of alkalis and alumina, one can distinguish here (Table 121, Fig. 93) quartz-pyrophyllite rocks (clusters I, II and samples 8, 3) and quartz-mica-pyrophyllite (clusters III–V). Apparently, they form a genetic series (arrows in Fig. 96), and the loss of mica may initially be accompanied by silicification (clusters III ⇒ IV), but as the amount of pyrophyllite increases, quartz is also leached, which

Table 121

Chemical composition of the Riphean pyrophyllite rocks of the Ovruch rift zone. *Compiled according to V. V. Zaikov et al., 1989 [107, p. 28]*

Oxides and modules	I	II	III	IV	V	3	6	8
	Myosilite	Super-siallite	Myosilite		Normo-siallite	Normosiallite		Myosilite
n	2	2	2	4	2			
SiO_2	76.24	59.62	71.56	76.53	67.15	68.13	67.50	77.19
TiO_2	0.65	0.62	0.62	0.58	0.69	0.86	0.54	0.67
Al_2O_3	14.98	29.95	15.10	13.05	16.38	19.61	17.41	14.70
Fe_2O_3	4.61	1.11	5.04	2.51	6.39	7.03	3.56	1.61
FeO	0.37	0.00	-	-	-	0.00	1.44	-
MnO	0.02	-	-	-	-	0.00	-	-
MgO	0.11	0.03	0.85	1.11	1.78	0.16	1.38	0.40
CaO	0.18	0.15	0.48	0.26	0.37	0.40	0.12	0.37
Na_2O	0.07	0.28	0.22	0.20	0.25	0.00	4.23	0.16
K_2O	0.18	0.12	2.59	2.89	3.68	0.20	-	1.52
P_2O_5	0.05	-	0.00	0.00	0.00	0.01	-	0.00
S	0.03	0.08	0.07	0.12	0.02	0.04	0.10	0.10
LOI	2.83	7.96	3.13	2.65	3.13	3.66	3.68	2.83
Total	100.32	99.92	99.66	99.90	99.84	100.10	99.96	99.55
HM	0.27	0.53	0.29	0.21	0.35	0.40	0.34	0.22
FM	0.07	0.02	0.08	0.05	0.12	0.11	0.09	0.03
AM	0.20	0.50	0.21	0.17	0.24	0.29	0.26	0.19
TM	0.043	0.021	0.041	0.044	0.042	0.044	0.031	0.046
FerM	0.32	0.04	0.32	0.18	0.37	0.34	0.28	0.10
NKM	0.02	0.01	0.19	0.24	0.24	0.01	0.24	0.11
AlkM	0.40	2.30	0.10	0.10	0.10	0.00	-	0.10

leads to an increase in HM (cluster I ⇒ sample 3 ⇒ cluster II). Sodium composition of sample 6 seems to reflect the albitization process, which may be the result of sodium removal.

The compact shape of the clusters is explained by significant preliminary averaging: most of the analyzes are averages of materials obtained by the authors from 2–67 analyses. For example, point *8* is the average of six analyses. Note that, if desired, pyrophyllite rocks can be interpreted not as metasomatites of a secondary quartzite formation, but as formations of ancient WCr after the Riphean substrate; however, the first diagnosis here looks much preferable.

Gay and Kyrvakar deposits. Pyrophyllite rocks are also described at the Gay sulfur-pyrite deposit. All nine compositions given by V. V. Zaikov et al. [107] are averages of 2–11 analyses. But even such averaging does not eliminate *the strong dispersion of compositions characteristic of allochemical*

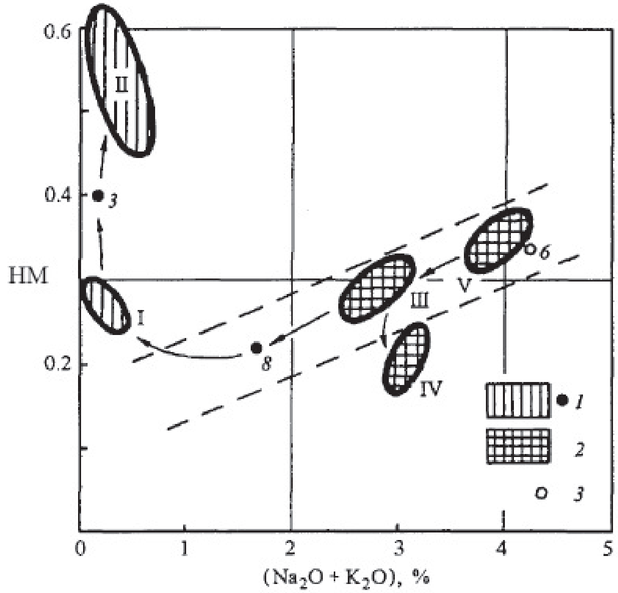

Fig. 93. Module diagram for pyrophyllite rocks of the Ovruch rift zone. *Compiled according to V. V. Zaikov et al., 1989 [107, p. 28].* 1, 2 – pyrophyllite rocks: low-mica (1), mica (2); 3 – quartz-albite (?)rocks. *Arrows*– the proposed sequence of rock formation

metamorphism. Varieties of metasomatites can also be distinguished here, corresponding, on the one hand, to quartz-sericite and sericite rocks, and, on the other hand, to highly variable pyrophyllite rocks with somewhat different total alkalinity.

At the Kyrvakar deposit in Armenia, metasomatites after Upper Jurassic tuffs are described: pyrophyllitized (norm- and supersiallites), alunitized (sulphurous supersiallites), and kaolinized (normohydrolysates). The six analyzes of these rocks given by V. V. Zaikov and colleagues represent the average of 4–17 analyzes [107]. It is curious that there is a positive correlation in the TM – FerM plot, which indicates a genetically unified series of metasomatites, the substrate of which was intermediate or basic rocks.

Pyrophyllite rocks of the Kul Yurttau deposit. These rocks are considered metasomatites based on the rhyolite substrate [107]. The 37 analyzes presented by V. V. Zaikov and co-workers (of which 29 represent the *average* of 2–16 analyses) clearly show the picture of allochemical metamorphism. As can be seen from the module diagram (Fig. 94) and Table 122, there is a dispersion of HM, NKM, and FerM values (the latter is partly due to intense pyritization of some rocks). Fluctuations in HM and NKM reflect varia-

Table 122

Average chemical composition of pyrophyllite metasomatites of the Kul-Yurttau deposit (Bashkiria, D_2–C).
Compiled according to V. V. Zaikov et al., 1989 [107, p. 47–48]

Oxides and modules	Ia	Ib	Ic	ld	le	II	III	IV	V
	Normo-silite	Myosilite	Normosilite				Super-siallite	Alkaline hypo-hydrolysate	Normo-hydrolysate
	6	2	11	3	3	3	4	2	3
SiO_2	84.54	75.89	82.68	82.08	82.30	82.23	59.58	45.27	42.61
TiO_2	0.25	0.42	0.22	0.25	0.25	0.21	0.66	0.63	0.96
Al_2O_3	11.24	17.20	12.29	12.16	12.44	11.48	30.88	36.59	46.10
Fe_2O_3	0.09	0.35	0.26	0.19	0.31	0.37	0.14	0.30	0.14
FeO	0.47	0.78	0.65	0.65	0.25	0.49	0.26	0.11	0.11
MnO	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.02	0.03
MgO	0.21	0.24	0.23	0.15	0.32	0.38	0.09	2.51	0.05
CaO	0.10	0.17	0.23	0.18	0.20	0.17	0.08	0.85	0.05
Na_2O	0.06	0.26	0.23	0.31	0.43	0.54	0.46	2.21	0.31
K_2O	0.10	0.39	0.43	0.66	1.02	1.98	1.35	4.74	0.49
P_2O_5	0.03	0.04	0.02	0.01	0.05	0.05	0.07	0.04	0.12
SO_3	0.10	0.05	0.04	0.05	0.05	0.05	0.06	0.05	0.06
LOI	2.65	4.15	2.56	3.00	2.54	1.85	6.11	6.54	9.15
Total	99.87	99.96	99.87	99.72	100.19	99.83	99.77	99.86	100.18
HM	0.14	0.25	0.16	0.16	0.16	0.15	0.54	0.83	1.11
FM	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.06	0.01
AM	0.13	0.23	0.15	0.15	0.15	0.14	0.52	0.81	1.08
TM	0.022	0.024	0.018	0.021	0.020	0.019	0.021	0.017	0.021
FerM	0.05	0.07	0.08	0.07	0.05	0.08	0.01	0.01	0.01
NKM	0.01	0.04	0.05	0.08	0.12	0.22	0.06	0.19	0.02
AlkM	0.60	0.70	0.50	0.50	0.40	0.30	0.30	0.50	0.60

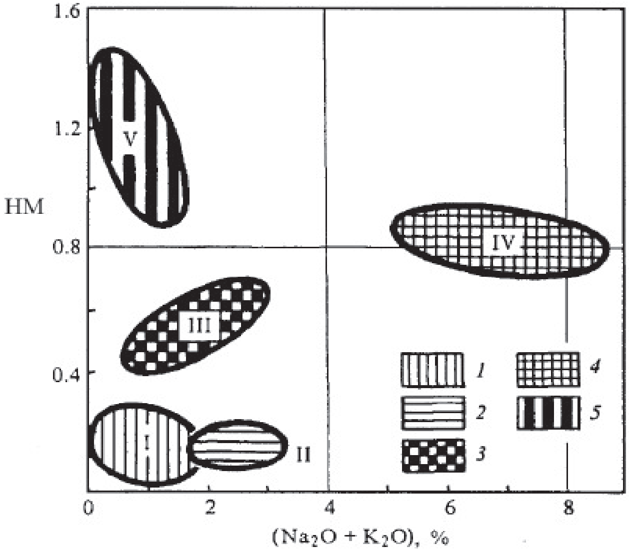

Fig. 94. Module diagram for pyrophyllite metasomatites of the Kul-Yurttau deposit (Bashkiria, D_2–C).

Compiled according to V. V. Zaikov et al., 1989 [107, p. 47–48].

Shales: 1 – sericite-pyrophyllite-quartz, 2 – quartz-pyrophyllite, 3 – (1+2+5), 4 – pyrophyllite-sericite, 5 – with diaspore

tions in the contents of pyrophyllite, diaspore, and quartz. Two groups of altered rocks are clearly visible, corresponding, as it were, to two branches of the metasomatic process: pyrophyllitization with the destruction of feldspars and the removal of alkalis (a number of clusters II ⇒ Ie ⇒ Ia) and the removal of silica with pyrophyllite and diaspore accumulation (a number of clusters III ⇒ V). A special group is formed by pyrophyllite-mica rocks (cluster IV), which, in terms of alkali content, can reach the level of alkalites (these rocks are referred in the original source as "secondary quartzites"). Apparently, these rocks represent a relic of the first – alkaline – stage of metasomatism (sericitization). They may correspond to the frontal zone of the metasomatic column. Low-alkaline pyrophyllite quartzites can correspond to its middle zone, and almost alkali-free diaspore-pyrophyllite rocks can correspond to its rear zone.

Note that the highlighted by V.V. Zaikov et al. [107] petrographic varieties – "pyrophyllite-quartz and quartz-pyrophyllite (low-alkaline) shales", "sericite-pyrophyllite-quartz shales, pyrophyllite-sericite-quartz, sericite-pyrophyllite (alkaline)", "shales with diaspores (aluminous)", as well as "secondary quartzites (apoextrusive)" – in some cases show a close chemical composition; thus, the first three varieties were found within cluster II. In cluster Ib – first and second varieties, in cluster Ia – second and fourth. This example once again shows the advantage of chemotypes over lithotypes. The corresponding (more correct) typification of rocks is given by us in the caption to Fig. 94.

Acidic apovolcanites of the Northern Urals. The diagnostic features of these metasomatic rocks, which were formed on the substrate of the Rifean–Vendian rhyolites [8], are not only the presence of alkalites among them (7 out of 16 analyzes), but also, mainly, an unusually wide range of normalized alkalinity NKM, which is not characteristic of sedimentary rocks: from 0.33 to 0.78 (Table 123, Fig. 95). This reflects variations in the contents of rock-forming sericite, pyrophyllite, and K-feldspar. An increase in the proportion of the first two minerals increases the alumina content (and, accordingly, reduces NKM), an increase in the K-feldspar proportion increases NKM. *It is quite probable that such an appearance of NKM diagrams is generally characteristic of allochemical metamorphism with alkali migration.*

Let us also pay attention to the lithochemical typification of rocks – the appearance of pyrophyllite and sericite in them does not at all make them hydrolysate: they are certified as silites, alkaline silites or alkalites. If we assume that the precursor of pyrophyllite was supergene kaolinite, then it is difficult to understand why the eluvial kaolinite rocks are so acidic. ***The pres-***

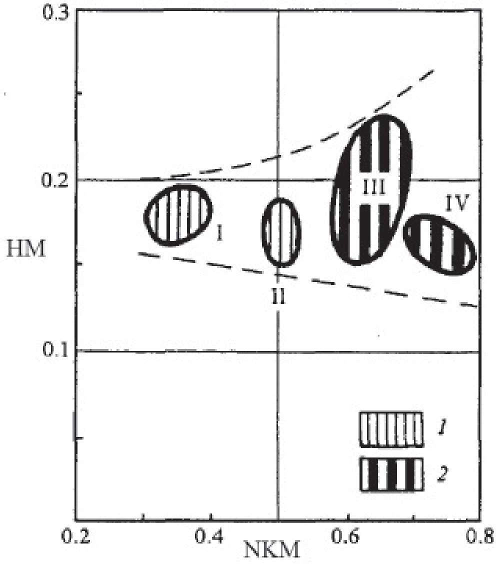

Fig. 95. Module diagram for porcelain stones – acid apovolcanites of the North Urals. *Compiled according to B. A. Goldin et al., 1987 [8, p. 12].*
Shales: 1 – pyrophyllite-sericite-quartz, 2 – sericite-K-feldspar-quartz

Table 123

The average chemical composition of porcelain stones of the North Urals.

Compiled according to B. A. Goldin et al., 1987 [8, p. 12]

Oxides and modules	I	II	III	IV
	Normosilite	Alkaline normosilite		Alkalite
n	3	3	6	4
SiO_2	77.59	78.55	75.66	77.69
TiO_2	0.17	0.21	0.16	0.17
Al_2O_3	12.14	11.99	12.42	11.32
Fe_2O_3	1.08	0.69	0.79	0.57
FeO	0.60	0.28	0.55	0.38
MgO	1.06	0.50	0.52	0.38
CaO	0.41	0.28	0.25	0.52
Na_2O	0.25	2.39	2.34	1.27
K_2O	4.05	3.68	5.51	7.13
LOI	1.82	1.23	1.29	0.39
Total	99.17	99.80	99.49	99.82
HM	0.18	0.17	0.18	0.16
FM	0.04	0.02	0.02	0.02
AM	0.16	0.15	0.16	0.15
TM	0.014	0.018	0.013	0.015
FerM	0.14	0.08	0.11	0.08
NKM	0.35	0.51	0.63	0.74
AlkM	0.10	0.70	0.40	0.20

ence of pyrophyllite (and often diaspore) in felsic rocks can be considered as one of the diagnostic features of the secondary quartzites formation.

Note that the two petrographic apovolcanites types identified by B.A. Goldin [8] (*Kapkanvozh* and *Sivyaga*) are distributed on the graph in such a way: clusters I–II are represented only by the first, and clusters III–IV – by a mixture of the first and second. Thus, the Sivyaga are simply the most K-feldspar varieties of the Kapkanvozh, hardly forming an independent type. Another illustration to the topic "lithotypes or chemotypes?".

Aluminous apovolcanics in the Southern Urals. In the eugeosynclinal zone of the Southern Urals, A.V. Govorova described several occurrences of high-alumina rocks that formed in the substratum of volcanic rocks because of their hydrothermal processing by acidic post-volcanic fluids. These rocks were very often mistaken for bauxites.

Layered and "pseudo-rhythmic" explosive breccias of quartz porphyries were described on Mount Sokolok. As a result of hydrothermal processing, the breccias turned into rocks, 90% consisting of the kaolinite group minerals. "*The well-preserved primary structural and textural features (detrital* *composition, fluidity) allow us to speak of felsic volcanic rocks kaolinization under conditions of low-temperature hydrothermal processes under the influence of acidic solutions containing mainly CO_2 <...> In our case, the minerals of the kaolinite group gave pseudomorphs over volcanic glass*" [79, p. 33]. The locality of hydrothermal alterations occurrence makes it possible to attribute these high-alumina rocks (29–37 % Al_2O_3) to the vent facies.

