ISSN 0016-7029, Geochemistry International, 2006, Vol. 44, No. 6, pp. 559–580. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.V. Maslov, Yu.L. Ronkin, M.T. Krupenin, G.A. Petrov, A.Yu. Kornilova, O.P. Lepikhina, O.Yu. Popova, 2006, published in Geokhimiya, 2006, No. 6, pp. 610–632.

Systematics of Rare Earth Elements, Th, Hf, Sc, Co, Cr, and Ni in the Vendian Pelitic Rocks of the Serebryanka and Sylvitsa Groups from the Western Slope of the Central Urals: A Tool for Monitoring Provenance Composition

A. V. Maslov, Yu. L. Ronkin, M. T. Krupenin, G. A. Petrov, A. Yu. Kornilova, O. P. Lepikhina, and O. Yu. Popova

Zavaritskii Institute of Geology and Geochemistry, Ural Division, Russian Academy of Sciences, Pochtovyi per. 7, Yekaterinburg, 620151 Russia
e-mail: maslov@igg.uran.ru

Received September 15, 2004

Abstract—This paper presents the first data on the systematics of rare earth elements (REE), Th, Hf, Sc, Co, Cr, and Ni and the Nd model ages of fine-grained aluminosilicate clastic rocks of the Serebryanka and Sylvitsa groups of the Vendian from the Kvarkushsko–Kamennogorskii meganticlinorium (western slope of the Central Urals). It was found that the REE distribution patterns of shales and mudstones of the two groups are similar to those of the majority of post-Archean fine-grained terrigenous complexes. The presence of pelitic rocks with $Gd_N/Yb_N > 2.0$ in a number of Vendian levels suggests a contribution from an Archean component in the composition of the fine aluminosilicate clastic material. This is probably also indicated by the high degree of heavy REE depletion in some mudstone samples. The REE systematics allow us to suppose a heterogeneity of Vendian paleocatchments and variations in their composition with time. The eroded areas had the most mature composition in the beginning of Serebryanka. Starting from the second half of Serebryanka, mafic and/or ultramafic rocks started playing a significant role in the provenances. The rocks of the lower portion of the Serebryanka Group show T_{Nd}(DM) values of about 2.0 Ga, whereas the upper part of the section is dominated by rocks with T_{Nd}(DM) ≅ 1.77–1.73 Ga. This indicates that during the Taninskaya and Koiva time periods, fine aluminosilicate clastic material was supplied into the sedimentation region mainly from the west, from the eastern areas of the east European platform, where Archean and Early Proterozoic crystalline complexes dominated. A decrease in model ages was related to the addition of juvenile mantle material to the mature continental crust. Such processes can be illustrated by the mafic–ultramafic complexes (Dvoretskii, Shpalorezovskii, Vil'vinskii, etc.) located in the field of Vendian sedimentary sequences, which show T_{Nd}(DM) values from 824 to 707 Ma. It was concluded that the history of the formation of an Early Vendian rift in the western slope of the central Urals included only one rifting event (rather than three, as was previously supposed), which was supported by a variety of recent geological and isotope geochemical data.

DOI: 10.1134/S0016702906060036

INTRODUCTION

The isotope geochemical characteristics of fine-grained terrigenous rocks (mudstones, shales, and fine-grained siltstones) occurring in the majority of sedimentary sequences of varying age are successfully used in reconstructions of the environments of their formation (composition and evolution of paleocatchments, paleotectonics, paleoclimate, paleogeography, redox conditions in basins, etc.) [e.g., 1–31].

An efficient method for the reconstruction of the compositions of catchment rocks is an analysis of the distribution patterns of rare earth elements (REE) and various indicator ratios of La, Th, Co, Sc, Cr, Ni, and some other trace elements, because these characteristics are not significantly disturbed by the processes of sedimentation, lithogenesis, and metamorphism. Such results have been extensively reported in international journals, but in Russia these studies are just beginning. Therefore, any publications in this field are interesting and may have important methodical applications.

This paper focuses on the isotope geochemical reconstruction of the composition and evolution of the upper crust during the accumulation of the Vendian deposits of the Serebryanka and Sylvitsa groups of the Kvarkushsko–Kamennogorskii meganticlinorium (western slope of the central Urals) and continues a series of our publications deciphering the formation conditions for the Precambrian sedimentary sequences of the Urals [32–35, etc.]. This study was also aimed at comparing our data with the results of previous lithological and petrographic investigations.

LITHOSTRATIGRAPHY OF THE SEREBRYANKA AND SYLVITSA GROUPS

The Vendian sequences of the Kvarkushsko–Kamennogorskii meganticlinorium are exposed over a distance of about 200 km from south to north by numerous right tributaries of the Chusovaya River (Fig. 1) and are composed of two large sedimentary groups, Serebryanka and Sylvitsa [e.g., 36–38].

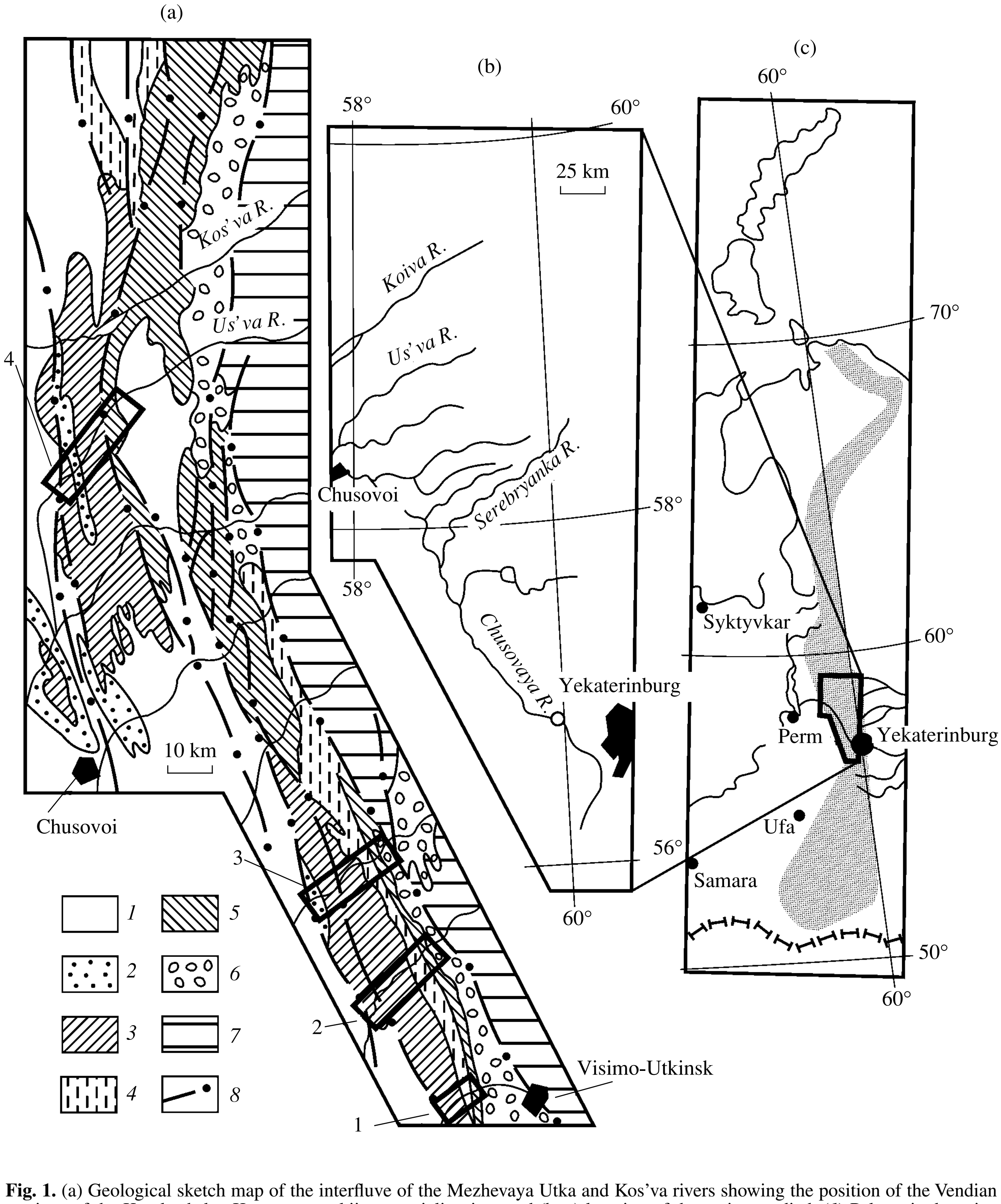

Fig. 1. (a) Geological sketch map of the interfluve of the Mezhevaya Utka and Kos'va rivers showing the position of the Vendian sections of the Kvarkushsko–Kamennogorskii meganticlinorium and (b, c) location of the region studied. (*1*) Paleozoic deposits, (*2*) Ust'-Sylvitsa Formation; (*3*) Chernokamenskaya Formation; (*4*) Perevalok and Staropechninskaya formations; (*5*) Koiva, Butonskaya, and Kernosskaya formations; (*6*) Garevskaya and Taninskaya formations; (*7*) Upper Riphean deposits; and (*8*) a fault. Numerals in Fig. 1a show sections along the (1) Mezhevaya Utka, (2) Serebryanka, (3) Sylvitsa, and (4) Us'va rivers.

The Serebryanka Group includes, from bottom to top, the Taninskaya, Garevskaya, Koiva, Butonskaya, and Kernosskaya formations. The *Taninskaya Formation* (up to 500 m thick) consists of tillite-like conglomerates with scattered pebbles interbedded with feldspar–quartz sandstones, siltstones, and silty shales. The *Garevskaya Formation* (up to 700–750 m thick) includes fine-grained sandstones and shales. The *Koiva Formation* (up to 250–300 m thick) is composed of thinly intercalated phyllite-like shales, siltstones, and variegated limestones; some sections of the formation include packages and beds of pebble conglomerates. The *Butonskaya Formation* (300–350 m thick) includes banded carbon-poor dark gray shales with occasional siltstone interbeds. The *Kernosskaya Formation* (200–350 m thick) is composed of sandstones and phyllite-like silt–clay rocks. In the northern part of the Kvarkushsko–Kamennogorskii meganticlinorium, the sections of the upper Kernosskaya Formation contain abundant volcanic rocks of the Dvoretskii complex. This complex is composed of moderately alkaline rocks of the first phase: picrites, trachybasalts, basaltic trachyandesites, trachyandesites, and trachytes and alkaline rocks of the second phase: hyalomelanephelinites, olivine hyalomelanephelinites (limburgites), alkali basalts (nepheline basalts and tephrites), basic phonolites, alkali trachytes, and phonolites.

The K–Ar isotopic ages of the Dvoretskii complex range within 285–420 Ma [e.g., 29, 40, 36]. Ronkin [41] determined the age of the Dvoretskii trachyandesites as 569 ± 42 Ma (Sm–Nd method for bulk-rock samples) and 559 ± 16 Ma (bulk-rock Rb–Sr method). The isotopic age of alkaline gabbros of the Kus'inskii complex, which is usually regarded as an intrusive analog of the Dvoretskii volcanic association, is 626 ± 57 Ma (Sm–Nd method) [42, 43]. The pyroxene picrites of the same complex were dated at 608 ± 3 Ma by the Rb–Sr method.

The Sylvitsa Group includes the Staropechninskaya, Perevalok, Chernokamenskaya, and Ust'-Sylvitsa formations. The *Staropechninskaya Formation* (up to 500 m) is composed of pebble-poor conglomerates (lower part) and dark-colored sandstones, siltstones, and shales (upper part). The rocks of the formation overlie the earlier sequences with a hiatus and fill a series of incised valleys [36, 44]. The *Perevalok Formation* (no more than 300 m) is composed of dark-gray mudstones, sandstones, and gravelstones. It is overlain by a thick (1500–1800 m) sequence of mainly fine-grained greenish-gray sandstones, siltstones, and mudstones distinguished as the *Chernokamenskaya Formation.* The section of the Sylvitsa Group is crowned by the polymictic and feldspar–quartz sandstones with thin interbeds of siltstones and mudstones of the *Ust'-Sylvitsa Formation.* Its thickness is 500–600 m.

THE ENVIRONMENTS OF THE FORMATION OF SEDIMENTARY SEQUENCES OF THE SEREBRYANKA AND SYLVITSA GROUPS: PREVIOUS WORK

The mineralogy and petrography of sandstones and conglomerates of the Serebryanka Group were studied mainly in 1960–1980. Kukharenko [45] argued that the boulder and pebble material in the conglomerates of the lower Taninskaya Formation was derived mainly from the internal highs of the Ural geosyncline located east of the present-day Kvarkushsko-Kamennogorskii meganticlinorium. Subsequently, Kurbatskaya [46], Kurbatskaya and Ablizin [47], and Ablizin et al. [36] showed that the tillite-like conglomerates of the Taninskaya Formation are dominated by rocks identical to the rocks of the base of the east European platform and minor fragments of Riphean rocks.[1] According to these authors, the main source area was located southwest and west of the modern Kvarkushsko–Kamennogorskii meganticlinorium, and part of the material was supplied into the basin from the east. According to the same authors, the scattered pebbles from the conglomerates of the Koiva level are dominated by fragments of quartzitic sandstones, felsic igneous rocks, cherts, and quartzites; fragments of carbonate rocks occur in some sections. During the Butonskaya time, the provenances were presumably located in the east. The conglomerates and gravelstones of the Kernosskaya Formation contain 90–95% fragments of the underlying Riphean rocks (Fig. 2). However, the analysis of the typomorphic characteristics and associations of quartz types in the base rocks and sandstones of the Kernosskaya Formation suggested that its source was also mainly the granite gneisses of the base of the east European platform [36].