As can be seen from Table 124, the most aluminous kaolinite rocks described by A.V. Govorova on Mount Sokolok are certified as hydrolysates and siallites (cluster I and sample 4), and the most siliceous – as myosilite. It is noteworthy that this rock (sample 2) retains the initial SiO_2 content for rhyolites (and the Al_2O_3 content increases very slightly) with almost complete alkalis removal. Thus, the metasomatic hydrothermal kaolinization of feldspars and micas is performed.

Table 124

Chemical composition of hydrothermally kaolinized liparitic breccias, Mount Sokolok, C_1, eastern slope of the Southern Urals.
Compiled according to A.V. Govorova, 1979 [79, p. 22–23]

	1	2	4
	Hypohydrolysate	Myosilite	Supersiallite
n	2		
SiO_2	49.10	74.98	57.88
TiO_2	0.57	0.33	0.42
Al_2O_3	35.60	17.62	29.08
Fe_2O_3	0.19	0.01	0.36
FeO	0.20	0.14	0.28
MnO	0.02	0.01	0.01
MgO	0.27	0.28	0.32
CaO	0.15	0.17	0.28
Na_2O	0.07	0.06	0.12
K_2O	0.06	0.08	0.44
F	0.07	0.08	0.06
LOI	14.14	6.65	10.55
Total	100.44	100.41	99.80
H_2O^+	13.75	5.27	10.45
CO_2	0.01	0.01	0.01
HM	0.74	0.24	0.52
FM	0.01	0.01	0.02
AM	0.73	0.23	0.50
TM	0.016	0.019	0.014
FerM	0.01	0.01	0.02
NKM	0.00	0.01	0.02
AlkM	1.20	0.80	0.30

In the core of one of the wells drilled in Magnitogorsk through diabases and their tuffs, "bauxite-like tuffs" containing up to 32 % Al_2O_3 and about 12 % Fe_2O_3, composed largely of halloysite, zeolites and goethite, were found. Having studied the core, A. V. Govorova concluded that "*more loose formations – tuffs of the basic composition, which ended up in the solution passage zone, were more favorable for their seepage and therefore underwent more processing than dense diabases. The near-contact parts of diabase bodies were also subjected to greater processing, but <...> to a lesser extent than tuffs*".

On the left bank of the river Ural, in the andesites contact zone (from the west) and porphyries (from the east), there is a narrow band of outcrops (about 300 m long) of cherry-red hematite-sericite rocks containing about 35 % Al_2O_3. It is assumed that this is a product of the liparites processing under the influence of hydrothermal fluids genetically related to andesites: "*apparently, andesites found the weakest place for their exposure to the surface – the junction of basic and acid volcanic-detrital rocks and found their way out through the same weakened zone and hydrotherms*" [79, p. 84].

In the area of vil. Martynovka in the Southern Urals, N.A. Skopina discovered unusual hornfelsed acidic volcanics containing about 37 % Al_2O_3 and many pink balls up to 1.5 cm in diameter. These rocks occur near the contact of felsite porphyries with granites. A.V. Govorova found out that the balls are composed of andalusite with a possible corundum admixture, and their enclosing mass is enriched in late sericite and paragonite. It was concluded that this is vent or near-vent felsite facies; the primary nature of the balls is liquation, and their composition is the result of working through the rock with very acidic post-volcanic fluids.

Diasporic apovolcanites in Kazakhstan. In Kazakhstan, on the northern slope of the ridge Tarbagatai in the interfluve of the Karabuga–Tebezga, L. N. Kotova in 1964 discovered the diaspore concretions occurrence containing 51–61 % Al_2O_3 in aluminous Upper Devonian pumice of trachyliparite composition. Concerning the origin of hydromica pumice rocks, she notes that in rocks without diaspore concretions, the correlation between Al_2O_3 and Fe_2O_3 is positive, while in rocks with such concretions it transforms into a negative one. "*Such a different behavior of Fe_2O_3 in these rocks is the result of the redistribution and migration of iron <...> The process of iron redistribution, apparently, was associated with the entry of acidic waters into the pumice rocks, which dissolved and partially removed Fe_2O_3 from them, redepositing it in the basalt porphyrites of the underlying layer.*

This is confirmed by the fact that among the dark red pumice rocks with a high Fe_2O_3 content there are small lenses of light, almost white pumice rocks with a low Fe_2O_3 content. In the underlying basaltic porphyrite, uneven strong ferrugination of the rock is observed. Likely, these same acidic waters also contributed

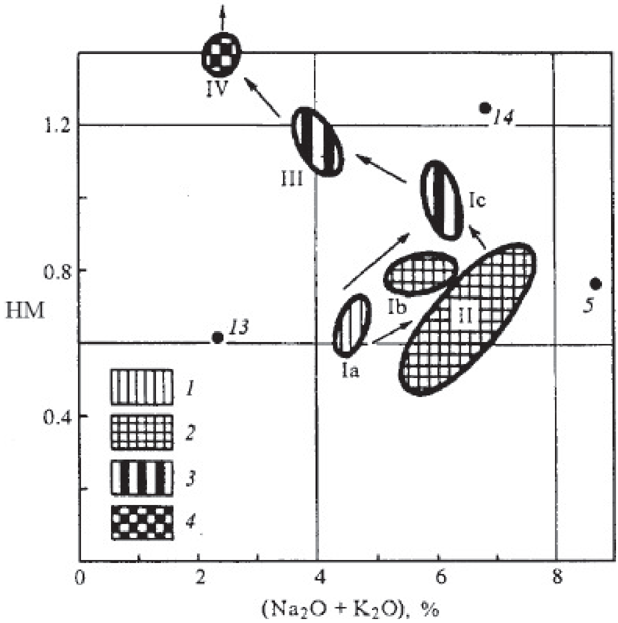

Fig. 96. Module diagram for aluminous rocks formed over a pumice tuff substrate.
Compiled according to L.N. Kotova, 1972 [146, p. 143–145]

to the aluminum redistribution: however, being more inert, it did not migrate from the formation, but was pulled together, forming concretions. Concretions were formed already after rock hydromica" [146, p. 152–153].

According to the description by V.A. Venkov et al., aluminous rocks occur in interlayers 0.5–4.0 m thick and in the form of lenses > 25 m thick and 100–300 m long. "*These are red, black, and dark grey dense formations, consisting of fine-scaly aggregates of 2M hydromica and hematite, the replacement products of the original pumice rocks and their tuffs, the primary textural and structural features of which have been preserved. Spherical diaspore concretions 5–20 cm in diameter were found in a lens of altered red rocks overlain by sintered pumice rock*" [48, p. 199]. However, these geologists believe that the available data are "*clearly insufficient for an unambiguous interpretation of concretions and their host high alumina rocks <...> It is possible that their formation is due to hypergenic metasomatism, which occurred during chemical weathering of igneous rocks on volcanic edifice slopes*" [48, p. 201].

L.N. Kotova [146] presented 3 analyzes of diaspore concretions and 21 analyzes of hydromica tuffs. As once can see from the module diagram with alkalis (Fig. 96), at the Karabugin ore occurrence, there are, as it were, two alteration process lines of the original pumice tuffs of trachyliparites. The first line is their hydromicasation (potassium introduction); in this process, the HM module also increases due to an increase in the alumina content: cluster Ia and sample 13 ("unaltered" tuffs) ⇒ clusters Ib, II (hydromica tuffs). The second line is the iron accumulation (clusters Ic and III), then a strong silica removal and a significant potassium loss – diaspore concretions are formed (cluster IV). It is curious that TM decreases in these formations: from 0.060 (on average) in the original and hydromica host tuffs to 0.022–0.020 (Table 125). Since the contents of TiO_2 do not noticeably change in this case, it can be assumed that during concretions formation, aluminum was mobile, and titanium was an inert component.

Note that this whole picture (including strong iron accumulations – up to 17.4 % Fe_2O_3 in hydromica tuffs) is very similar to that described in detail by us (see Section 9.4) in the Subpolar Urals, where the substrate is sericite, sericite-pyrophyllite and hematite-diaspore-pyrophyllite shales with abundant diaspore concretions served as Vendian-Cambrian rhyolites and their tuffs.

Thus, the Karabuginsky ore occurrence shows characteristic signs of allochemical alteration of the initial acidic substrate: a strong dispersion of petrochemical parameters and the presence of a lithotypes regular genetic series, reflecting successive stages of the hydrothermal-metasomatic process.

Apovolcanites of Armenia. Clay rocks are known within the Middle Eocene Sevan-Shirak zone of Armenia – products of porphyrites hydrothermal alteration, their tuffs and vein rocks. They serve as industrial raw materials to produce refractories (Tumanyan deposit). According to the description of I.Kh. Petrosov, one can see four genetic groups of minerals in these rocks: orthomagmatic, hydrothermal-metasomatic, hydrothermal proper, and hypergenic. Clay minerals are mainly hydrothermal-metasomatic: they are chlorite, sericite (hydromica), pyrophyllite, kaolinite, dickite, montmorillonite, disordered montmorillonite-pyrophyllite (pyrophyllite-montmorillonite). Part of the kaolinite presumably belongs to the hypergenic group. The development of clay minerals depends on both the substrate and the degree of hydrothermal alteration. For example, "*in weakly altered porphyrites, pyrophyllite is the most important; almost constantly present: mixed-layer pyrophyllite-montmorillonite, montmorillonite with a homogeneous composition of interlayer spaces, hydromica (sericite) <...> In intensely altered varieties, kaolinite (or dickite) dominates; as impurities are present: pyrophyllite, hydromica, montmorillonite, less often chlorite and disordered mixed-layer pyrophyllite-montmorillonite <...>*" [205, p. 163].

The module diagram (Fig. 97) shows a wide variation in HM values, which allows the formation of seven clusters that only partially coincide with

Table 125

Chemical composition of aluminous rocks formed on the pumice tuffssubstrate.

Compiled according to L.N. Kotova, 1972 [146, p. 143–145]

Oxides and modules	Ia	Ib	Ic	II	III	IV	5	13	14
	Hypohydrolysate	Pumice tuffs				Diaspore concretion (superhydrolysate)	???????? Пемзовые туфы ????????		
		Alkaline hypohydrolisate	Alkaline Ti normohydrolisate	Alkaline hypohydrolisate	Ti normohydrolisate		Alkalite	Hypohydrolisate	Alkaline Ti normohydrolisate
n	2	4	3	7	2	3			
SiO_2	53.91	49.03	43.94	50.76	41.85	18.43	48.07	58.84	39.02
TiO_2	1.44	1.54	2.05	1.60	2.18	1.34	1.12	1.13	2.97
Al_2O_3	22.39	26.82	22.94	24.73	28.66	58.20	33.63	27.82	27.86
Fe_2O_3	9.96	9.40	16.75	8.65	12.71	7.12	1.79	6.85	16.89
FeO	0.57	0.60	1.73	0.92	4.16	0.75	0.18	0.65	1.01
MnO	0.07	0.04	0.10	0.06	0.09	0.16	0.01	0.01	0.03
MgO	0.72	0.55	1.27	0.51	0.09	0.01	0.00	0.00	0.12
CaO	2.63	1.25	1.10	1.77	1.45	0.90	0.55	0.24	1.13
Na_2O	1.18	0.89	0.61	0.83	2.43	0.54	1.11	0.55	1.49
K_2O	3.41	4.85	5.53	5.91	1.62	2.01	7.61	1.82	5.40
P_2O_5	0.12	0.09	0.18	0.13	0.07	0.09	0.03	0.05	0.14
H_2O^+	3.33	4.78	3.44	3.50	4.74	10.24	6.02	2.20	3.50
Total	99.69	99.88	99.64	99.36	100.01	99.79	100.12	100.16	99.56
HM	0.64	0.78	0.99	0.71	1.14	3.67	0.76	0.62	1.25
FM	0.21	0.22	0.45	0.20	0.41	0.43	0.04	0.13	0.46
AM	0.42	0.55	0.52	0.49	0.68	3.16	0.70	0.47	0.71
TM	0.064	0.052	0.090	0.065	0.076	0.023	0.033	0.041	0.107
FerM	0.44	0.35	0.74	0.37	0.55	0.13	0.06	0.26	0.58
NKM	0.20	0.21	0.27	0.27	0.14	0.04	0.26	0.09	0.25
AlkM	0.30	0.20	0.10	0.10	1.50	0.30	0.10	0.30	0.50

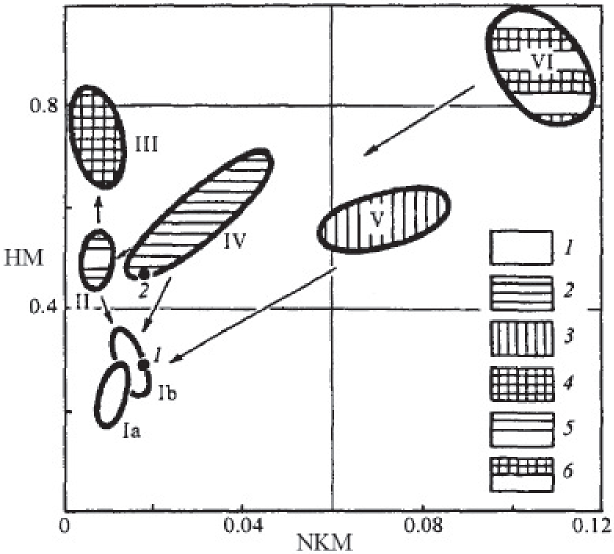

Fig. 97. Module diagram for hydrothermally altered rocks of the Tumanyan deposit (Armenia, Middle Eocene).

Compiled according to I.Kh. Petrosov, 1983 [205, p. 164].

1 – kaolinite rocks, 2 and 3 – altered rocks of the substrate: vein (2), porphyrites and tuffs (3); 4, 5 and 6 – mixtures of lithotypes, respectively (2 + 3), (1 + 2) and (1 + 2 + 3); arrows – the expected direction of the processes

the lithotypes identified by I.Kh. Petrosov (Table 126). At the same time, *more altered kaolinite rocks* (clusters Ia, b and partly II) *are less hydrolyzed* than less altered rocks of the substrate – pyrophyllitized porphyrites, their tuffs and vein rocks (clusters II–VI). The reason is that secondary quartz also appears in kaolinite rocks. Note that such zoning would be very strange for a hypergenic eluvial process: here the upper, most developed (rear!) zones of the weathering crust profile are always more hydrolyzed than the lower ones.

Concerning the genesis of these rocks, I.Kh. Petrosov proves the inconsistency of the judgment about their hypergenic nature; in his opinion, "*the formation of all mineral associations can be easily explained by a hydrothermal process, complicated by the subsequent hypergenic redistribution of matter.*" It is assumed that hydrothermal activity was initiated by the intrusion of the basic dikes into the Eocene strata: "*This is evidenced, for example, by the confinement of the most intense leaching zones to the dikes endocontacts and the gradual weakening of change processes with distance from them.*" Another important evidence of the hydrothermal process is the presence of characteristic minerals, such as pyrite, barite, gypsum, secondary quartz, alunite,

Table 126

Chemical composition of hydrothermally altered rocks of the Tumanyan deposit, Middle Eocene, Armenia. *Compiled according to I.Kh. Petrosov, 1983 [205, p. 164]*

Oxides and modules	Ia	Ib	II	III	IV	V	VI	1	2
	Myosilite		Supersiallite	Hypohydrolysate			Normo-hydrolysate	Timyosilite	Siferlite
n	2	2	2	4	2	2	3		
SiO_2	75.30	70.54	61.06	51.16	56.59	55.04	42.63	70.82	61.57
TiO_2	1.91	1.33	0.99	0.77	0.86	0.97	1.11	2.83	1.94
Al_2O_3	15.44	18.68	28.58	21.93	25.34	29.32	21.94	11.88	9.94
Fe_2O_3	0.99	0.86	0.56	14.33	6.09	1.24	14.15	6.20	17.34
FeO	0.08	0.15	0.08	0.19	0.15	0.15	0.20	0.15	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00
MgO	0.00	0.17	0.07	0.21	0.28	0.25	0.32	0.00	0.26
CaO	1.35	1.16	0.87	0.80	1.46	0.98	1.55	1.09	0.87
Na_2O	0.12	0.13	0.17	0.12	0.23	0.63	1.10	0.16	0.13
K_2O	0.07	0.15	0.07	0.05	0.58	1.50	1.22	0.05	0.05
H_2O^+	3.15	3.77	6.51	7.63	4.28	4.27	4.93	3.23	5.70
LOI	1.91	2.62	1.48	3.42	4.20	5.28	10.90	3.17	2.47
Total	100.32	99.56	100.44	100.61	100.06	99.65	100.06	99.58	100.27
HM	0.24	0.30	0.49	0.73	0.57	0.58	0.88	0.30	0.47
FM	0.01	0.02	0.01	0.29	0.12	0.03	0.34	0.09	0.29
AM	0.20	0.26	0.47	0.43	0.45	0.53	0.51	0.17	0.16
TM	0.124	0.071	0.034	0.035	0.034	0.033	0.050	0.238	0.195
FerM	0.06	0.05	0.02	0.64	0.24	0.05	0.62	0.43	1.46
NKM	0.01	0.01	0.01	0.01	0.03	0.07	0.11	0.02	0.02
AlkM	1.80	0.90	2.60	2.60	0.40	0.40	0.90	3.20	2.60

pyrophyllite. "*Hydrothermal solutions were characterized by an acidic reaction and the presence of sulfate ion as the main component. This is evidenced by the presence of sulfide mineralization in altered rocks, barite, gypsum (the latter also forms independent lenses), as well as intensely pronounced leaching processes*" [205, p. 201–202].