The pebbles of conglomerates from the Staropechninskaya Formation are composed of sedimentary rocks of the underlying Kernosskaya Formation (sandstones, quartzitic sandstones, cherts, carbonate rocks, siltstones, and phosphorites), occasional mafic igneous rocks similar to the rocks of the Dvoretskii complex, and granitoids. The main heavy minerals are rutile, zircon, and chromite.

The sandstone matrix of the Chernokamenskaya Formation includes abundant fragments of andesite and basalt porphyries, trachyte porphyries, and sedimentary rocks [36].

There is still no consensus concerning the history of the basin that existed in the Vendian in the junction zone between the east European platform and the central Urals. Mitrofanov and Kozakov [49] believe that the geosyncline process accompanied by the formation of the oceanic crust began in the Urals during the Vendian or Cambrian, and continental rifting prevailed in

[1] Suslov et al. [41] detected volcanics of the Shchegrovitskaya Formation (complex) among the fragments of the Taninskaya conglomerate. The volcanics of the Shchegrovitskii complex were dated at 672 ± 22 Ma by the whole rock Rb–Sr method [48].

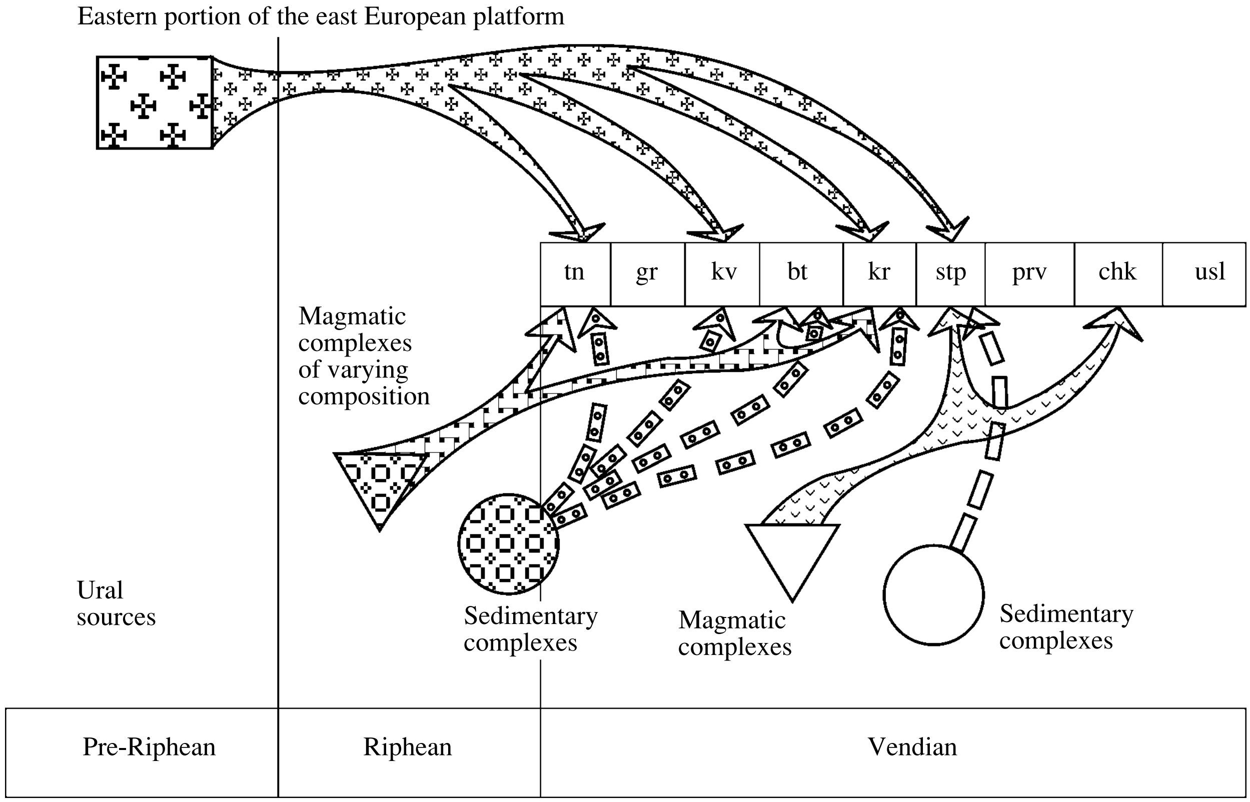

Fig. 2. Diagram showing the mineral supply of a fragment of the basin that existed in the Vednian in the territory of the present-day western slope of the central Urals according to the data of mineralogical and petrographic investigations [36, 46, 47]. tn, Taninskaya Formation; gr, Garevskaya Formation; kv, Koiva Formation; bt, Butonskaya Formation; kr, Kernosskaya Formation; stp, Staropechninskaya Formation; prv, Perevalok Formation; chk, Chernokamenskaya Formation; usl, Ust'-Sylvitsa Formation.

this area in the Riphean. Khain and Bozhko [50] supposed that an increase in the extent of rifting in the Urals occurred in the Vendian. In contrast, Klyuzhina [37] argued that the sequences of the Serebryanka Group were accumulated in an epoch of passive tectonic conditions.

Based on an analysis of paleogeodynamic aspects of the Vendian–Early Paleozoic stage of the development of the Urals, Koroteev et al. [51] concluded that a series of rift-related grabens and depressions was formed during this time period over the whole Ural fold belt. They were filled with terrigenous and volcanosedimentary rocks. Necheukhin [e.g., 52] assigned the Vendian complexes of the Urals to epicontinental rift associations.

According to Puchkov [53, 54], the Early Vendian decrease in the sea level was accompanied by a crustal uplift and local eruptions of subalkaline basaltoids in the area considered. The period of the formation of Serebryanka Group deposits can be characterized as mainly a tectonically calm epoch, when shallow terrigenous and carbonate sequences of the shelf type were mainly accumulated. In Puchkov's opinion, the deposits of that time period bear no resemblance to the associations of active rift zones. The Sylvitsa Group is characterized by an increase in the role of polymictic sandstones upsection; the composition of heavy minerals changes dramatically, which, similar to southern Ural sections, is probably indicative of a fundamental change in the position of provenances. It was supposed [54] that a folding phase occurred in the Urals between approximately 620 and 540 Ma. This phase is correlated with the Cadomian orogeny of western Europe. The paleo-Urals, paleo-Taimyr, and peri-Gondwana Cadomides were probably parts of a large orogenic belt of the Vendian supercontinent during that time.

Karpukhina et al. [42, 43] analyzed the petrochemical and geochemical characteristics of mafic–ultramafic complexes in the western slope of the central Urals and concluded that these complexes were formed in intraplate environments during an early evolutionary stage of the paleo-Ural rift. A longitudinal and transverse zoning in the distribution of the Vendian igneous complexes was established in [55]. The northernmost Krasnovisherskii complex is composed of high-Ti and high-Fe essexite gabbro of the subalkaline potassic series. The Dvoretskii intrusive–volcanic area is located to the south and includes extrusive rocks of the strongly differentiated K–Na subalkaline series and comagmatic intrusions. The same area hosts the alkaline ultrabasic rocks of the Blagodat' complex and tholeiites of the bimodal association of the Troitsk complex. It is supposed that these complexes are surrounded by the Shpalozerovskii and Vil'venskii trachybasalts. By analogy with Cenozoic rifts, the absence of continental tholeiites probably indicates a slow spreading rate. A series of local spreading zones with distinctive geodynamic characteristics probably existed in the Riphean and Vendian within the present-day western slope of the Urals.

Geologists from Perm supposed that a large slotlike continental rift was formed at the boundary of the Late Riphean and Early Vendian in the junction zone between the western Urals and the east European platform [e.g., 56–59].[2] It was supposed that the beginning of the Vendian was distinguished by the formation of a system of large tectonic depressions filled with coarse clastic deposits of the sparagmite association. The development of the Early Vendian rift involved three large stages marked by three cycles of the formation of volcanic–carbonate–terrigenous associations [57].[3] The periods of tectonic activation were accompanied by local occurrence of alkali basalt volcanism (dikes, sills, flows, etc.). The regions of ultrabasic and basic magmatism host numerous phosphate occurrences, which are most widespread among the deposits of the Butonskaya and Kernosskaya formations [62]. At the Early–Late Vendian boundary, the extensional regime was changed by compression. The sections of the Staropechninskaya level are dominated by shallow marine and glacial–marine deposits [e.g., 63]. The accumulation of relatively deep phosphate-bearing fine-grained terrigenous sediments probably prevailed during the Perevalok time in the region of the Kvarkushsko–Kamennogorskii meganticlinorium.

It was recently established that the deposits of the Chernokamenskaya Formation contain extensive prodelta and delta facies formed during a period of gradual shoreline regression and shallowing of the basin. Two sedimentary complexes were distinguished in the lower subformation of the Chernokamenskaya Formation [64, 65]. The lower complex is composed of silty mudstones and silty sandstones making up recyclites, which were formed in coastal environments with wave-induced sedimentation. The upper complex is dominated by sandstones and silty sandstones composing procyclites. During the Ust'-Sylvitsa time, sandy and sandy–silty deposits were mainly accumulated. They often show diverse cross-bedding, ripple marks, and desiccation cracks. The examination of the orientation of inclined laminae suggested that clastic material was transported into the basin from the north or northeast [36, 66, 67].

SOME METHODIC ASPECTS OF THE USE OF RARE EARTH AND TRACE ELEMENTS FOR THE RECONSTRUCTION OF THE COMPOSITION OF SOURCE PROVINCES

As was mentioned above, REE, Th, Sc, and high-field-strength elements are the most efficient tools for the reconstruction of the composition of provenances and their monitoring. They are poorly soluble in water and, consequently, are transported almost without losses from source regions to sedimentation basins. In most cases, the distribution patterns (spectra) of REE in provenances are retained in the sedimentary rocks [3, 16, 18, 68–73, etc.]. The REE usually do not enter the crystal lattice of clay minerals and are sorbed on the surface of clay particles or occur in their interlayer space. The major portion of REE in clastic sedimentary rocks is confined to the clay fraction and the fraction finer than 2 μm [e.g., 3, 74].

The diversity of REE spectra in post-Archean sedimentary rocks is largely controlled by the tectonic conditions of their formation and the composition of provenances [e.g., 24, 75]. The reconstruction of provenance compositions from REE distribution patterns is based on the fact that basic igneous rocks show low light to heavy REE ratios (LREE/HREE) and no distinct Eu anomaly, whereas felsic rocks are characterized by high LREE/HREE ratios and a pronounced Eu anomaly [3, 76, 77, etc.].

The use of geochemical features of fine-grained clastic aluminosilicate sediments for the reconstruction of the composition of paleocatchment rocks (=upper crust) is based on the analysis of various geochemical indexes (La/Th, Cr/Ni, La/Co, Th/Sc, Th/Co, etc) and a comparison of their values in pelitic rocks with those typical of indicator igneous associations and a number of geochemical standards, such as PAAS (average post-Archean Australian shales), NASC (North American shale composite), RPSC (general Russian platform sample of clays), etc. The main approaches used in such studies were described in detail in [3, 16, 18, 20, 74, 78–83, etc.].

For instance, relatively high Cr/Zr and Sc/Th values are indicative of a significant proportion of basic and ultrabasic rocks in the provenance, whereas high Th/Co

[2] A comparison of the sections of the Taninskaya–Koiva level of the Serebryanka Group and spatial distribution in them of pebble-poor conglomerates (mixtites) with model glacial sedimentary sequences showed, however, that the formation of the deposits of the lower part of the Serebryanka Group occurred probably in conjugate shelf (western sections) and slope (eastern sections) environments of a sedimentary basin [60].

[3] The volumes of particular cycles were not given by Kurbatskaya in [57], but three cycles of sedimentation in the section of the Serebryanka Group were distinguished in her earlier publication [61]: Taninskaya, Koiva, and Kernosskaya. Each of them shows a transgression–regression structure, beginning from terrigenous rocks with tillite-like conglomerates and volcanics and terminating by sandy–shale units. However, the extent of the Serebryanka Group accepted by Kurbatskaya is different from that proposed by the IV Ural Stratigraphic Conference [38]: the lower boundary of the group was drawn at the base of the Us'va Formation, and the upper boundary corresponded to the roof of the Perevalok Formation.

values imply the predominance of felsic rocks. It was shown by the example of the Precambrian fine-grained terrigenous rocks of the Kaapvaal craton that the combined use of Cr/Th, Th/Sc, and Co/Th ratios is efficient for monitoring the composition of provenances, because the Cr/Th ratio is a more sensitive indicator of paleocatchment composition than Eu/Eu*, La/Yb, or Th/U. Low Cr/Th and Co/Th values indicate the prevalence of felsic rocks in the eroded areas, whereas high or variable Cr/Th values suggest a prominent role of basic and ultrabasic rocks in the paleocatchments. Another efficient indicator of the presence of ultrabasic rocks in the eroded areas is the Cr/Ni ratio [84]. Pelitic rocks with Cr/Ni ratios of about 1.4 are characteristic of settings where ultramafic rocks are directly eroded in provenances; Cr and Ni are closely related in such a case. If Cr/Ni > 2.0, it is reasonable to suppose that there was a substantial transformation of the suspension of fine ultrabasic terrigenous particles along their migration paths from the eroded areas (in such a case, Cr is more closely related to V and Ti).