As for hypergenesis, it is not excluded, but its role was clearly subordinate: "*The hypergenesis change was expressed mainly in the oxidation of sulfides, the formation of a new generation of limonite and iron caps, i.e., mainly in the iron and sulfur redistribution. In addition, as a result of hypergenic processes, the stratification (zonality) of mineral facies was disturbed*" [205, p. 205].

Having considered all the materials, I. Kh. Petrosov concludes that the refractory rocks of the Tumanyan deposit should be attributed to the secondary quartzites formation, despite the absence of a clearly defined mineral zonality here:

"*It is appropriate to speak not about mineral facies (zones), but rather about the most common mineral associations, paragenesis of minerals coexisting side by side without replacement phenomena.*" In total, he singled out seven such associations, which "*can be considered as relics of primary mineral facies*" [205, p. 206).

Dumortierite concretions. In the Lower Carboniferous volcanic and volcanogenic-sedimentary Karkaraly formation around the Kentyube iron ore deposit (Kazakhstan), M.M. Kayupova and Z.T. Tilepov described a horizon with dumortierite concretions, having a thickness 30–100 m and traced for 3 km long. The concretions content sometimes reaches 60 %, their size is from 2×3 to 30×40 cm. Concretions are composed of densely blue radially radiant borate silicate dumortierite $(Al, Fe)_7[BO_3][SiO_4]_3$.

As the authors believe, "*the formation of dumortierite concretions is apparently due to the delivery <...> of groundwater associated with fumarole activity during periods of volcanic paroxysms attenuation. According to S. I. Naboko, boron is one of the most characteristic elements of the exhalations of the world <...> In our case, in addition to boron, the solutions contained mobile compounds of iron and aluminum, which later became isolated in the form of independent concretion-forming minerals – hematite, hydromica and dumortierite*" [129, p. 928]. Since nothing similar has been described for weathering crusts, these data make it possible to use boron as an indicator of metasomatic formations such as secondary quartzites.

Hydrothermal-metasomatic formation of argillisites. These formations are lower temperature than secondary quartzites. According to A. D. Rakcheev, the term "argillisation" was first used in the petrographic dictionary by F. Yu. Levinson-Lessing in 1893 and became firmly established in the literature after the work of T. Lovering, who designated clay products of hydrothermal alteration with the term *argillic alteration*. Like secondary quartzites, argillisites are divided not according to their own characteristics, but according to the deposits they accompany. In contrast to the "massifs" of secondary quartzites, the zones of argillisites are characterized, as a rule, by a linear arrangement, and the thickness of the aureoles of argillisation usually does not exceed 1–5 m. However, "*it sharply increases in the near-surface setting up to 150–200 m. Stratiform deposits are formed in separate layers of tuffs*" [204, p. 265–266].

Argillisites can be marginal, low temperature facies within secondary quartzite formations. V.N. Razumova calls them "volcanogenic clay metasomatites" and writes the following: "*In modern hydrothermal fields near faults leading hydrothermal fluids <...>, deposits of opalites and secondary quartzites with alunite and sulfur are formed (in higher temperature facies – with diaspore, boehmite and pyrite). Far from the faults, the increased rocks water content promotes the development of hydrothermal clays (areal low-temperature argillisation). The formation of clay metasomatites is associated with fissure and fissure-areal circulation of groundwater, mainly along the horizons of volcaniclastic rocks, therefore, cloak-like <...>, reservoir <...> and multi-tiered form of occurrence is typical for volcanogenic clay metasomatites. The thickness of volcanic clays, according to volcanologists, is often 300–400 m, and in tuffs it reaches many hundreds of meters, which allows us to speak of regional argillisation and clayization (Volostnykh, 1972; Kazitsyn, 1972) <...> When volcanogenic montmorillonite and kaolin clays are found among ancient volcanic sequencees, they are usually taken for eluvial formations – areal weathering crusts – even when deposits of clay metasomatites are accompanied by bodies of secondary quartzites containing high-alumina minerals*" [220, p. 109].

Argillisites have been studied in most detail by geologists at hydrothermal uranium deposits, where they are often a typical prospecting feature. We will limit ourselves to only one example of kaolinite rocks – indisputable argillisites.

Apogranitic kaolinites of the Czech Republic. One spectacular example of argillisation was described by Czech geologists in the vicinity of Karlovy Vary [40]. Here lies a body of kaolin rock formed over the substrate of the Varissian granitoids of the Karlov massif driven by the famous Karlovy Vary carbon dioxide waters generated by Miocene volcanism. A steeply dipping block of biotite adamellites 500 m long, 25 m wide, and to a depth of more than 60 m was subjected to kaolinization. Along with granitoids, basalt dikes are also altered, turning them into montmorillonite. For our topic, it is essential that the kaolin rock has several features that distinguish it from the weathering crust kaolins that are regionally distributed here.

Firstly, the completeness of granite decomposition is characteristic, i.e., high content of kaolinite in the clay fraction. Kaolin is unusually strong (a result of secondary compaction), very well formed crystallographically, has high water absorption, and exhibits low drying shrinkage. Secondly, there is a low Fe_2O_3 content (siderite, goethite) and TiO_2, and in fine fractions they are even less. Thirdly, there is a paradoxical decrease in the content of Al_2O_3 in fine fractions; for example, the 10–5 μm fraction contains 36.5 % Al_2O_3, while the < 1 μm fraction contains only 20.16 %. Since there is almost no quartz in the latter, the presence of either amorphous silica, or a decomposition product of biotite or chlorite, high-silica anoxite-kaolinite, is allowed here.

Elements-indicators of argillisites. Although in this book we have avoided consideration of the trace elements' indicator role, limiting ourselves to rock-forming elements, in the case of argillisites, the involvement of the latter may be of decisive importance for diagnosis.

A. A. Kremenetskii et al. [189] described clay-carbonate rocks in the volcanogenic-sedimentary strata with coal-type biogenic organic matter. Their peculiarity is that they contain lithium mica and, as a result, are highly enriched in lithium, cesium and fluorine, on average (in %) 0.516 Li (0.434–0.610), 0.026 Cs (0.017–0.030), 2.77 F (0.96–3.75). In addition, there are strong geochemical anomalies of Mo, As, as well as U, Bi, Pb, Be, and W. It is assumed that these unusual formations are the products of hydrothermal argillisation of tuffaceous material. Argillisation could be either synchronous with volcanism, or later, low-temperature. Note that in the proposed substrate (potassium trachybasalts), the F, Li and Cs contents are already clearly increased: 0.15–0.40, 0.01–0.03 and 0.005–0.010 %, respectively. In this situation, the rocks in their lithological composition (in particular, the carbonate presence) are not at all similar to the formations of the weathering crust, which allows us to qualify them as hydrothermal argillisites (probably based on the substrate of tuffoids, and not the basalts themselves – otherwise it is difficult to explain the presence of C_{org}).

Metamorphogenic hydrolysates. Into this group we include such regional metamorphism products, for which one has to really consider the occurrence of allochemical metamorphism processes that can give rise to rocks of hydrolysate composition: a) products of retrograde metamorphism, b) aluminous and ferruginous granulites.

Archean metamorphites of North Karelia. At the regressive stages of regional metamorphism, the process of acid leaching often develops, which gives rocks that are very difficult to distinguish from the ancient metamorphosed weathering crust. In the Archean gneisses of North Karelia, metamorphosed in the moderate pressure facies (kyanite-sillimanite type), zones of acid leaching with an area of about 4 km^2 have been described. In isolated metasomatite bodies, a complete metasomatic column consisting of five zones was observed. In the rear zone I, the inert component is one silica, the rest are all taken out; in the frontal zone V, only Na_2O and H_2O are mobile, while the other components are inert. A sequence paragenesis of garnet, hornblende, staurolite, kyanite, quartz, and plagioclase forms here. As noted by Leningrad geologists, the first zone is "*similar in composition to shales formed from highly differentiated sediments that arise during the redeposition of chemical weathering crusts and is often taken for them. The marginal zone, in which the displaced inert components are deposited, is represented by highly exotic multimineral rocks of increased magnesia content, which are distinguished by a high ratio of aluminum to calcium. In principle, it is possible to imagine primary sediments with a similar composition, but the presence of these rocks among high-alumina formations should alert the researcher involved in paleolithological reconstructions and force him to analyze parageneses in order to identify metasomatic zoning*" [257, p. 20].

Aluminous and ferruginous granulites of the Tatar arch. B.S. Sitdikov and colleagues in their work give 15 analyzes of aluminous granulites of the Tatar arch, penetrated by deep wells [239, p. 35]. These are garnet-cordierite, cordierite-sillimanite-biotite shales and plagiogneisses, etc., including those with garnet and hypersthene. As can be seen from Table. 127, the rock composition is diverse: among them are hydrolysates (cluster IV), pseudohydrolysates (cluster V and sample 10), siallites (clusters I, II), including alkaline with a high manganese content (sample II), pseudo-siallites (cluster III and sample 13). The wide spread of points on the module diagram (Fig. 98) emphasizes the heterogeneity of the population, in which clusters and individual compositions do not show noticeable trends.

One can note two petrochemical features of the rocks, which are in a certain antagonism.

1. Low titanium value; 9 compositions are hypotitanic (TM < 0.035), 5 – normotitanium, only one – supertitanium and at the same time the most ferruginous (sample 10: TM 0.068, FerM = 0.89, ∑Fe – 16 %). This, as well as the generally relatively low TiO_2 content (maximum 1.67 %), low CaO content, and low sodium value (AlkM < 1) allow us to agree with the author's diagnosis of these metamorphites as metapelites, but not as metabasites. We would classify the compositions in clusters II and III as such rocks. However, the rocks in cluster I are distinguished by extremely low titanium value and, in addition, high sodium value (AlkM 2.4 versus 0.5–0.3). These may be metaarkoses or even low alkaline metarhyolites.

2. Presence of pseudohydrolysates, i.e., rocks with high HM, but also with a fairly high MgO value. This feature, as a rule, characterizes the basic material.

One can think that this contradiction is easy to resolve, because metapelites are closely associated in the section with metabasites and seem to give them all the transitions – through biotite-plagioclase, garnet-biotite, plagioclase-hyperstenbiotite gneisses. Perhaps they simply contain an admixture of basic pyroclastics? It was this idea that Tatar geologists came up with: "*The facts indicate the presence of gradual transitions between the distinguished rock classes, which, apparently, is explained by the mixed nature of some initial rocks (tuffites, siltstones with clay-carbonate cement, etc.)*" [239, p. 34].

However, the most important contradiction is alarming: why are these mixed rocks aluminous? After all, the Al_2O_3 content in them reaches 30.6 %, and the AM

Table 127

Chemical composition of aluminous Archean granulites from the Tatar arch basement of the Russian platform.

Compiled according to B. S. Sitdikov et al., 1980 [239, p. 35]

Oxides and modules	I	II	III	IV	V	10	11	13
	Hyposiallite	Normosiallite	Pseudosiallite	Hypohydrolysate	Alkaline pseudo-hydrolysate	Pseudo-hydrolysate	Alkaline normosiallite	Pseudosiallite
n	2	2	2	4	2			
SiO_2	68.47	63.82	57.56	52.78	42.18	52.29	63.04	66.41
TiO_2	0.09	0.50	1.13	0.81	1.69	1.16	0.48	0.94
Al_2O_3	19.03	18.81	21.68	28.17	30.40	16.97	16.46	15.70
Fe_2O_3	0.81	3.55	3.95	2.42	3.34	4.20	2.49	2.18
FeO	1.91	3.30	4.89	6.22	6.83	11.77	4.70	2.97
MnO	0.02	0.09	0.07	0.07	0.08	0.20	0.68	0.10
MgO	1.25	2.65	3.30	2.19	5.00	4.70	1.29	3.08
CaO	2.33	0.53	0.56	0.68	1.88	0.48	2.31	2.76
Na_2O	3.29	1.06	0.71	1.19	1.58	0.41	3.50	1.88
K_2O	1.37	1.94	2.38	2.44	3.55	3.93	3.43	1.75
P_2O_5	0.03	0.03	0.02	0.03	0.03	0.03	0.05	-
SO_3	-	0.00	0.19	0.04	0.11	0.01	0.00	-
LOI	1.37	3.33	2.49	2.82	2.28	3.45	1.51	1.15
Total	99.97	99.58	98.93	99.86	98.95	99.60	99.94	98.92
HM	0.32	0.41	0.55	0.71	1.00	0.66	0.39	0.33
FM	0.06	0.15	0.21	0.21	0.36	0.40	0.13	0.12
AM	0.28	0.29	0.38	0.53	0.72	0.32	0.26	0.24
TM	0.004	0.027	0.052	0.029	0.055	0.068	0.029	0.060
FerM	0.14	0.36	0.39	0.30	0.32	0.89	0.46	0.32
NKM	0.24	0.16	0.14	0.13	0.17	0.26	0.42	0.23
AlkM	2.40	0.50	0.30	0.50	0.40	0.10	1.00	1.10

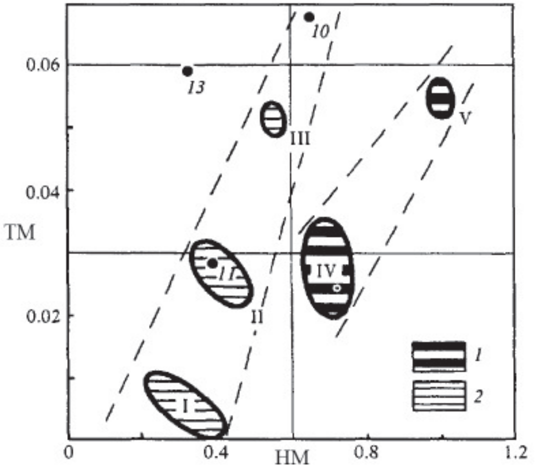

Fig. 98. Module diagram for aluminous Archean granulites
from the Tatar arch basement of the Russian platform.
Compiled according to B. S. Sitdikov et al., 1980 [239, p. 35].
1 – hydrolysates and pseudohydrolysates. 2 – siallites and pseudosiallites

value in nine out of fifteen analyzes corresponds to hyper- (> 0.40) and superaluminous (0.35–0.40). It turns out that we must operate with approximately the following models of premetamorphic rocks: a) kaolinite-hydromica clays + basic pyroclastics; b) kaolinite-hydromica clay + dolomite; c) basic greywackes with kaolinite-hydromica matrix + dolomitic cement.

However, model a) does not agree well with low TM, models with dolomite are doubtful due to the low CaO content in the rocks, and model c) contradicts model a) in facies: it is difficult to combine humid platform weathering and greywacke formation.

All this forces us to assume that during the formation of the Archean aluminous granulites of the Tatar arch, allochemical metamorphism processes widely occurred. Apparently, these are not isochemical metapelites, but restites – rocks from which significant amounts of Na, Ca, Mg and Si were removed during regional granitization.

The ferruginous granulites of the Tatar arch (Table 128) are distinguished by an increased magnetite content: 5–10, sometimes up to 25–30 %. As shown by the study of 12 analyzes given by B. S. Sitdikov et al. [239, p. 90], among them are hypohydrolysates, more magnesian pseudohydrolysates, and one siferlite (sample 4).