The lack of significant Cr/Th variations in fine-grained terrigenous rocks over rather long time periods is regarded as an indicator of the stability of the tectonic regime, which is favorable for the efficient mixing of fine clastic aluminosilicate material along migration paths. In order to minimize the effect of mineral sorting, La/Th, La/Sc, and Th/Sc ratios are used. Low Th/Sc and La/Sc values suggest the dominance of mafic–ultramafic associations in the source regions. The same is indicated by high Ni/Co and Cr/V and low V/Ni ratios. According to McLennan [18], the Th/Sc ratio is a more sensitive indicator of the average composition of eroded regions than La/Th.

The Th–Hf–Co and La–Th–Sc diagrams are also regarded as powerful tools in provenance analysis. If the compositions of shales and siltstones plot near the Th, Hf, and La apexes in these diagrams, felsic rocks are probably predominant in the source regions. If the compositions plot closer to the Co and Sc apexes, it is suggested that basic and ultrabasic rocks are most abundant in the eroded areas.

The average values of La/Th, Th/Sc, and La/Sc ratios for Archean schists are 3.5, 0.43, and 1.3, respectively. Very high abundances of Cr and Ni are characteristic of fine-grained terrigenous rocks from many Early Archean complexes. Early Archean shales show anomalously high Cr/V (~5.3) and Ni/Co (~11.6) ratios but low V/Ni values (~0.51). In Late Archean shales, these parameters are 1.5, 3.0, and 1.7, respectively. Taking into account these distinctions, the geochemical characteristics of fine-grained terrigenous rocks can probably be used for discrimination between provenances of different ages [3, 70].

SAMPLES AND METHODS OF THEIR PROCESSING

For our investigations, 85 samples were collected from natural sections of the Serebryanka and Sylvitsa groups of the Kvarkushsko–Kamennogorskii meganticlinorium along the Us'va, Sylvitsa, Serebryanka, and Mezhevaya Utka rivers. The samples were visually identified during field work as shales and mudstones. The further discrimination of the collection into silty–sandy and pelitic rocks was based on petrographic examination and the position of the compositional points on the $\log(SiO_2/Al_2O_3)$–$\log(Fe_2O_3/K_2O)$ diagram [85].

After these operations, 74 samples of shales and mudstones were analyzed for trace elements (40 elements, including 14 REE, Li, Be, Sc, Ti, Cr, Ni, V, Co, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Sb, Cs, Ba, Hf, Ta, Tl, Pb, Th, and U) using an inductively coupled plasma mass spectrometer of high sensitivity and mass resolution for element analysis and isotope measurements. About 50 mg of finely powdered material was digested in a mixture of fluoric and nitric acids (in the proportion 5 : 1) at temperatures of about 150–170°C in Teflon autoclaves up to complete decomposition. After evaporation the samples were transferred into a 3% nitric acid solution with a dilution factor of the initial sample of about 10^3 and then measured with an Element2 ICP/HR-MS. Indium (^{115}In) was used as an internal standard; BCR-1 and BCR-2 (Columbia River basalt) samples of the U.S. Geological Survey were used as external standards. The external standards were measured after every 5–10 sample analyses in order to account for fluctuations in the characteristics of the instrument with time. The accuracy of analysis depended on the concentration of a particular element and ranged from 3 to 20–50% relative (approaching the detection limit for very low concentrations). The accuracy of the data was additionally checked by the repeated analysis of randomly selected samples.

Sm and Nd isotopic compositions were determined by isotope dilution mass spectrometry on a Finnigan MAT-262 high-precision solid-phase analyzer. All chemical operations were performed in a clean room with a forced inflow of filtered (HEPA filters) atmospheric air using Teflon and quartz labware and specially purified reagents. The procedure of chemical preparation of samples for the analysis of Sm and Nd concentrations and isotopic compositions included the following sequential operations: (1) sample decomposition, (2) extraction of bulk REE, and (3) separation of Sm and Nd.

The samples were decomposed by a mixture of fluoric and chloric acids in Teflon autoclaves. An aliquot with a certain amount of the $^{150}Sm + ^{149}Nd$ spike (using the optimum proportion of 0.15 g spike per 1 μg of Nd in the sample) was kept at 150–180°C until complete decomposition. The reaction mixture was evaporated to dryness and treated with 10 N HCl for the decomposition of fluorides. Then, the samples were kept for 6–12 h under decomposition conditions. After this, the solutions were again evaporated, and the dry residue was dissolved in 2 ml of 2.3 N HCl and centrifuged. The obtained transparent solution was loaded into the first chromatographic column filled with Dowex 50 × 8 200–400 mesh cation exchange resin. In this column, the bulk REE was separated from the major components of the sample by stepwise elution with 2.3 N and 3.9 N HCl. The eluate fraction containing Nd, Sm, other REE, and traces of some other elements was evaporated and dissolved in 0.6 ml of 0.1 N HCl. The final separation of Sm and Nd was carried out in the second chromatographic column filled with di-(2 ethylhexyl) orthophosphoric acid coated on polytrifluochloroethylene (KEL-F).

In order to more efficiently separate Nd and Sm from traces of alkali earth elements, a gradient elution with 0.1 N and 0.3 N HCl was carried out. The laboratory blank was usually no higher than 0.3 ng Nd and 0.2 ng Sm. The Sm and Nd isotopic compositions of the mixtures of the $^{150}Sm + ^{149}Nd$ spike and samples were determined on a Finnigan MAT-262 multicollector instrument operated in a static mode.

The analysis of Sm and Nd was performed using two-filament Re of ion sources preliminarily annealed in a vacuum chamber to eliminate contaminants. The Nd isotopic ratios were normalized to $^{146}Nd/^{144}Nd$ = 0.7219. The internal statistics of mass spectrometric analysis provided a convergence of better than 0.002% relative for the $^{143}Nd/^{144}Nd$ ratio. The precision of measurements was estimated from the parallel analyses of the La Jolla standard (California, USA). The accuracy of measured Sm/Nd ratios was calculated from the long-term precision of the measurements of the BCR-1 and BCR-2 standards as 0.2–0.5% relative. The parameters of the evolution diagrams were evaluated using the regression programs of Ludwig [86]. Age calculations were based on a decay constant of 6.54×10^{-12} yr^{-1}.