There is a significant scatter of points on the module diagrams; three clusters can be distinguished with great conventionality in terms of iron content, alkalinity, and titanium content. It is essential that half of all compositions have TM > 0.065

Table 128

Chemical composition of ferruginous Archean granulites
from the Tatar arch basement of the Russian platform.
Compiled according to B. S. Sitdikov et al., 1980 [239, p. 90]

Oxides and modules	I	II	III	3	4	6	8
	Pseudohydrolysate			Hypohydrolysate	Siferlite	Pseudohydrolysate	
n	2	4	2				
SiO_2	47.44	47.95	33.45	55.63	67.08	49.36	35.96
TiO_2	0.58	1.39	1.49	0.01	0.14	1.88	0.01
Al_2O_3	12.16	16.19	8.93	0.00	7.17	13.18	14.68
Fe_2O_3	6.23	6.85	17.52	28.65	11.97	7.47	3.85
FeO	20.79	9.23	26.87	10.75	6.72	8.56	16.00
MnO	0.59	0.20	0.13	0.06	0.02	0.23	0.14
MgO	4.13	4.07	4.57	1.13	1.75	6.00	10.51
CaO	5.25	5.66	2.37	1.72	2.90	6.35	8.84
Na_2O	0.47	2.56	0.34	0.31	1.33	2.24	0.66
K_2O	0.46	2.25	0.90	0.21	0.52	1.03	1.24
P_2O_5	0.38	0.47	0.90	0.12	0.30	0.14	0.40
LOI	1.48	3.19	2.69	1.40	0.20	3.24	7.50
Total	99.96	100.01	100.16	99.99	100.10	99.68	99.79
HM	0.85	0.71	1.64	0.71	0.39	0.63	0.96
FM	0.66	0.42	1.46	0.73	0.30	0.45	0.84
AM	0.26	0.34	0.27	0.00	0.11	0.27	0.41
TM	0.047	0.086	0.167	-	0.020	0.143	0.001
FerM	2.17	0.93	4.27	3946.00	2.56	1.08	1.36
NKM	0.08	0.30	0.14	-	0.26	0.25	0.13
AlkM	1.00	1.10	0.40	1.50	2.60	2.20	0.50

(up to 0.191 in pseudohydrolysate within cluster III). Along with increased Mg value (many pseudohydrolysates) and appreciable CaO amount (>5 % in almost half of the samples), all this clearly indicates the relationship of these rocks with metabasites. However, the presence of primary hydrolysate metamorphites is also not excluded: the increased phosphorus content in four analyzes (0.55–1.17 %) seems to be too high for metabasites. This fact can be interpreted as a result of phosphate sorption on iron hydroxide sediments.

At the same time, the absence of clear correlation fields on the module diagrams, at least in the TM – FerM coordinates, suggests that there should be products of allochemical metamorphism, which was also admitted by Tatar geologists: "*Among <...> ferruginous rocks, there are also metasomatites of the skarnoid type, apparently formed under the conditions of the amphibolite facies: garnet-carbonate-quartz rocks, garnet-magnetite-(pyroxeno-hornblend)-quartz gneisses, etc.*" [239, p. 89].

9.3. Apocrust metahydrolysates

As a rule, these are stratiform bodies of considerable thickness in the rank of stratons (formations, subseries, and even series) and, less often, thin members. Thickness, characteristic paragenesis of rocks in the section (combination of hydrolysed shales with quartz sandstones and quartzites), significant distribution in the area, obligatory location in the section above the surfaces of large and largest stratigraphic unconformities – all this makes us interpret such strata as metamorphosed "weathering crust formations" in V. P. Kazarinov's understanding [122] or *lepigenic formations* [294]. As the materials discussed in the previous chapter show, these objects can be divided into two large groups: a) low alkaline, including low potassium ones; b) high potassium. The former are usually more hydrolysatic (higher HM module) than the latter. However, this feature is less important here than the difference in potassium contents – it reflects a significant difference in the conditions for the formation of eluvial-crustal products. The further presentation is largely based on the excellent book by V. K. Golovenok "High-alumina formations of the Precambrian" [82] and our publications: "The nature of anomalous potassium accumulations in clay rocks" [298] and "Lepigenic formations" [294].

Low-alkaline metahydrolysates

Usually, these are shales containing aluminous and (or) ferruginous minerals (kyanite, sillimanite, diaspore, pyrophyllite, chloritoid, staurolite, hematite) in close paragenesis with oligomictic or monoquartz sandstones and quartzites.

Archaean and Karelian. Keiv shales. In the Upper Archean Keiv series on the Kola Peninsula, the Chervurt formation 50–400 m thick is known, represented by alternating quartzites and garnet-mica shales with shales containing kyanite, staurolite, and sometimes ilmenite. Contrary to B. M. Mikhailov's doubts [181], V.K. Golovenok cites convincing geological, structural and petrographic data in favor of the existence of a large stratigraphic unconformity at the Keiv series basement – in the top of the biotite gneisses of Lebyazhinskaya series [82, p. 126–133].

Aluminous rocks of the Witwatersrand. A remarkable feature of the Lower Karelian Witwatersrand strata is the association of "reefs" (gold-bearing quartz conglomerates) with shale containing chloritoid and pyrophyllite. Such rocks lie not only at the "reefs" bottom, but sometimes even form their cement. In many researchers' opinion, which is shared by T. Reimer [349], aluminous shales are nothing but weathering crusts (paleosoils) and the products of their redeposition. In table 129 we processed 14 analyzes provided by him, finding a strong alkalinity and hydrolysate dispersion. Seven compositions are certified as hydrolysates (five of them are alkaline), two are clearly related to them as alkalite (sample 10) and supersiallite, four are siallites (two of them are alkaline). A special place is occupied by the magnesian pseudohydrolysate analysis, which contains almost no alkalis (sample 4). It can be assumed that 12 analyzes characterize the weathering products of acidic rocks (clusters I–III and samples 2, 3, 10, 11), and sample 4 is a weathering product of metabasites. The rocks represented by sample 9 (myosilite) appears to be arkose sandstone or siltstone.

Early Karelian gneisses of the Teterev–Bug formation and Karelian phyllites of Western Taimyr. In the west of the Ukrainian crystalline shield, in the middle reaches of the Southern Bug River, there are several outcrops of sillimanite gneisses associated with other gneisses and quartzites. Usually graphite-garnet-sillimanite (± cordierite) gneisses form members up to 300m thick and up to several kilometers long [82, p. 161]. It is difficult to doubt that such large bodies are metasedimentary formations. The statistical sample of Karelian phyllites (quartz-sericite shales) analyzes of Western Taimyr (Table l 30) is divided into cluster I – hydrolysates and a single composition of sample 4 – siallite. We can agree with M.G. Ravich [219, p. 146], who interpreted these rocks as metapelitolites. Let us only add that the increased rock hydrolysation in cluster I is due not so much to alumina as to iron (super- and hyperferrous compositions). This circumstance, as well as "traces" of the former Mg value (in one of the three analyses, 3.50 % MgO) make it possible to interpret these shales as products of redeposited weathering crust metamorphism after rocks of basic or intermediate composition. Moderate TM values allow two interpretations: either weathering proceeded in a reducing environment (titanium removal), or the substrate was relatively low in Ti, for example, andesitic or granodiorite.

Riphean. Akitkanii (?)[3] *Anai formation and Lower Riphean Purpol formation.* The Anai formation is developed in the Baikal mountainous region in the upper reaches of the river Lena; its middle subformation, more than 700 m thick, is represented by alternating sericite- and disthene-chloritoid shales with light-colored quartz sandstones. The upper subformation (at least 900 m thick) is composed mainly of quartz and quartz-feldspar sandstones with subordinate interlayers of sericite-chloritoid shales [82, p. 67]. In the Baikal mountainous region, in the interfluve of the rivers Vitim and Chara, the Teptorgin series of the Riphean is developed. At its basement lies the Purpol formation, 150–200 to 950–965 m thick, overlying the Karelides with a large break and angular unconformity. The middle subformation of

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[3] Akitkanii is a stratigraphic unit in the rank of a subgroup, identified by L.I. Salop [234]. It is dated in the interval of 1900–1600 Ma, i.e., it partially captures the upper Karelian and the lower Riphean in the generally accepted Precambrian time scale.

Table 129

Chemical composition of Witwatersrand aluminous shales and some rocks associated with them.

Compiled according to T. Reimer, 1985 [349, p. 39, 40]

Oxides and modules	I	II	III	2	3	4	9	10	11
	Alkaline supersiallite	Hypohydro-lysate	Alkaline hypo-hydrolysate	Normo-siallite	Hypo-hydrolysate	Pseudo-hydrolysate	Myosilite	Alkalite	Hypo-hydrolysate
n	2	2	4						
SiO_2	59.83	54.67	50.98	67.20	51.00	52.02	75.47	54.78	58.11
TiO_2	0.75	0.72	1.02	0.93	1.12	1.66	0.53	1.01	0.97
Al_2O_3	25.48	29.42	34.92	24.39	28.85	28.47	16.03	29.99	31.93
Fe_2O_3	3.36	6.15	2.12	2.27	5.73	9.59	0.99	0.99	1.32
MgO	1.61	2.41	1.01	1.45	2.05	4.19	1.15	0.87	0.05
CaO	0.05	0.04	0.01	0.01	0.66	0.01	O.O!	0.48	1.02
Na_2O	0.64	0.36	0.45	0.11	1.11	0.22	0.20	0.52	0.00
K_2O	4.55	2.26	4.82	0.58	5.20	0.08	3.09	7.95	1.10
LOI	4.32	4.36	4.98	2.92	3.92	4.66	2.49	4.12	5.65
Total	100.59	100.39	100.31	99.86	99.82	100.90	99.96	100.71	100.15
HM	0.49	0.66	0.75	0.41	0.70	0.76	0.23	0.58	0.59
FM	0.08	0.16	0.06	0.06	0.15	0.26	0.03	0.03	0.02
AM	0.43	0.54	0.68	0.36	0.57	0.55	0.21	0.55	0.55
TM	0.029	0.024	0.029	0.038	0.039	0.058	0.033	0.034	0.030
FerM	0.13	0.20	0.06	0.09	0.19	0.32	0.06	0.03	0.04
NKM	0.20	0.09	0.15	0.03	0.22	0.01	0.21	0.28	0.03
AlkM	0.10	0.20	0.10	0.20	0.20	2.80	0.10	0.10	0.00

Table 130

Chemical composition of Precambrian phyllites of Western Taimyr.
Compiled according to M. G. Ravich, 1954 [219, p. 146]

Oxides and modules	1	4
	Hypohydrolysate	Normosiallite
n	3	
SiO_2	53.46	59.70
TiO_2	1.14	0.67
Al_2O_3	18.65	14.78
Fe_2O_3	6.04	5.50
FeO	6.13	4.88
MgO	2.89	2.50
CaO	1.18	2.89
Na_2O	1.11	0.98
K_2O	2.34	1.87
LOI	6.99	6.08
Total	99.93	99.85
HM	0.60	0.43
FM	0.28	0.22
AM	0.35	0.25
TM	0.061	0.045
FerM	0.61	0.67
NKM	0.19	0.19
AlkM	0.50	0.50

the Purpol formation (up to 350 m) is composed mainly of high-alumina shales with diaspore, disthene and chloritoid, while the lower (60–240 m) and upper (60–400 m) ones are mainly composed of quartz sandstones and gravelites [82, p. 50–57].

There is no doubt that the aluminous metamorphites of both strata are of primary sedimentary nature.

Riphean strata of the Yenisei ridge. In the Middle Riphean Tungusik Series (Potoskuy, Shuntar, and Kirgitei formations), there are shale units with chloritoid, the content of which reaches 40–50 %. Sometimes pyrophyllite was also noted in these rocks. The overlying Upper Angara formation of the Oslyan series (Upper Riphean?) also contains chloritoid shales. Their feature is the high iron oxide content, and in some varieties – the presence of pyrophyllite and kaolinite. Typically, chloritoid shales are associated with quartz sandstones; Upper Angara shales lie directly above the stratigraphic break, which is marked by the “ore-bearing horizon” – iron ores at the very formation basement [82, p. 98–103].

Ovruch Group and Middle Riphean Zigalga formation. The Tolkachev formation up to 900 m thick, composed mainly of quartz sandstones and quartzites with interlayers of pyrophyllite and hematite-sericite shales, is located in the Ovruch Riphean series in the northwestern part of the Ukrainian crystalline shield. The pyrophyllite content in shales reaches 30 %, hematite – up to 15% [82, p. 175].

In the Southern Urals, at the basement of the Middle Riphean, there is a thick Zigalga formation, composed mainly of quartz sandstones and quartzites and containing shales and phyllites with chloritoid in the middle subformation, and with staurolite in areas with more intense metamorphism (Uraltau ridge). According to V.K. Golovenok, the presence of a large Pre-Zigalga break is beyond doubt [82, p. 114–118].

Riphean-Vendian hematite sandstones. Specific formations are hematite red sandstones containing cakes and extended thin layers of hematite. Such rocks are known as part of the ancient humid "red-colored carbonate-free hematite formations" identified by A. I. Anatolyeva. "*It has become obvious that some Late Precambrian red-colored rocks show a close paragenetic relationship with hematite layers of varying thickness*" [5, p. 173]. Associated with them are red-colored argillites with hematite, which have a hydromica-chlorite and kaolinite composition. For example, in the Upper Riphean-Vendian section of the SW Siberian Platform (Taseev series), hematite sandstones contain SiO_2 79.5–79.9, Al_2O_3 1.6, Fe_2O_3 14.3–24.5, FeO 0.14, TiO_2 0.18–0.20%. Based on these data, the rocks are certified as hypertitanous and hyperferruginous myosilites. ***Some varieties of sandstones are so rich in hematite that they turn from silites (which is normal for sandstones) into hydrolysates.*** Such, for example, is one of A. I. Anatolyeva's analyzes: SiO_2 50.72, TiO_2 0.65, Al_2O_3 7.05, Fe_2O_3 34.77, MnO 0.28%; this rock is certified as Fe-normohydrolysate (HM 0.84).

One should join A. I. Anatolyeva's conclusion about the genesis of this unusual sedimentary formation: "*Along with the dominant products of mechanical rocks destruction, likely, a significant amount of chemical weathering products entered the sedimentation basin, due to which the hematite inclusions and interlayers observed in the formation were formed*" [5, p. 188].

True, here the question remains in the shade: how did the hematite *concentration* in sandstones occur, capable of transforming ordinary feldspar-quartz sandstones into real hydrolysates? Apparently, the point is that particles of terrigenous Fe hydroxides from weathering crusts had the same hydrodynamic size as a certain-sized sand fraction. Another fraction of iron oxide particles, apparently, was smaller and precipitated together with aleuropelitic material, forming red-colored argillites with hematite.

Paleozoic. The considered examples belonged to the Precambrian. However, metahydrolysates are also known among the metamorphic strata developed in the Paleozoic folded belts. We restrict ourselves to three examples.

Upper Cambrian-Lower Ordovician chloritoid shales of the Subpolar Urals. In the ancient metamorphic strata in the Subpolar Urals (the Rosomaha and Maldynyrd ridges), chloritoid has been known at least since the early 1960s, when its presence was noted in the Man'inskaya formation (R_3mn) in the upper reaches of the river Kozhim.

Judging by the outcrop numbers given in M. V. Fishman and B. A. Goldin's book [260], they found chloritoid shales on the creek Sanashor, a large left tributary of the Big Katalambiu river. A hydrothermal genesis of the chloritoid was assumed.

In 1966, in a report on the Suraiz geological survey party (basin of the Balbanyu and Limbekoyu rivers) L. T. Belyakova described a thick member of chloritoid shales in the northern watershed part of the ridge Maldynyrd near the lake with a height mark 1242.1 m. She suggested that the chloritoid was formed due to the metamorphism of the primary rock rich in alumina and magnetite.

In 1978, R. G. Timonina, in her Ph.D. thesis, described in detail shales with chloritoid and kyanite on an unnamed stream flowing into the Kozhim 2 km below the mouth of the Big Katalambiu. Later this stream was named after her [75]. In addition, she noted chloritoid-disthene, hematite, and pyrophyllite shales in the basal quartzites of the Telpos formation O_1tp. R. G. Timonina interpreted chloritoid and kyanite as minerals of the metasomatic column, a product of acid leaching [253, p. 25–29]; however, recent studies have shown that such an interpretation is doubtful – both minerals are products of redeposited products metamorphism of the Upper Cambrian weathering crust [317]. In 1985, V. S. Ozerov established the regional development of shales with chloritoid in the southern part of the ridge Maldynyrd and in several points on the ridge Lapcha, and later (1989) and much to the south – up to the basin of the river Shchugor. According to him, shales with chloritoid (and some other aluminous and ferruginous minerals) are a metamorphosed Cambrian weathering crust on the substrate of the Riphean-Vendian formations [187, 188].