REE SYSTEMATICS OF THE MUDSTONES OF THE SEREBRYANKA AND SYLVITSA GROUPS

The bulk REE content (ΣREE) of the shales and mudstones of the Serebryanka and Sylvitsa groups ranges from 164 to 266 ppm (Table 1). Ash-tuff interbeds from several levels in the sections of the Chernokamenskaya Formation of the Sylvitsa Group show

Table 1. Median values of REE concentrations (ppm) in shales and mudstones from various lithostratigraphic units of the Serebryanka and Sylvitsa groups

Component	tn	gr	kv	bt	kr	stp	prv	chk_1	chk_2	usl
La	60.38	48.60	33.31	46.45	41.09	45.01	40.37	37.67	50.26	54.63
Ce	120.48	89.66	70.69	84.66	83.54	89.51	87.23	79.76	109.79	110.60
Pr	12.51	10.69	7.69	10.64	9.37	10.47	9.70	8.94	12.22	11.76
Nd	47.73	38.79	28.95	37.87	34.34	38.83	36.58	33.74	46.44	43.47
Sm	7.09	6.52	5.52	6.02	5.91	6.81	6.87	6.05	7.89	8.01
Eu	1.63	1.36	1.07	1.06	1.19	1.29	1.29	1.21	1.45	1.45
Gd	5.78	5.33	5.17	4.48	4.91	5.33	5.89	5.22	6.66	6.93
Tb	0.82	0.84	0.80	0.65	0.78	0.80	0.87	0.83	0.97	1.03
Dy	4.28	5.04	4.69	3.49	3.96	4.62	4.98	4.83	5.87	6.16
Ho	0.87	0.97	0.94	0.73	0.84	1.02	1.07	1.03	1.26	1.30
Er	2.25	2.62	2.43	1.98	2.21	2.79	2.94	2.76	3.41	3.51
Tm	0.32	0.36	0.36	0.28	0.33	0.41	0.44	0.40	0.51	0.52
Yb	2.10	2.36	2.29	1.87	2.09	2.73	2.89	2.72	3.28	3.43
Lu	0.29	0.35	0.37	0.28	0.31	0.41	0.43	0.39	0.49	0.53
Total	266.53	213.49	164.28	200.46	190.87	210.03	201.55	185.55	250.49	253.33
*n**	5	3	11	7	7	6	8	13	8	5

Note: Formations: tn, Taninskaya; gr, Garevskaya; kv, Koiva; bt, Butonskaya; kr, Kernosskaya; stp, Staropechninskaya; prv, Perevalok; chk_1, lower subformation of the Chernokamenskaya Formation; chk_2, upper subformation of the Chernokamenskaya Formation; and usl, Ust'-Sylvitsa.

*Number of analyses used for the calculation of median values.

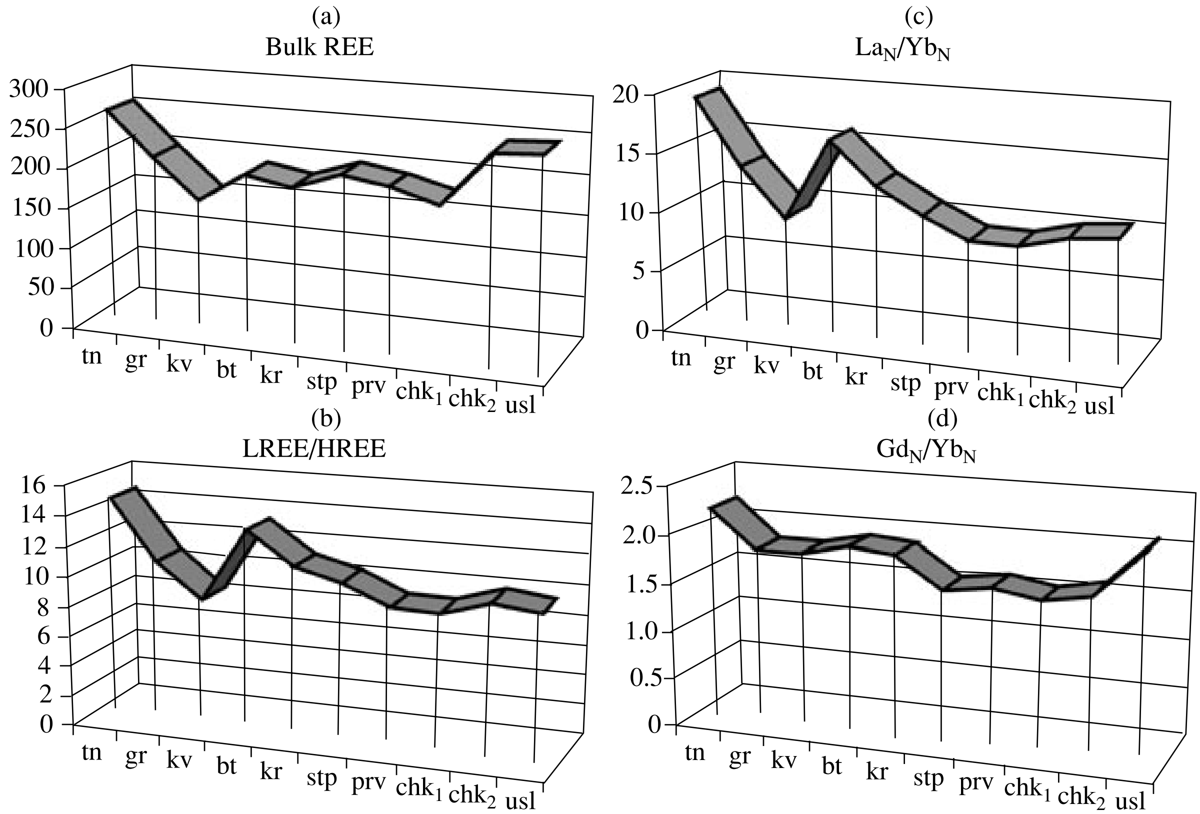

Fig. 3. Variations in (a) the bulk REE content and the median values of (b) LREE/HREE, (c) La_N/Yb_N, and (d) Gd_N/Yb_N ratios in the shales and mudstones of various lithostratigraphic units of the Serebryanka and Sylvitsa groups.

significantly lower ΣREE values (~138 ppm). Variations in this parameter from bottom to top in the Vendian section of the Kvarkushsko–Kamennogorskii meganticlinorium are shown in Fig. 3a. It is seen that the ΣREE of shales decreased gradually in the first half of Serebryanka time (Taninskaya, Garevskaya, and Koiva time). The second half of Serebryanka time and the beginning of Sylvitsa time (from Butonskaya to early Chernokamenskaya time) were characterized by slightly higher and approximately constant amounts of REE entering the basin, from 180–190 to 210 ppm. At the end of Sylvitsa time (late Chernokamenskaya and Ust'-Sylvitsa time), the input of ΣREE into the basin increased; Ust'-Sylvitsa time is similar in this respect to Taninskaya time. Since the abundances of ΣREE in PAAS and NASC are 183 and 173.2 ppm, respectively [3], the above data imply that during the whole time interval the paleocatchments were composed mainly of a rather mature crust with a certain compositional heterogeneity of sources in some particular periods.