The idea of the ancient weathering crust existence in the Subpolar Urals was put forward in 1962 by G. A. Chernov. Subsequently, using the petrochemical method, we identified several probable substrates of such a crust and discovered a chloritoid at several new points on the ridge Rosomakha. Analyzes of chloritoid from the stream Timonina have been published, and a scheme of its normative calculation was given [75]. The study showed [317] that chloritoid is usually the latest metamorphic mineral, producing well-formed poikiloblasts up to 1 cm in size, but more often 0.1–0.3 mm. According to the chemical composition, chloritoids form two groups. In the first, the TiO_2 content is 1.52–2.43 %, CaO 0.02–0.18, Na_2O 0.06–0.25, K_2O 0.06–0.15 %. In the second group TiO_2 content is an order lower, Ca and alkalis are usually not detected by analysis. Titanium chloritoids are found in shales along the substrate of Upper Riphean metabasite, Upper and Middle Riphean metatuffoid shales. These are always poikiloblasts overflowing with microinclusions of rutile, leucoxene, apatite, epidote, kyanite, tourmaline, hematite, micas, and chlorite. Relatively low-titanium chloritoid is found in aporhyolitic Maldy shales; tourmaline is characteristic of mineral inclusions, rare-earth elements are characteristic of trace elements at the level of hundredths %, due (as recent microprobe studies have shown) to the presence of micron-sized inclusions of rare-earth phosphates.

It is known that chloritoid is a polygenetic mineral and is formed in the processes of isochemical regional metamorphism of both low and relatively high stages in contact aureoles of acid intrusions and in quartz veins [57]. However, L.Halferdahl's indication is very important [57, p. 486] that the chloritoid is stable only in aluminous rocks. Indeed, a literature review convinces us that, ***at least in greenschist facies, chloritoid (as well as its frequent companion pyrophyllite) is not inherent in any metamorphic metapelite shales, but only in hydrolysate shales, which are enriched in aluminous and ferruginous erosion products of weathering crusts.***

The frequent paragenesis of chloritoid with pyrophyllite and hematite suggests the most probable reactions of isochemical metamorphism, in which kaolinite or pyrophyllite and some iron-bearing mineral (chamosite, hydrogoethite, goethite, magnetite) served as the starting material for the formation of chloritoid. Some difference in the chlorites chemical composition reflects the difference in the primary substrates of the weathering crust, and the low crystallinity degree of the mineral indicates its formation at low $P-T$ metamorphism parameters [215].

The foregoing allows us to state that the chloritoid regional development in the Subpolar Urals at the basement of the Uralide Sequence (O_1–C), including the Alkesvozh strata €$_3$–O_1al and partly in the Telpos formation O_1tp, and in the Upper Pre-Uralides (PR_2–V), indicates the regional development of ancient weathering crusts enriched in iron and alumina [92, 111, 187, 317].

However, this concept is not suitable for all our chloritoids. Manganese chloritoid from aporhyolite shales (or from apoarcosic derivatives of rhyolites) and alpine quartz veins dissecting them is associated with abundant tourmaline (up to 2 %), kyanite, and probably also fluorite. This indicates a superimposed process, where the chloritoid could have been formed according to the "pyrophyllite + magnetite" pattern, as evidenced by the poikiloblastic appearance of the chloritoid, which "devours" the pyrophyllite base tissue and is not subject to rock schistosity. According to St. Petersburg and Yekaterinburg geologists, metasomatic processes on the ridge Maldynyrd were the result of repeated Paleozoic activations of ancient (Riphean-Vendian) breaks [137, 255]. Apparently, the unique fuchsite-allanite-gold-palladium mineralization, discovered by V. S. Ozerov, is associated with one of these activations [187, 188].

Devonian "sparkling shales" of the Northern and Subpolar Urals. In the upper reaches of the river Lemva, on the ridge Tisvaiz the D_2 strata outcrops, composed of black shales (beds and lenses? up to 40 m thick), quartz sandstones, and limestones. According to V. S. Tsyganko [270] and A. I. Pershina [19], the age of the strata is Eifelian.

In 1962, the outstanding Vorkuta geologist K. G. Voinovsky-Krieger first described these strata, calling the black shales “sparkling” in their characteristic appearance. These rocks are very difficult to diagnose and were originally identified by him as clinocoisitic. It was only in 1975 that we discovered that they contain pyrophyllite (~36 %), chloritoid (~25 %), whose porphyroblasts give the rocks “sparkle”, and sericite (~26 %), and the normative recalculation did not even exclude the presence 1–2 % free alumina [39]. Similar rocks in similar strata were described in 1973 by V. N. Puchkov 200 km to the south – in the Malo-Pechora allochthon – in the upper reaches of the river Malaya Pechora in the Northern Urals. “*It became clear that these rocks are metamorphosed products of the weathering crust, which originally had a hydromica-chamosite-kaolinite composition...”* [295, p. 192]. Lithochemical data processing showed that “sparkling shales” are certified as normotitanic hypohydrolysates; this allowed us to suggest that “*the substrate for the Devonian weathering crust was most likely sedimentary rocks, and not mafic rocks or granitoids*” [74, p. 96].

Tanamys strata of the Northern Pamirs. According to K. F. Budanova [33], this is a “phyllite-shalet high-alumina formation” (Silurian–Devonian), represented by strata of alternating shale with chloritoid, chlorite-muscovite parashales, green orthoshales and marbled limestones with a thickness > 900 m. In the overlying Sarykol series (C–P), composed mainly of quartzite-like sandstones, there are also thin interbeds of shale with chloritoid. According to K. F. Budanova, chloritoid shales were formed by the metamorphism of redeposited weathering crusts, although she does not exclude their formation due to the erosion of hydrothermal hydrolysates along the volcanic substrate. Shales richest in chloritoid contain 36.5 % Al_2O_3 and 15 % Fe_2O_3 + FeO.

High-potassium metahydrolysate shale

We call high-potassium shales containing at least 5 % K_2O. Among them there are varieties containing 8–10 and even 11–12 % K_2O. In such rocks, potassium bearers are light micas and potassium feldspar, the presence of which is indicated by the potassium module KM value (K_2O/Al_2O_3) > 0.31, i.e., more than the muscovite norm. ***As a rule, high-potassium shales are part of thick red-colored strata and are closely associated with high-potassium arkoses.*** Like low-alkaline aluminous shales, these rocks are also undoubtedly derivatives of thick weathering crusts. As shown in Chapter 8, the difference lies in the fact that low alkaline hydrolysate shales were formed due to the processes of acidic humid weathering, during which Na, Ca, Mg, K, and Si were removed from the substrate, while high potassium shales and associated potassium arkoses were formed under conditions of arid alkaline weathering, in which potassium was an inert element.

Karelian. Huron, Taimyr, Segozero, Vepsian shales. In the southern part of the Canadian shield, there are thick strata of Karelids as part of the Huronian superseries. They lie on the metamorphosed Pre-Huronian weathering crust (which Canadian geologists call paleosol), represented by high-potassium shales containing up to 11% K_2O and 33.1% Al_2O_3. The Huron contains several formations (Mak-Kim, Pekors, Gouganda) with high-potassium shales containing up to 8.5% K_2O and up to 23.7% Al_2O_3 [82, p. 207].

In Western Taimyr, the Karelides contain a very thick Voskresenskaya formation (2500–2700 m), represented by alternating quartz and feldspar-quartz sandstones and dark ilmenite-bearing phyllites somewhat enriched in alumina and containing up to 5% K_2O [82, p. 94-95]. Moderately increased K_2O values do not seem to allow these shales to be classified as high-potassium. However, we noted that "the genetic relationship of the Taimyr black shales with mafic or ultramafic rocks is clarified" [300, p. 51]. Naturally, the weathering of a low-K substrate cannot give rise to such high potassium contents as the weathering of granitoids or acid gneisses; therefore, for a basic substrate, such potassium contents should be considered anomalous.

In the Lower Yatulia set of Central Karelia, a thick Segozero series is developed, sedimentary in its lower part (700–1000 m), and in its upper part (up to 750 m) – sedimentary-volcanogenic [234, p. 136]. In the middle and lower parts of the sedimentary strata section (below the stromatolitic dolomites crowning it), high-potassium shales are developed, which on average contain 6.5–8.9% K_2O and 7.8–25.0% Al_2O_3. The presence of a significant amount of K-feldspar in them has been proven [298].

Table 131 presents analyzes of the Lower Yatulian argillites and sandstones – one of the most ancient red-colored rocks on Earth [245]. The initial compositions are predominantly represented by K-alkalites and alkaline (also potassium) siallites. The relationship of these taxa is quite obvious here, so that the boundary between them (8% of alkalis) in this case has a formal character. It is very remarkable that the normalized alkalinity (NKM) of argillites is not only not lower, but on average even slightly higher than that of sandstones, a pattern that never occurs in humid deposits. Despite the absence of formally hydrolysate compositions among argillites, they should also be interpreted as formations of peculiar (arid) weathering crusts [298]. Just unlike the Vepsian red-colored rocks [245, p. 92] (see about them below) in the substrate of the Lower Yatulian crusts, apparently, there were more uniform rocks of acidic composition.

Among the Jatulian sandstones, K-arkoses predominate, and only one composition (sample 12) can be certified as quartzite. The presence of compositions with increased magnesian value (pseudosilites) among the arkoses is curious. Sometimes

Table 131

Chemical composition of argillites and sandstones
of the Lower Jatulian of Central Karelia.
Compiled according to A. V. Sochava, 1979 [245, p. 94]

n	I	II	3	12
	Argillites (alkaline normosiallite)	Sandstones (myosilite)	Argillites (alkaline hyposiallite)	Sandstone (supersilite)
n	8	7		
SiO_2	60.11	71.37	67.00	87.52
TiO_2	0.82	0.38	0.96	0.09
Al_2O_3	18.91	12.76	16.81	4.87
Fe_2O_3	5.21	1.61	2.68	0.63
FeO	0.59	0.26	0.14	0.14
MnO	0.03	0.05	0.02	0.04
MgO	2.46	2.37	1.23	0.96
CaO	0.50	2.21	1.33	1.71
Na_2O	0.13	0.08	0.14	0.30
K_2O	7.85	4.60	6.00	1.54
P_2O_5	0.11	0.10	0.20	0.05
SO_3	0.02	0.03	0.01	-
CO_2	0.68	2.75	1.03	1.16
LOI	2.74	1.79	2.36	0.84
Total	100.16	100.36	99.91	99.85
HM	0.43	0.21	0.31	0.07
FM	0.14	0.06	0.06	0.02
TM	0.043	0.029	0.057	0.018
FerM	0.30	0.15	0.16	0.16
NKM	0.42	0.37	0.37	0.38
AlkM	< 0.10	< 0.10	< 0.10	0.20

this can be confidently associated with increased carbonate content (dolomite), but in other cases, apparently, magnesium silicate (biotite?) is present. sample 3, judging by its intermediate position between argillites (cluster I) and sandstones (cluster II), should probably be qualified as siltstone.

Table 132 and in fig. 99 show red-colored argillites and sandstones analyzes of the Vepsian series of Karelia (upper Karelian sequence) [245]. Attention is drawn to the great originality of argillites. Of the seven compositions, only two are certified as alkaline siallites, and among the remaining ones we find K-alkalites, hydrolysates, pseudosiallite with a geochemical Mn anomaly (sample 2), strong phosphorus accumulations at a level of 0.70–4.13 % (cluster IV and sample 4) and even sulfate (cluster III). All this forces us to interpret the Vepsian argillites as products of arid weathering crusts redeposition, and in the substrate of these crusts there were various

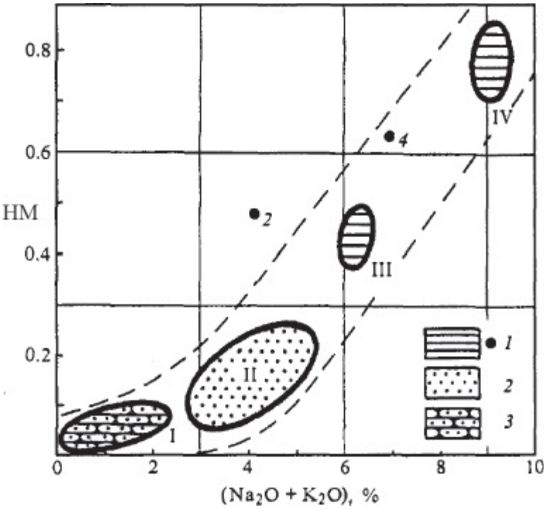

Fig. 99. Module diagram for the red-colored rocks
of Karelia's Mesoprotozoic Vepsian series.
Compiled according to A. V. Sochava, 1979 [245, p. 94].
1 – argillites and aleuroargillites, 2 – arkosic sandstones, 3 – feldspar quartzites

rocks, up to evaporites. As a result of this diversity, only one more or less homogeneous cluster IV (hydrolysate-alkalite) can be formed among argillites, while cluster III should be interpreted as silty clay. The Vepsian sandstones are also heterogeneous, including potassium arkoses (cluster II) and quartzites with K-feldspar (cluster I). The presence of a composition with elevated TM (0.098) among the latter may indicate the process of dynamic material sorting in shallow water facies.

Charodokan, Udokan, Kursk shales. In the Oldongsinsk grabensinklinal in the west of the Vitim-Aldan shield, on the surface of Archean granites with signs of weathering crust, at the basement of the Karelids Uguy series, the Charodokan formation, 350–425 m thick, with arkosic conglomerates, gravelites, and pudding breccias in its lower part, occurs. Above are strata of medium-grained arkosic and quartz sandstones with rare interlayers of red-brown argillites. As A. V. Sochava, who studied these strata, notes, "the degree of sand grains roundness increases from polymictic to monomictic sandstones" [246, p. 38], which can be considered an indication of additional mechanical differentiation of the arkosic material during the quartz sandstones formation. The Charodokan formation has characteristic features of the "weathering crust formation" with a strong differentiation of the original petrofund: the SiO_2 content in sandstones reaches 96.8 %, and the Al_2O_3 content in argil-

Table 132

Chemical composition of the red-colored deposits of the Vepsian series of the Karelian Mesoprotozoic.

Compiled according to A. V. Sochava, 1979 [245, p. 94]

Oxides and modules	I	II	III	IV	4	2
	Sandstones		Argillites		Argillites	
	Hyper-silite	Normo-silite	Alkaline normosiallite	Alkalite	P alkaline hypohydrolysate	Pseudo-siallite
n	3	3	2	3		
SiO_2	93.15	79.48	61.28	46.18	47.39	57.85
TiO_2	0.12	0.26	0.67	1.39	1.10	0.86
Al_2O_3	2.24	9.62	21.61	24.57	19.48	17.85
Fe_2O_3	1.25	1.95	4.13	9.12	9.30	3.19
FeO	1.17	1.82	0.40	0.43	0.29	5.72
MnO	0.02	0.02	0.02	0.07	0.05	0.48
MgO	0.30	0.64	0.97	1.17	0.64	3.86
CaO	0.26	0.30	0.45	1.63	6.40	0.30
Na_2O	0.11	0.19	0.11	0.07	0.09	0.36
K_2O	0.88	3.98	6.20	9.05	6.90	3.80
P_2O_5	0.05	0.14	0.24	1.09	4.13	0.16
SO_3	0.05	0.09	0.80	0.02	0.01	0.04
CO_2	0.60	0.25	0.48	0.93	3.19	0.86
LOI	0.26	1.39	2.83	3.86	0.68	4.69
Total	100.46	100.13	100.19	99.58	99.65	100.02
HM	0.05	0.17	0.44	0.77	0.64	0.49
FM	0.03	0.06	0.09	0.23	0.22	0.22
TM	0.055	0.027	0.031	0.056	0.056	0.048
FerM	1.03	0.38	0.20	0.37	0.47	0.50
NKM	0.44	0.43	0.29	0.37	0.36	0.23
AlkM	0.10	0.10	< 0.10	< 0.10	< 0.10	0.10

lites reaches 26.5 %. Particularly remarkable is the strong potassium accumulation and iron enrichment. The average K_2O content in argillites is 7.52 % (maximum up to 9.5 %), Fe_2O_3 is about 8 % (maximum up to 9.88 %). There is even more iron in siltstones – on average 12, maximum – up to 14.69 %. Based on redness and the hematite presence, the strata could probably be attributed to the "red-colored hematite formations" of the humid type identified by A. I. Anatolyeva [5]. However, this conclusion seems unfounded here. The high KM value in argillites (0.36), which exceeds the muscovite norm of 0.31, clearly indicates the presence of K-feldspar. This is difficult to reconcile with the assumption of the kaolinite presence in the pelitoids composition, which is required by the humid weathering model.

The Udokan series of Karelids is developed in the Olekma-Vitim mountainous country and includes the thick Sakukan formation. High potassium shales are concentrated in the middle and Upper Sakukan subformations. “And in this case, one can hardly doubt that these shales are the derivatives of strongest weathering crusts on the acidic rocks substrate” [298, p. 693].

In the lower part of the Kursk series of Karelids on the Voronezh shield, in the K_1^2 unit, which lies under the ferruginous quartzites, there are shales, which, even according to the average data compiled by V.K. Golovenok, contain 4.6–5.8% K_2O. Contrary to the of B.M. Mikhailov’s objections [181], there are numerous and rather convincing evidences for the Pre-Kursk weathering crust existence on granites and gneisses of the Mikhailovskaya series [82, p. 182–183].

Riphean. “Agalmatolites” of Northwest Scotland. The table 133 processed five analyzes of Riphean “agalmatolitic” (quartz-muscovite) “paleosoils” on the substrate of pink Karelian granite-gneisses (Lewisian sequence, NW Scotland [321]). With the substrate weathering, the feldspars content decreases (decrease in NKM) and the mica content increases (increase in HM) to values that are close to the hydrolysates boundary (0.55): cluster I ⇒ cluster II ⇒ sample 5. In this series, rocks are certified as alkalites – alkaline normosiallites – supersiallites.

Jalagun formation. It dates to the early Riphean, developed in the Middle Vitim mountainous country. Its middle subformation (850–1200 m) is mainly shale and, along with quartz-muscovite-chloritoid shales, contains quartz-chlorite-muscovite with 5.6–6.2 % K_2O and up to 30.7 % Al_2O_3 [82, p. 77].

Shales of Timan and the Southern Urals. In the Riphean section of the Middle and Southern Timan, the Chetlass, Bystrinsk and Vizing series are distinguished. In the Western structural zone of Timan, the Chetlass, Obdyrsk, and Dzhezhimsk uplifted basement blocks are located, where the Chetlass series is developed as part of the Svetlinsk, Novobobrovsk, and Vizing formations and the lower part of the Bystrinsk series, the Anyugsk formation. According to our graduate student L. I. Oparenkova, the Novobobrovsk formation contains interlayers of aluminous shales containing, on average, 5.52 % K_2O and 27.04 % $A1_2O_3$ in three analyzes. At the base of the Anyug formation, O. S. Kochetkov described metamorphosed weathering crusts composed of shales of very similar composition: 5–6 % K_2O and up to 26 % Al_2O_3. The Anyug formation itself is represented by a red-colored strata dominated by potassium arkoses and subarkoses. According to V. V. Tereshko, S. I. Kirillin, and G. Ya. Kazantseva, they contain up to 6.3 % K_2O.

In the Southern Urals, in the stratotype section of the Riphean, high-potassium rocks are found in all three sections, which are represented by

Table 133

Chemical composition of Riphean quartz-muscovite (“agalmatolite”) paleosols based on the granite and pegmatite substrate of the Lewisian sequence, NW Scotland. *Compiled according to I. Allison et al., 1992 [321, pp. 25–26]*

Oxides and modules	I	II	5
	Alkalite	Alkaline normosiallite	Supersiallite
n	2	2	
SiO_2	68.60	60.61	57.57
TiO_2	0.23	0.62	0.44
Al_2O_3	15.61	23.67	30.73
Fe_2O_3	0.88	2.29	0.73
FeO	0.73	0.26	0.01
MnO	0.03	0.02	0.01
MgO	0.56	0.95	0.32
CaO	0.89	0.03	0.02
Na_2O	1.72	0.15	0.13
K_2O	8.99	7.67	4.55
P_2O_5	0.06	0.03	0.02
H_2O^+	0.83	3.47	4.77
Total	99.13	99.77	99.30
HM	0.25	0.44	0.55
FM	0.03	0.06	0.02
AM	0.23	0.39	0.53
TM	0.014	0.026	0.014
FerM	0.10	0.11	0.02
NKM	0.69	0.33	0.15
AlkM	0.20	< 0.10	< 0.10

sedimentary series – megacycles. The thickest and most sustained horizons of high-potassium clay shales and arkoses are known at the basement of Burzyanian (Bolsheinzer formation) and Karatavian (red-colored Biryan subformation of the Zilmerdak formation). In both cases, the position of high-K strata directly above the surface of large stratigraphic unconformities clearly indicates their connection with weathering crusts [298, p. 693].

Dalred and Katangese shales. In Scotland, the Dalred metamorphic series is known, which dates to the Late Riphean–Early Cambrian interval. According to data compiled by V.K. Golovenok [82, p. 190–191], the K_2O content in the Dalred shales reaches 5.4–6.2 %, Al_2O_3 – 33.2 %.

According to A. V. Sochava [245], the Upper Riphean copper-bearing shales of the Katanga formation (Central Africa), according to four analyzes, contain an average of 9.88 % K_2O.

9.4. Metahydrolysates and alkalites of controversial genesis

These include aluminous, ferruginous, or highly alkaline metamorphic rocks, the genesis of which is not as clear as those described above, and the "endogenous or exogenous" alternative cannot be considered resolved, since it is very difficult to separate isochemical metamorphites from metasomatites among them. Of course, the boundary between the objects of "established" and "controversial" genesis is very subjective. For example, the aluminous and ferruginous granulites considered above may well be placed in the category of "controversial". And vice versa, some of the "controversial" objects may not be considered as such since arguments in favor of one of the two genetic hypotheses are sometimes much more weighty than alternative ones.

Aluminous gneisses of the White Sea sequence. O. I. Volodichev gave 43 analyzes of the Belomor Katarchean sequence gneisses, metamorphosed into disthene gneiss facies [55, p. 77–80]. Among these rocks, there are at least six separate petrographic varieties, of which two belong to the "subfacies of disthene-orthoclase gneisses" and four belong to the subfacies of "disthene-microcline and disthene-muscovite gneisses". Lithochemical data processing makes it possible to notice some features of these rocks [Table 134, Fig. 100].

1. Petrographic varieties of gneisses form "pure" (or almost pure) clusters I, V, VII–IX and mixed clusters II–IV, VI, which differ significantly in composition. At the same time, not only different gneisses differ (garnet-biotite from those with kyanite), but significant dispersion is also observed within the petrographic group of kyanite-garnet-biotite (clusters V, VII–IX). This means that lithochemical information is much richer than petrographic information.

On fig. 100, one can see an almost uncorrelated field, and on the HM – TM plot, a positive correlation trend emerges. This allows all (or most) analyzes to be considered as a single set – a certain set of related rocks. According to the HM, TM, and FerM values, the compositions could correspond to pelitoids and, partly, to psammoids (HM < 0.30). However, in most analyses, AlkM value > 1, which is not characteristic of even the most sodium Archean shales [228].

There is a wide development of alkaline (21 analyses) and magnesian (28 analyses) compositions. It is clear that this is due to the biotite presence. However, it is symptomatic that the presence of magnesian rocks – pseudosiallites and even pseudohydrolysates – is not accompanied by anomalies in titanium value and iron content.

These features allow us to draw two in general non-trivial conclusions.

1. The Belomor gneisses were formed mainly on the greywacke substrate, among which there were also more acidic varieties, as well as, apparently, rocks with an abundance of clay matrix, which brought them closer to

Table 134

Chemical composition of Catharhean metamorphites (garnet-biotite gneisses with kyanite and muscovite) of the White Sea sequence.

Compiled according to O. I. Volodichev, 1975 [55, p. 77–80]

Oxides and modules	I	II	III	IV	V	VI	VII	VIII	IX
	Myosilite	Pseudosiallite		Alkaline normosiallite	Alkaline pseudosiallite		Pseudosiallite	Alkaline pseudohydrolysate	Alkaline pseudosiallite
n	7	2	5	4	4	3	3	2	2
SiO_2	69.11	60.97	64.63	65.76	60.33	62.77	59.72	55.44	54.63
TiO_2	0.64	0.81	0.71	0.57	0.81	0.70	0.97	0.89	0.86
Al_2O_3	13.93	18.32	16.12	16.04	18.23	16.36	18.83	19.70	20.03
Fe_2O_3	1.04	1.56	0.86	1.14	1.29	1.46	0.85	2.79	1.59
FeO	4.87	7.34	5.83	4.58	6.30	5.25	7.19	7.44	7.58
MnO	0.09	0.13	0.09	0.11	0.10	0.08	0.08	0.12	0.15
MgO	2.72	3.20	3.31	2.88	4.11	3.33	4.39	4.94	4.62
CaO	3.48	1.65	2.83	2.90	2.56	2.73	2.45	2.09	2.17
Na_2O	2.13	0.93	2.97	3.34	3.01	3.51	2.36	2.15	3.06
K_2O	1.17	2.84	1.65	1.77	2.23	2.43	2.22	3.51	3.67
P_2O_5	0.13	0.05	0.17	0.12	-	0.05	0.08	-	0.12
LOI	0.91	2.25	1.26	0.99	1.19	1.53	1.15	1.13	1.69
Total	100.22	100.05	100.43	100.20	100.16	100.20	100.29	100.20	100.17
HM	0.30	0.46	0.37	0.34	0.44	0.38	0.47	0.56	0.55
FM	0.12	0.20	0.15	0.13	0.19	0.16	0.21	0.27	0.25
AM	0.20	0.30	0.25	0.24	0.30	0.26	0.32	0.36	0.37
TM	0.046	0.044	0.044	0.035	0.044	0.043	0.052	0.045	0.043
FerM	0.41	0.47	0.40	0.35	0.40	0.40	0.41	0.50	0.45
NKM	'0.24	0.21	0.29	0.32	0.29	0.36	0.24	0.29	0.34
AlkM	1.80	0.30	1.80	1.90	1.30	1.40	1.10	0.60	0.80

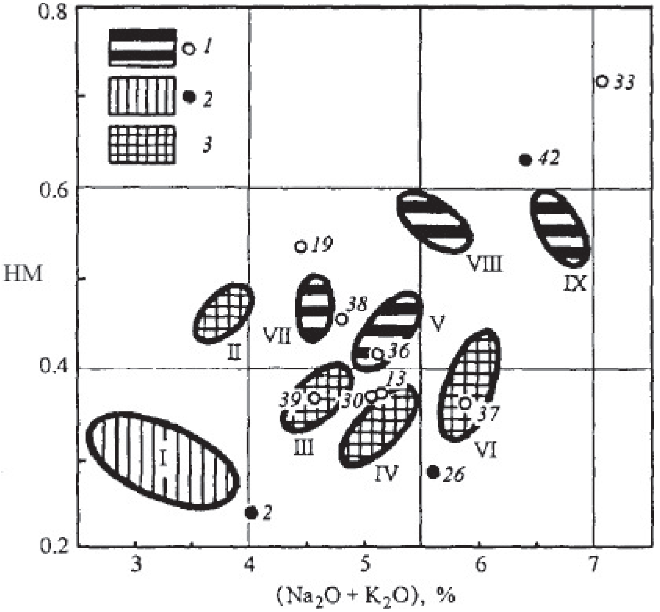

Fig. 100. Module diagram for gneisses of the Belomor sequence.
Compiled according to O. I. Volodichev, 1975 [55, pp. 77–80].
1 – kyanite-garnet-biotite gneisses (some with muscovite), 2 – fine-grained garnet-biotite gneisses, 3 – mixture of lithotypes (1 + 2)

pelitoids. Greywackes were probably derivatives of andesites (or granodiorites?), but not basalts. Only under such a condition can sands with increased magnesian content be formed, but with normal iron and titanium values.

2. In the processes of regional metamorphism, phenomena of allochemical metamorphism undoubtedly took place, affecting mainly alkalis and partly titanium (?). This is evidenced by the wide dispersion of points on all module diagrams, which does not allow any trend to be identified, as well as the abundance (11 out of 43!) of individual compositions that cannot be averaged.

It should be noted that, according to O. I. Volodichev, the White Sea gneisses were formed during migmatization and metasomatism of magmatic rocks of basic composition, partly eclogite-like.

Karelian metamorphites of Pechenga. E. T. Bobrov and I. G. Shchipakina [21], who described the ancient (Karelian) weathering crust developed after the Pechenga basalts (Kola Peninsula), in addition to the "unaltered" crusts (since we are talking about metamorphic rocks, this term should be understood conditionally) also identified "metasomatically altered rocks". However, it is very difficult to distinguish them (Table 135).

Clusters I and II correspond to the compositions of “unaltered” cores, which are very peculiar in themselves – in particular, they are represented by potassium alkalites, which, as we know, is very characteristic of ancient WCrs. However, it is very strange that such rocks could be formed on the basalt substrate. Nevertheless, in cluster III we find points of both “unchanged” (IIIa) and “metasomatically altered” WCs (IIIb). In general, the three samples of the latter are characterized by a lower total and normalized alkalinity and a significantly lower titanium value, but these features are also characteristic of the two samples of the former ones. This ambivalent situation allows two interpretations: (a) what is considered to be metasomatites, in fact, is not, but represents some zone of the ancient WCr; b) on the contrary, two more samples should be classified as metasomatites, which were characterized as “unchanged”. Additional information is needed to select an alternative.

Riphean sandstones of the Aldan shield. Terrigenous and carbonate deposits of the Uchur R_2 series were studied by E.M. Pinsky in the middle part of the Uyano-Ulkan trough (lower Uyan depression), where they are subdivided into the Gonam (below) and Omakhta formations. Table 136 and fig. 101 processed 27 analyzes of sandstones, siltstones and dolomites, among which 8 clusters and 5 individual compositions can be distinguished, i.e., the initial information is halved. Most of the composition points fall within a narrow band of positive correlation of parameters, which may indicate the petrogenic nature of sedimentary rocks.

Clusters Ia and Ib correspond to the Gonam sandstones, which are classified as supersilites and alkaline supersilites. High values of the normalized alkalinity NKM at low sodium content (AlkM < 1) show that potassium feldspar is the alkalis-bearer. It is obvious that these are quartz sandstones with K-feldspar, but practically without plagioclases. Such rocks could be formed during arid weathering of an acidic (granite or gneiss) substrate. The division of the samples into clusters Ia and Ib is conditional – it is obvious that they form a single set.

The IIIa and IIIb clusters combine the Gonam (IIIa) and Omakhta (IIIb) siltstones with a very high total alkalinity ($Na_2O + K_2O$ 11.7–12.05 %, and up to 12.4 % in some samples). Therefore, these rocks are certified as alkalites. In Chapter 6 it was shown that the genetic interpretation of alkalites allows several options, in particular: acidic (or alkaline) pyroclastites, alkaline metasomatites, weathering crust formations. In this case, the inclusion of clusters IIIa and IIIb in the same correlation band with quartz sandstones of cluster I indicates their relationship. In the case of alkaline metasomatites, one would expect some differences between the latter and the substrate, in particular, points falling out of the correlation band. More acceptable seems to be the idea that these rocks are alkaline or acid tuffs. However, this is contradicted by the TM values equal to 0.034–0.050 on average. For acidic pyroclastics, these values are too high; in rhyolites, the TM value is usually < 0.020, and often falls to such miserable values as 0.005 or even lower [310, 315].