The REE distribution patterns of the shales of the Serebryanka Group are similar to those of typical post-Archean fine-grained terrigenous deposits (Fig. 4a): they show a moderate slope in light REE, a distinct negative Eu anomaly, and no significant heavy REE depletion relative to middle REE [3]. The LREE/HREE ratio of the shales of the Serebryanka Group varies from almost 15 to 8.5 (Table 2). The lower value is characteristic of the fine-grained terrigenous deposits of the Koiva Formation. The $(La/Yb)_N$ ratio of the majority of pelitic rocks and fine-grained siltstones from this level ranges from 13 to 19, and only the Koiva shales show significantly lower values of ~9.8. The Gd_N/Yb_N value of the fine-grained terrigenous rocks of the Serebryanka Group is 1.9–2.2; the highest ratios (~2.23) were observed in the basal levels of the group. The magnitude of Eu anomaly in the pelitic rocks of the Serebryanka Group is either slightly higher or slightly lower than the Eu/Eu* value that is typical for average post-Archean Australian shale. Only the fine-grained terrigenous rocks of the Kernosskaya Formation are similar to PAAS in this parameter.

The REE distribution patterns of the fine-grained terrigenous rocks of the Sylvitsa Group are similar to those of typical Archean mudstones (Fig. 4b). Their negative Eu anomalies are either similar to that of PAAS or even more pronounced (Eu/Eu* from 0.59 to 0.65). The LREE/HREE ratio is more stable than in the pelitic rocks of the Serebryanka Group: this parameter ranges from 9.14 (lower subformation of the Chernoka-

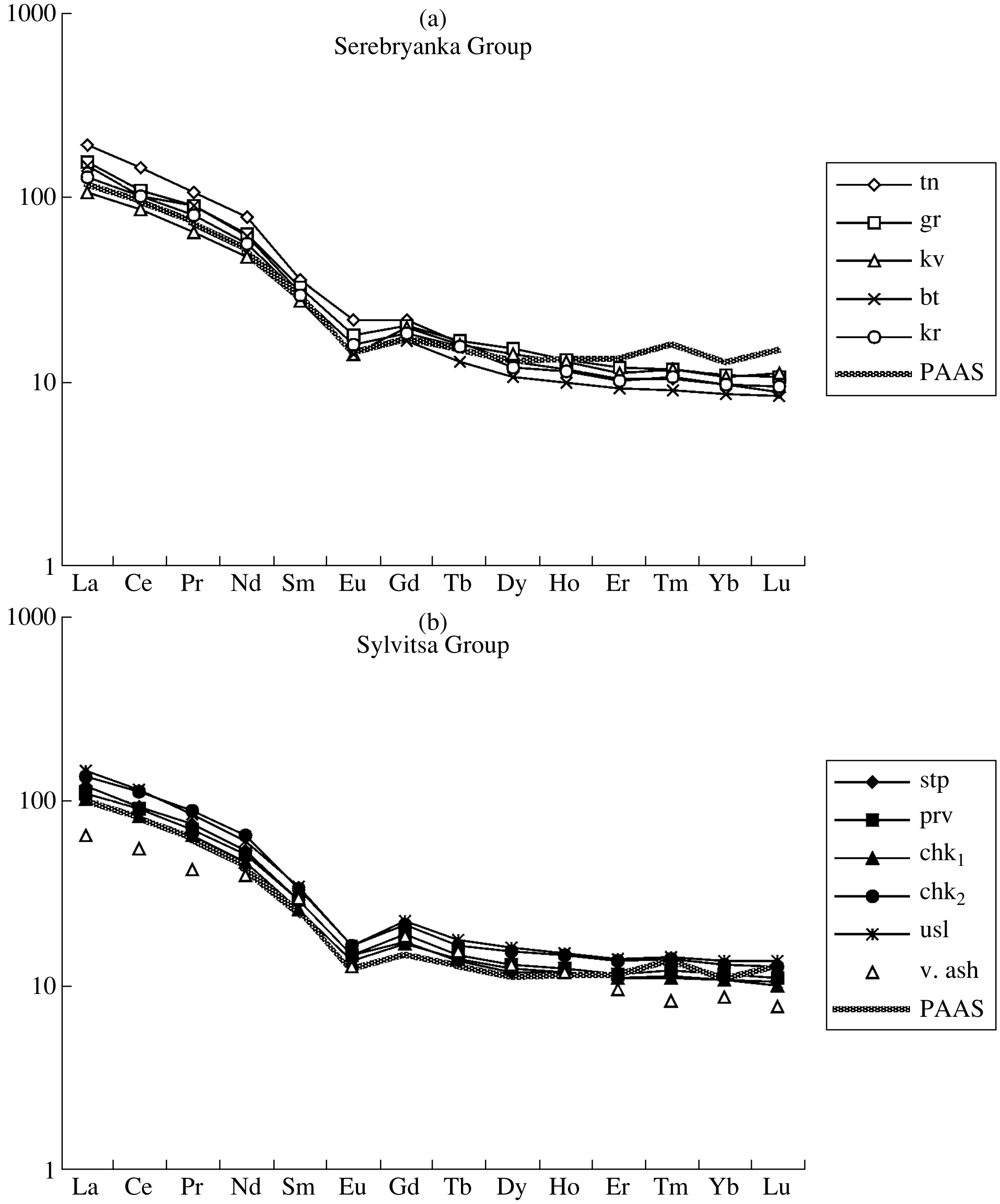

Fig. 4. REE distribution patterns for the shales and mudstones of the (a) Serebryanka and (b) Sylvitsa groups. tn, Taninskaya Formation; gr, Garevskaya Formation; kv, Koiva Formation; bt, Butonskaya Formation; kr, Kernosskaya Formation; stp, Staropechninskaya Formation; prv, Perevalok Formation; chk_1, lower subformation of the Chernokamenskaya Formation; chk_2, upper subformation of the Chernokamenskaya Formation; usl, Ust'-Sylvitsa Formation; v. ash, crystalloclastic tuffs from the Chernokamenskaya Formation; and PAAS, post-Archean Australian shale.

menskaya Formation) to 10.5 (Staropechninskaya Formation). The La_N/Yb_N ratio of the mudstones of all levels of the Sylvitsa Group is lower than that of the Serebryanka Group shales (except for the Koiva level). Ash-tuff interbeds from the lower portion of the Chernokamenskaya Formation show lower La_N/Yb_N values of about 7.47. The LREE/HREE ratio of the tuffs is 6.6. The average Gd_N/Yb_N ratio of the mudstones of the Sylvitsa Group is also significantly lower than that of the shales of the Serebryanka Group, which is reflected by gentler slopes in the right part of most REE spectra.

The shales and mudstones of the Serebryanka and Sylvitsa groups differ in the magnitude of the Eu anomaly. The Eu/Eu* ratio of the Serebryanka level shales is usually higher than that of PAAS, whereas the same parameter in the Sylvitsa mudstones is mostly similar to or higher than the PAAS value.