Table 135

Chemical composition of the ancient metamorphosed weathering crust after the Pechenga basalts.
Compiled according to E. T. Bobrov and I. G. Shchipakina, 1991 [21, p. 42]

Oxides and modules	I	II	IIIa	IIIb	31	35
	Metasomatites (Ti alkaline)		Unaltered rocks (pseudohydrolysate)	Metasomatites (pseudosiallite)	Unaltered rock (alkaline carbonate pseudosiallite)	Metasomatite (pseudosiferlite)
n	2	2	2	2		
SiO_2	56.71	50.84	46.67	52.92	32.90	60.06
TiO_2	2.81	2.91	0.74	1.02	0.50	1.76
Al_2O_3	15.50	15.42	14.15	14.57	10.70	10.11
Fe_2O_3	3.81	9.81	7.09	2.11	3.35	7.76
FeO	2.27	3.02	6.48	8.89	3.12	6.11
MnO	0.08	0.10	0.20	0.20	0.13	0.16
MgO	0.20	1.00	5.63	7.70	11.85	4.13
CaO	2.66	2.05	10.93	5.12	15.97	1.67
Na_2O	0.10	0.10	2.42	3.30	0.18	0.10
K_2O	13.00	11.60	0.29	0.40	6.58	2.70
P_2O_5	0.33	0.33	0.11	0.11	0.08	0.44
LOI	2.10	2.43	4.60	3.25	14.27	4.25
Total	99.57	99.61	99.31	99.59	99.63	99.25
CO_2	0.77	0.44	2.04	0.45	11.52	0.22
HM	0.43	0.61	0.61	0.51	0.54	0.43
FM	0.11	0.27	0.41	0.35	0.56	0.30
AM	0.27	0.30	0.30	0.28	0.33	0.17
TM	0.181	0.189	0.052	0.070	0.047	0.174
FerM	0.34	0.71	0.92	0.72	0.59	1.18
NKM	0.85	0.76	0.19	0.25	0.63	0.28
AlkM	< 0.10	< 0.10	8.30	8.20	< 0.10	< 0.10

Table 136

Chemical composition of the Middle Riphean deposits

Compiled according to E. M. Pinsky, 1996

Oxides and modules	Ia	Ib	IIa	IIb	Ша	IIIb	IV
	Sandstones				Siltstones (alkalite)		Sandstones (carbonate-alkaline)
	Super-silite	Alkaline supersilite	Alkaline normosilite	Alkalite			
n	4	5	2	3	3	2	2
SiO_2	88.15	84.80	65.80	76.50	67.30	58.05	44.50
TiO_2	0.15	0.16	0.26	0.22	0.76	0.56	0.43
Al_2O_3	4.68	7.43	8.80	11.27	15.17	16.55	10.20
Fe_2O_3	0.39	0.41	0.33	1.07	3.23	1.85	2.25
FeO	0.10	0.00	0.78	0.12	0.21	0.55	0.17
MnO	0.01	0.03	0.03	0.01	0.01	0.01	0.08
MgO	0.60	0.10	3.55	0.20	0.42	2.15	6.10
CaO	0.85	0.24	5.75	0.29	0.21	3.25	13.85
Na_2O	0.20	0.20	0.20	0.20	0.20	0.20	0.20
K_2O	3.58	5.80	7.00	9.00	11.50	11.85	8.10
P_2O_5	0.06	0.05	0.07	0.07	0.12	0.07	0.15
BaO	0.014	0.038	0.726	0.061	0.039	0.035	0.066
LOI	0.92	0.48	7.01	0.59	0.79	4.92	14.51
Total	99.70	99.74	100.31	99.60	99.96	100.05	100.61
HM	0.06	0.09	0.15	0.17	0.29	0.34	0.30
FM	0.01	0.01	0.07	0.02	0.06	0.08	0.19
AM	0.05	0.09	0.13	0.15	0.23	0.29	0.23
TM	0.032	0.022	0.029	0.020	0.050	0.034	0.042
FerM	0.10	0.06	0.13	0.10	0.22	0.14	0.24
NKM	0.81	0.81	0.82	0.82	0.77	0.73	0.81
AlkM	0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10

Thus, the most probable is the interpretation of the alkalites of the clusters IIIa and IIIb as formations of an arid weathering crust over a granitoid substrate, potassium arkoses [298].

As for the Gonam sandstones in clusters IIa and IIb, their intermediate position between the extreme compositions of the clusters I and III rocks is obvious. In this case, which of the extreme compositions (I or III) should be considered initial? Apparently, the arkose sandstones of cluster I should be considered as such, and the alkalites of cluster III should be considered as more transformed. The position of the latter in the section also seems to be consistent with this: the samples in cluster I were taken in the upper part of the section, and in cluster III, in the lower one, which should take place during the WCr column redeposition.

Separate fields on the module diagram form the Omakhta carbonate sandstones (cluster IV) and dolomites (cluster V). The former are also characterized by high al-of the Uchur series, the Uyano-Ulkan trough, the Aldan shield.

V	26	29	32	36	50
Dolomites (carbonatolite)	Silty sandstone (alkalite)	Sandstone	Dolomite	Sandstones	
		Carbonatolite		Mn-Ba myosilite	Alkaline carbonate pseudosilite
2					
11.20	57.90	15.10	15.40	72.70	49.40
0.09	0.27	0.02	0.06	0.15	0.23
2.20	11.90	1.40	2.00	6.40	8.10
0.97	2.80	3.20	5.10	2.50	0.75
1.75	0.00	0.27	0.00	0.00	1.10
0.18	0.20	0.30	0.42	7.20	0.13
16.15	3.30	12.20	9.00	0.10	6.80
26.75	6.90	32.60	33.50	0.01	12.80
0.20	0.20	0.20	0.31	0.20	0.20
1.55	10.00	1.10	1.70	4.60	6.60
0.16	0.16	0.32	0.25	0.22	0.05
0.880	0.110	0.061	0.120	3.000	0.890
37.95	5.72	32.92	31.72	2.92	12.97
100.03	99.46	99.69	99.58	100.00	100.02
0.46	0.26	0.34	0.49	0.22	0.21
1.68	0.11	1.04	0.92	0.04	0.18
0.20	0.21	0.09	0.13	0.09	0.16
0.039	0.023	0.013	0.028	0.023	0.028
1.27	0.25	2.66	2.68	1.48	0.24
0.79	0.86	0.93	1.01	0.75	0.84
0.10	< 0.10	0.20	0.20	< 0.10	< 0.10

kalinity, clearly similar to the I–III series of rocks. In the latter, the clastic part (constituting approximately 15–16%) is obviously dominated by quartz. In these rocks, there is also a noticeable Ba accumulation in the form of barite; the same geochemical feature is characteristic of the Gonam sandstones in the cluster IIa.

Finally, two Gonam rocks have a specific composition: highly enriched in Mn and Ba (sample 36) and highly dolomitic sandstone (sample 50). In the latter, the silicate base is the same as in the sandstones of rocks series I–III (alkaline silite). Its composition is apparently identical to the sandstone composition in the clusters IIa, b (and the HM is increased, most likely due to carbonate iron).

The reason for the barium accumulation is of independent interest, but it is quite likely that this is also a result of arid weathering of potassium granitoids, initially enriched in barium. In such WCrs, barium removed from silicates could be fixed in the carbonate form.

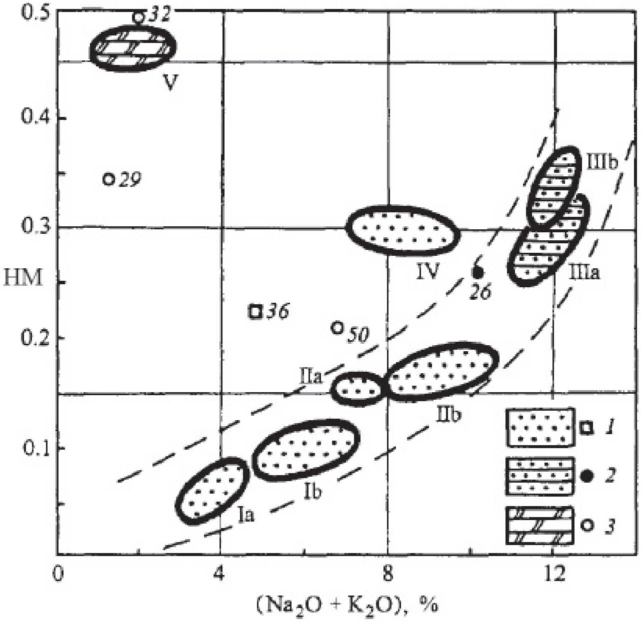

Fig. 101. Module diagram for the Middle Riphean deposits of the Uchur series of the Uyano-Ulkan trough.

Compiled according to unpublished data by E. M. Pinsky[4]*, 1996*

1 – sandstones, 2 – siltstones, 3 – dolomites.

Other objects of disputable genesis treated by us in the lithochemical standard include the Late Archean and Early Karelian metamorphosed eluvium based on various substrates on the Kola Peninsula [21], the Middle Riphean Beletarian metamorphic sequence of the Southern Urals [202], the Riphean diaspora bauxites of Mongolia [98), and recently discovered aporhyolitic diasporites of the Subpolar Urals. We will limit ourselves to consideration of the latter only, because even for this already well-studied object, the alternative – "metasomatic-hydrothermal or metamorphosed eluvial-crustal" – continues to be very acute [111, 304, 308].

Diasporic rocks of the Subpolar Urals. Concretionary diasporites and enclosing hematite-pyrophyllite shales with a diaspore in the Subpolar Urals were discovered by the Vorkuta geologist V.S. Ozerov only in 1985, although they literally lie on the surface, closely associated with apriolitic shales on the ridge Maldynyrd [304, 308].

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[4] We express our heartfelt gratitude to our friend E. M. Pinsky for providing these interesting materials.

The discoverer himself interprets diasporites as the most convincing evidence of the existence of metamorphosed Cambrian weathering crusts, calling diasporites “laterite conglomerates” [187, 188]. Although the eluvial-crustal nature of other metahydrolysates in this region – chloritoid, pyrophyllite, kyanite and other shales (not by rhyolites) – does not raise doubts in our minds, some features of the geology and geochemistry of aporhyolitic rocks make us seriously consider their alternative interpretation – as metasomatic formations like secondary quartzites [111, 304, 308].

So far concretionary diasporites are known in three parts of the ridge Maldynyrd (Fig. 102): 1) “Arch”, 2) a plateau to the NE from kar of the lake Grudependity (here is the unique gold-palladium deposit “Chudnoye”, discovered by V.S. Ozerov), 3) located somewhat to the north from the canyon of the creek Alkesvozh – the left tributary of the river Balbanyu, a large left tributary of the river Kozhim.

The “Arch” site is a flat swampy lowland (an ancient leveling surface?) 1.5×2 km^2 in size, where in 1988 the ditches of the A. V. Voznesensky’s party uncovered monotonous strata of red-colored hematite-diaspores of pyrophyllite shales with abundant diaspore concretions. Neither the thickness of the shales nor their relationships with the surrounding conglomerates, rhyolites, and diabases have been reliably established. On the rhyolite plateau near the Chudnoye gold-palladium deposit, outcrops of pyrophyllite-hematite-diaspore rocks form isometric spots or narrow bands surrounded by little altered rhyolites. Finally, in the rocky canyon the creek Alkesvozh throughout 0.5 km, the contact of Alkesvozh conglomerates and gravelites with aporhyolitic shales is exposed. The latter form a series of small wedges (apophysis?) in gravelites, which is very reminiscent of intrusive contact with zones of endo- and exocontact “hornfelses” – along the substrate of rhyolites and gravelites, respectively. Here, according to research data of the detailed profiles we passed, a very sequence picture was revealed, which is described in detail in [304].

In general, in the zone of interformational contact between Uralides and Pre-Uralides, the rocks relationships turned out to be so difficult, and the processes of their change are so intense, that almost all the facts obtained allow an alternative interpretation in terms of two models: a) metamorphosed Cambrian weathering crust along the rocks substrate of the Pre-Uralides sequence; b) metasomatites of several types (quartz-sericite, pyrophyllite, etc.), which include diasporites [137, 255].

According to the first model (V. S. Ozerov), the established mineral zonality of aporhyolitic shales is the zoning of the former lateritic weathering crust along rhyolites, where diasporites correspond to laterite-bauxites proper[5],

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[5] However, in recent years (1997–2000), V.S. Ozerov began to actively develop the idea of diasporites development on a substrate not of rhyolites, but of diaparems of kimberlite or alkaline-ultrabasic composition. Findings in diasporites of such minerals as ganite (zinc spinel) testify in favor of this, but there are no other confirmations of this idea yet (and are unlikely to be).

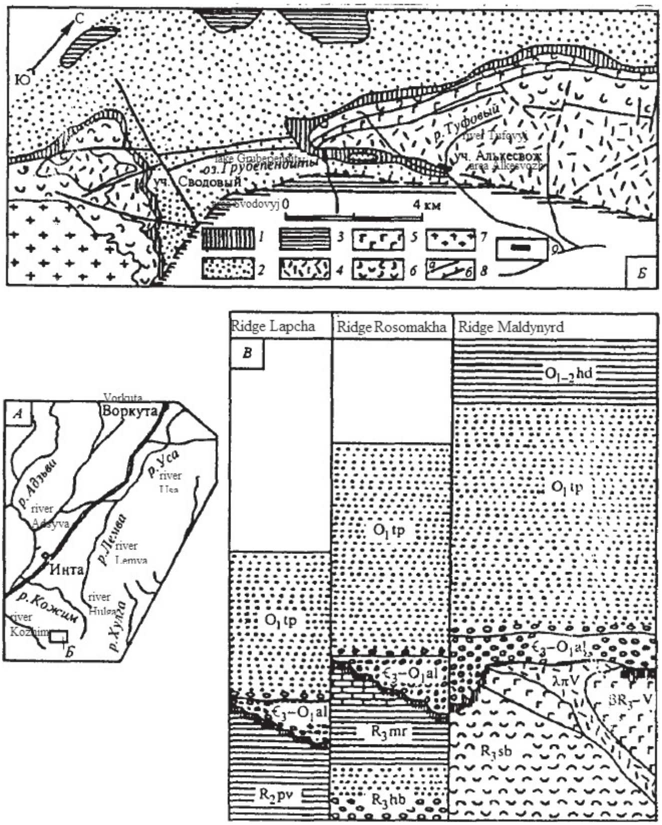

Fig. 102. Location of aporhyolitic diasporites outcrops on the ridge Maldynyrd, the Subpolar Urals. Materials by Ya. E. Yudovich, L. T. Belyakova, A. M. Pystin, S. A. Repina and V. S. Ozerov.

A – study area, B – the geological structure diagram of the southern part of the ridge Maldynyrd, C – conceptual scheme of interformational contact of Uralides and Pre-Uralid essequences [304, p. 82].

On the geological map. 1–3 – the basement of the *Uralidessequence*: 1 –gravelites, conglomerates and porphyroblastic chloritoid shales of the Alkesvozh strata (-€$_3$O$_1$al) and the underlying Cambrian weathering crust along the basement rocks; 2 – conglomerates, gravelites and quartzite-sandstones of the Telpos (Obeiz) formation (O$_1$ tp); 3 – silty shales of the Khydei (Saled) formation (O$_{1\text{-}2}$ hd); 4–6 – tops of the *Pre-Uralides sequence*: 4 – rhyolites of the Maldy sequence (λϖ–€$_1$), 5 – dolerites of the Manaraga sequence (βR$_3$–V), 6 – metabasites, rhyolites and their tuffs of the Sablegorsk formation (R$_3$–Vsb); 7 – granites of the Maldinmassif γV; 8 – breaks (a) and thrusts (b); 9 – areas with diasporic rocks. *Schematic columns*: metapelites and metatuffoids of the Puiva formation (R$_2$ pv), conglomerates and quartzites of the Khobeinskaya formation (R$_3$ hb), metapelites, metagreywackes (?) and dolomites of the Moroya formation (R$_3$ mr), aporhyolitic diasporites (*black*). Vertical strokes conditionally show the Cambrian weathering crust pyrophyllite shales – to kaolinite, sericite-pyrophyllite – to hydromica-kaolinite, and sericite shales – to hydromica zones of the weathering crust. At the same time, "anomalous" diasporites sharply enriched in hematite are interpreted as formations of the cuirass type.

In the second model, all zones are interpreted as facies of a single metasomatic-hydrothermal formation of secondary quartzites, while the presence of quartz veins is also of great importance, which is typical for the final process stage.

Obviously, it is necessary to extract new facts that will allow one of the alternative genetic models to be preferred. So far (1999), the metasomatic interpretation of diasporites has some advantage over the eluvial one [111, 304, 308].

9.5. Diagnostic signs of the metahydrolysates genesis

The presented material shows that the convergence of metahydrolysates features does not extend to **all** their features. If we approach the matter with an open mind and try to avoid extremes, then we can identify a number of such signs that should (with varying degrees of reliability) be considered diagnostic for metahydrolysates of a certain genesis.

Formation sign: finding metahydrolysates in lepigenic sedimentary formations. All the materials presented in Section 9.3 make it possible to generalize them within the concept of *lepigenic* sedimentary (and corresponding sedimentary-metamorphic) formations [294].

Lepigenic sedimentary formations are distinguished by the presence of weathering crust material, both autochthonous (in situ) and allochthonous (near redeposition) types. They are located on interformational boundaries between strata that differ significantly in age, composition and genesis, separated in time by large breaks in sedimentation and, accordingly, by surfaces of stratigraphic, angular, and sometimes azimuthal unconformity.

The strato- and tectonotype of the lepigenic formation is the *Alkesvozh stratum* - $€_3$–O_1 al identified by V. S. Ozerov in the Subpolar Urals [187], which lies at the interformation contact between the two largest tectonic sequences by N. P. Kheraskov: the Baikalian (Pre-Uralides) and the Caledonian-Hercynian (Uralides) [75, 111]. The Alkesvozh terrigenous strata lies at the base of the thick oligomict Telpos (Obeiz) formation O_1, which V. N. Puchkov [218] identified with the B. M. Keller's Falakh formation. The strata are highly variable laterally and are a sequence interbedding of conglomerates, gravelites and sandstones, mostly converted into slates. A distinctive strata feature is the presence in its composition of metamorphosed products of the Cambrian weathering crust: sericite, diaspore, pyrophyllite, chloritoid, abundant hematite (the last three in large spectacular crystals are redeposited in late Alpine-type veins), sometimes also kyanite and paragonite. If it overlies the Vendian-Cambrian rhyolites, then it contains (and/or underlies) diaspore-bearing pyrophyllite and sericite shales enriched in REE inherited from rhyolites, and if it occurs on Riphean-Vendian diabases, then it is dominated by sericite-pyrophyllite-chloritoid shales, often with high contents of leucoxene and hematite [111, 304]. A similar “geochemical inheritance” is also noted when the Alkesvozh strata occurs on sericite-chlorite shales of the Puiva (R_2 pv) or Moroin (R_3 mr) formations [317].

The lower contact of the Alkesvozh strata is very distinct because this is the interformational boundary between the Uralides and the Pre-Uralides. So, in a kar of the lake Grubependity L. T. Belyakova demonstrated this contact, where stratigraphic, angular, and azimuthal unconformity is visible, by the commission for the preparation of the III Ural Stratigraphic Conference (1977) [111]. During the periods of the Caledonian and Hercynian diastrophisms, the interformation contact “tectonized”: a massive plate of Telpos conglomerates with the Alkesvozh strata “soldered” to it could easily slip over the surface of the ancient weathering crust – pyrophyllite and sericite shales with the formation of various cataclasites [304]. As a result of such movements on mount Lesvie and mount Lapcha (upper reaches of the Karavanny brook) “pseudoconglomerates” with magnetite, chloritoid and pyrophyllite in cement were formed; quartz pebbles here are turned into narrow long lenses with a length to width ratio of up to 10:1.

The picture of a clear tectonic contact can lead to a suggestive but erroneous conclusion that all metahydrolysates in the contact zone, for example, shales with chloritoid and kyanite, were formed as a result of late hydrothermal metasomatic processes. We noted above that it was precisely this idea that was developed in the book by V. N. Razumova [220], but just the example of the already well-studied zone of interformation contact in the Subpolar Urals casts doubt on the correctness of some V. N. Razumova’s constructions. Here the cause should be interchanged with the effect: it was the presence of ancient weathering crusts that “provoked” the development of disjunctives, followed by hydrothermal working out of tectonically weakened zones, which is observed everywhere in the “Ural unconformity”, that is, in the zone of interformation contact “Uralides–Pre-Uralides”.

At the same time, the V. N. Razumova’s correctness was confirmed, who allowed the multi-stage formation of hydrolysate formations in the contact zone between the folded basement and the sedimentary cover. In any case, in the Subpolar Urals, isotopic data fix at least three diastrophisms: in the Late Riphean–Vendian, Devonian, and Permian [111]. The imposition of late hydrothermal metasomatic processes both on the metamorphosed Cambrian weathering crusts and on the Alkesvozh strata greatly complicates the whole picture observed at the interformation contact [111, 255, 304].

In contrast to the lower one, the upper contact of the Alkesvozh strata with deposits O_1 is not quite distinct and, according to V. S. Ozerov, has an adjoining character. It is recognized with a certain work experience by a number of more subtle features: color (variegation and the presence of "black" hematite conglomerates are characteristic for Alkesvozh), pebble composition (an abundance of quartzites, the presence of rhyolites, aporhyolitic shales and diabases, and the predominance of vein quartz are characteristic of Alkesvozh) and some others.

The V.S. Ozerov's pioneering work and additional data obtained by us in 1992-1998 revealed the wide distribution of the Alkesvozh strata in ten points of the Kozhim region of the Subpolar Urals. As it turned out, earlier these deposits were either considered to be part of the Telpos O_1 tp or Sablegorsk formation R_3–V_1 sb or were identified with the Laptopai formation V_2 lp [111]. According to V.S. Ozerov, the proluvial-deluvial strata of the Alkesvozh strata has been preserved from complete erosion by the waters of the Early Ordovician transgression in sublatitudinally oriented paleodepressions of the Cambrian relief [187]. Its accumulation was preceded by the epoch of continental weathering, covering the Middle and, probably, part of the Early Cambrian, i.e., at least 50 million years [75].

In 1985–1997, remarkable rocks and minerals were discovered in the Alkesvozh strata and underlying metamorphosed weathering crusts in the interformation contact zone: diaspore rocks, silicate-oxide manganese ore composed of brownite, spessartite and piemontite; gold-bearing and manganese-bearing rocks of acid composition – apoarcosic shales with an abundance of spessartine and piemontite; amazing vein and nodule-like segregations: giant-crystalline pyrophyllite-chloritoid, chlorite-tourmaline, and pink spessartine-epidote-quartz with arsenic monazite and, accordingly, with hurricane concentrations of REE; occurrences of lazulite in quartz veins associated with the initial sorption accumulation of phosphorus on iron hydroxides in the Cambrian weathering crust; unique in composition accessory zinc-manganese chrome-spinels and rare-earth minerals – monazite-1 with high As content, high-manganese epidote, unusual xenotime-1, closely associated with gold and yttrium arsenate – chernovite; unusually rich occurrences of visible gold, the content of which in individual hand samples is calculated in kilograms per ton; a diamond crystal in a small-volume sample of the Alkesvozh conglomerates [73, 111].

As a result, the identification of the Alkesvozh strata and the findings of a metamorphosed weathering crust at its basement acquired the importance of the most important stratigraphic criterion for metallogenic forecasting in the Subpolar Urals. In addition to gold and diamonds, Vorkuta geologists

L. T. Belyakova, M. V. Ilyin, A. V. Voznesensky and ourselves discovered commercial concentrations of REE (especially yttrium) in diaspore and pyrophyllite-diaspore shales, and the shales themselves can be considered as ores of alumina and refractory raw material.

In Chapter 8, it was shown that the weathering crust formations, the material of which formed the lepigenic formations, belong to two main types: humid and arid. In the case of acidic humid weathering, complementary pairs “quartz sandstones + kaolinite-containing clays” (acidic substrate) or “hematite-containing quartz sandstones + ochers, allites, bauxites” (basic substrate) are formed. The latter, by the way, reveals the nature of the phenomenon of red-colored strata of the humid type described by A.I. Anatolyeva [5]. Such are some ancient strata of quartz sandstones with abundant hematite, for which only igneous rocks rich in iron could serve as a terrigenous source of iron – at least not more acidic than andesite-diorite.

If we exclude the disputable case of the association of Catharhean quartzites with sililimanite gneisses (see Section 8.2), then in all other cases the sedimentary formation of the quartz sandstone + alumina shale association remains the most probable. Of course, purely theoretically, quartz sandstones may not necessarily be formed due to the erosion of high-quartz eluvium (although, we note, the formation of quartz sands due to “multiple washing and redeposition”, according to N. M. Strakhov, has long been refuted by observations of the large rivers alluvium [249]). However, it is the *association* of quartz sandstones with high alumina rocks that is important in this case.

In the case of alkaline arid weathering, complementary pairs are formed: potassium arkoses and high-potassium clays with K-feldspar (according to the acidic substrate) or quartz greywackes and Fe-Mg hydromica-montmorillonite and palygorskite clays (according to the basic substrate).

Thus, the presence of metahydrolysate rocks in lepigenic sedimentary formations is an important evidence of their supergene (rather than hydrothermal-metasomatic) primary nature.

Substrate-formational sign: attraction of hydrolysates to volcanogenic strata. Theoretically, it is far from easy to imagine the formation of thick weathering crusts in areas of active volcanism. The high frequency of eruptions allows the development of only a thin soil layer, which is destroyed by the next lava flow and can be fossilized only under an ash layer. It is even more difficult to explain why weathering crusts develop only over tuffs (this is precisely the predominant confinement of metahydrolysates), avoiding lava covers. And vice versa, as we have seen, the formation of secondary quartzites (not to mention the genetically related propylites, the hydrothermal nature of which is indisputable) is a typical feature of volcanogenic strata.

Therefore, the paragenesis of metahydrolysates with volcanogenic strata can serve as a diagnostic feature. However, it is rather weak and more informative only in combination with others.

Zonal-morphological criterion. If in a column containing metahydrolysates it is possible to determine the position "top-bottom" at the time of its formation, then the eluvial-crustal zoning (hypsometrically, the upper zone is the most mature) should be opposite to the zoning formed by ascending hydrotherms (the lower zone is the most mature). If the metasomatic column is oriented subhorizontally or obliquely to the horizon, then the occurrence of some symmetry can serve as a diagnostic feature: near-vein (near-fissure) metasomatites develop on both sides of the cracks, and later hydrothermal veins are often located in the center of the column. Naturally, this feature is completely uncharacteristic of eluvial-soil cores – they should not have any symmetry. Therefore, the presence of symmetrical zoning is a good indication of the hydrolysates' hydrothermal nature.

The "non-canonical" order of the zones in the column can also be diagnostic. Such a picture was observed, for example, by Ukrainian researchers in argillisites at the Slavyansk mercury deposit in Donbass (Kukovsky et al., 1982). Here, in relatively low-temperature argillisites, the following *diabase argillisation zoning* was observed: *montmorillonite zone ⇒ kaolinite zone ⇒ hydromica and paragonite zone*. The interpretation by the authors of the paragonite presence is interesting (it is believed that the paragonite formation at temperatures below 350 °C is thermodynamically impossible). They explain this by the proximity of the salt stock, which obviously gave rise to sodium chloride hydrothermal brines. However, for our topic, t***he extreme position of the hydromica zone in the argillisite column*** is more important, while in the weathering crust along the basic rocks, the order of zones is known to be different: montmorillonite ⇒ hydromica ⇒ kaolinite.

Mineralogical signs. As shown above, the acid leaching areas associated with retrograde metamorphism are characterized by a metasomatic column, the frontal zone of which is characterized by a sequence multimineral paragenesis, including both clearly hydrolyzed minerals (kyanite, staurolite) and calcium-iron-magnesian (amphiboles, phlogopites, biotites, celadonites, plagioclases). We can confidently assume that such rocks are not found among the eluvial-crustal metahydrolysates. Therefore, their presence can be considered a diagnostic sign. Using the example of pyrophyllite deposits in Armenia, one could see that mixed-layer pyrophyllite-montmorillonite, as well as silicates rich in halogens and boron, are a typical feature of secondary quartzites.

An important mineralogical feature is the sulfates presence. In weathering crusts, sulfates are characteristic only of the "alum process", which owes its origin to the oxidation of sulfide-rich black shales (or sulfide ores). However, as the studies by Acad. N. P. Yushkin and his students show, in this case, very specific semi-amorphous mineraloids and sequence aquatic iron and aluminum sulfates are formed in paragenesis with exotic aquatic iron-aluminophosphates and phosphate sulfates [74, p. 218–220; 318–320]. The very specificity of this paragenesis serves as an excellent diagnostic sign of hypergene sulfuric acid weathering. Conversely, the formation of alunite in paragenesis not only with pyrophyllite or kaolinite, but also with sulfides (pyrite), barite, gypsum, boron minerals (dumortierite), halide silicates (zuniite, topaz) is a reliable sign of the formation of secondary quartzites or their low-temperature facies – argillisites. The presence of high-temperature modifications of silica (tridymite) should also be attributed to the same feature.

Metastable phases and pseudomorphs can serve as other important mineralogical features. As noted by V. G. Bogolepov [24], there are two signs that distinguish exogenous (low-temperature) metasomatism from endogenous (thermal). First, with exogenous metasomatism, the process proceeds in cascades – step by step – and therefore slowly. As a result, many metastable phases arise. On the contrary, high-temperature endogenous metasomatites are characterized by a fast process, so the metastable phases do not last long. Secondly, pseudomorphoses are very characteristic of an exogenous process, while they are uncharacteristic of an endogenous process, since the period of pseudomorphism is very short (reduced).

To this we would add *the variability of the mineral composition and the presence of poorly crystallized phases*, indicating their formation at low temperatures during diagenesis. We observed such a pattern in shales at the Uralides–Pre-Uralides interformational contact for rare-earth phosphates, arsenates, molybdotungstates, as well as for epidotes, hematites, and some other minerals. Apparently, these minerals were formed in the Cambrian weathering crust. During subsequent transformations (associated with the metamorphism imposition), they were replaced by better crystallized phases of a simpler composition (a typical example is the transformation of microaggregate "shale-like" arsenic-containing monazite-1 into pure regular monazite-2 crystals) [111].

Geochemical features. Among the signs of hydrothermal-metasomatic hydrolysates or alkalites, their *acidic composition* should be attributed. So, on the rhyolites and dacites substrate, rocks of the "pyrophyllite quartzites" type are formed, sometimes even with diaspores, in which, despite the increased alumina content, the silica content is *higher* than in the original volcanic rocks. There is no place for such rocks in the eluvial WCr column – kaolinite formations are always poorer in silica than the substrate.

Another sign of hydrothermal-metasomatic hydrolysates can apparently be considered a deep aluminum and iron separation (with the formation of spatially isolated mineral accumulations). Such separation is possible only in very acidic (and, moreover, reducing) media, which are not characteristic of the Phanerozoic eluvial process.

The presence of geochemical anomalies of rare alkalis and some their hydrothermal companions (fluorine, arsenic, etc.) in clay hydrolysates can also serve as evidence of argillisites, since these elements usually do not accumulate in weathering crusts. A useful diagnostic feature may be the presence in such formations of carbonates – minerals “forbidden” during humid crust formation. It is true that carbonates are common in arid-type WCr, but the latter can be recognized by potassium accumulations; if none is observed, then the specified geochemical association (Li, Rb, Cs, F, As, Be, W plus carbonates) indicates a hydrothermal process.

A characteristic metahydrolysate feature in areas of progressive granulite and regressive amphibolite (or greenschist) metamorphism is the *chemotypes diversity* (association of hydrolysates with alkaline and magnesian compositions) and *a wide scatter of points on module diagrams without clearly expressed trends.* Taken together, these features testify to allochemical thermal metamorphism.

Brief conclusions

1. Hydrolysed rocks, i.e., the products of natural hydrolysis, their metamorphosed analogs – metahydrolysates, as well as the residual deep leaching products closely associated with them, have a dual, convergent nature. They can form both in eluvial and endogenous hydrothermal-metasomatic processes. Since hydrolysates and metahydrolysates are important minerals, the problem of their genetic diagnosis is very relevant.

2. In addition to the chemical and mineral composition convergence, the genetic diagnosis of hydrolysates is very complicated by the similarity of geological settings favorable for their formation. In particular, zones of large and largest structural unconformities between tectonic sequences, break and fractures zones, for example, surfaces of regional thrusts, layers or packs of layers of increased permeability – all of them are equally favorable for the formation of both low-temperature supergene and hydrothermal-metasomatic hydrolysates.

3. Several objects of hydrolysate and metahydrolysate nature of both main types are considered: endogenous (hydrothermal-metosomatic and metamorphogenic) and exogenous (metamorphosed eluvial-crustal). It has been established that among the eluvial crustal products there are formations of two types: a) low alkaline, including low potassium, and b) high potas-

sium. The wide distribution of the latter in the ancient strata gave rise to particularly persistent discussions among geologists. Meanwhile, red-colored formations of this type (in the rank of entire stratons) are, as a rule, derivatives of ancient weathering crust strata of the arid type, which are very characteristic of the Precambrian.

4. This analytical review allows us to see that, along with the signs of convergent similarity, objects of different genesis also have indisputable features of difference. The criteria for such a difference can be: a) formational, b) zonal-morphological, c) mineralogical and d) geochemical. The combination of these criteria makes it possible to establish the genetic nature of many, if not most, metahydrolysates.

5. Undoubtedly, the most difficult to diagnose are *polychronic metamorphites*, for which the occurrence of both exogenous and endogenous processes of leaching and hydrolysis is quite realistic – in different sequence. For example, it is possible to superimpose allochemical metamorphism on metahydrolysates of an eluvial-crustal nature, or, conversely, the weathering crust development along the allochemical metamorphite substrate. However, even for such objects of disputable genesis, the methodological approaches outlined in this chapter can be productive. They at least give the geologist information for consideration and clearly define the range of additional studies that are necessary for a more reliable diagnosis.

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