Table 2. Median values of the REE indicator ratios in the shales of the Serebryanka and Sylvitsa groups

Indicator ratio	tn	gr	kv	bt	kr	stp	prv	chk_1	chk_2	usl
LREE/HREE	14.85	10.87	8.57	13.49	11.29	10.53	9.26	9.14	10.09	9.76
La_N/Yb_N	19.43	13.92	9.83	16.79	13.29	11.14	9.44	9.36	10.36	10.76
Gd_N/Yb_N	2.23	1.83	1.83	1.94	1.91	1.58	1.65	1.56	1.65	2.13
Eu/Eu*	0.78	0.71	0.61	0.62	0.68	0.65	0.62	0.66	0.61	0.59

Note: Indexes of formations are given in Table 1.

In general, the REE distribution patterns of the Sylvitsa mudstones are more uniform than those of the Serebryanka shales. The latter exhibit two remarkable differences from the PAAS REE distribution patterns: lower, heavy, REE contents and a less pronounced Eu anomaly.

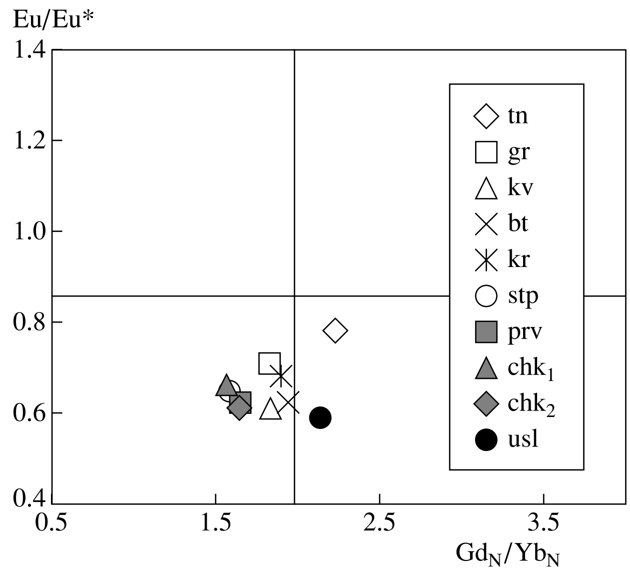

Fig. 5. Diagram of Eu/Eu* versus Gd_N/Yb_N for the shales and mudstones (median values) of various lithostratigraphic units of the Serebryanka and Sylvitsa groups of the Kvarkushsko–Kamennogorskii meganticlinorium. Symbols are the same as in Fig. 4.

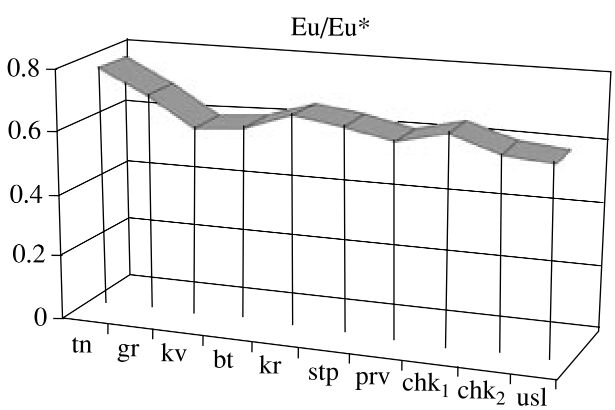

Fig. 6. Variations in the median Eu/Eu* values of the shales and mudstones of various units of the Serebryanka and Sylvitsa groups. Symbols are the same as in Fig. 4.

Let us analyze the behavior of the main parameters of the REE spectra (LREE/HREE, La_N/Yb_N, Gd_N/Yb_N, and Eu/Eu*) in the relative time scale, i.e., from bottom to top within the Vendian section.

The highest LREE/HREE values of 13–15 were detected in the shales of the Taninskaya and Butonskaya formations. Other Vendian lithostratigraphic units of the Kvarkushsko–Kamennogorskii meganticlinorium usually show LREE/HREE values of 8.5–10.5 (Fig. 3b). We remind the reader that the bulk upper continental crust (UCC) has a LREE/HREE value of about 9.5 [3]. The ash tuffs of the Chernokamenskaya level show the lowest LREE/HREE value of ~6.63, which is only slightly higher than that of average andesite.

The La_N/Yb_N ratio shows a similar behavior (Fig. 3c). The highest values (~16–19) are typical of shales and mudstones of the Taninskaya and Butonskaya formations, whereas the rocks of most other units of the Serebryanka and Sylvitsa groups range between 9.4 and 11. Similar to the LREE/HREE ratio, the lowest La_N/Yb_N values were detected in ash tuffs of the Chernokamenskaya Formation.

The Gd_N/Yb_N ratio of the fine-grained terrigenous rocks of most lithostratigraphic units of the Serebryanka and Sylvitsa groups falls within the range 1.5–1.9 (Fig. 3d), which is in general characteristic of post-Archean rocks. Only the shales and mudstones of the Taninskaya and Ust'-Sylvitsa levels show $Gd_N/Yb_N > 2.1$. This may be indicative of a role for the Archean component in the composition of the fine clastic aluminosilicate rocks of these levels [24]. The distribution of the median compositions of the Vendian fine-grained terrigenous rocks in the Gd_N/Yb_N–Eu/Eu* diagram (Fig. 5) is also symptomatic.[4] Most pelitic rocks from

[4] We used the median values of ratios, because these statistical parameters provide generalized estimates for a set of raw analytical data with an unknown distribution [31, 87].

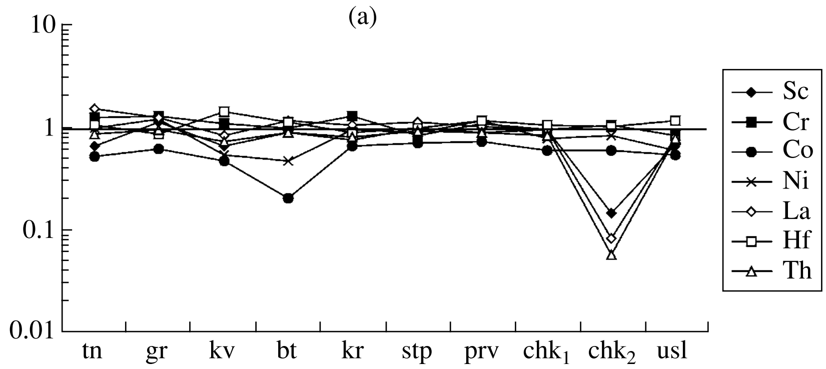

Fig. 7. Variations of PAAS-normalized median values of a number of trace elements for the shales and mudstones of various Vendian lithostratigraphic units of the (a) Kvarkushsko–Kamennogorskii meganticlinorium and (b) various samples of the Koiva Formation. See Fig. 4 for formation symbols.

various formations plot within the field of typical post-Archean cratonic sediments [24], but some points of the Taninskaya shales and Ust-Sylvitsa mudstones with strongly depleted heavy REE are similar in this parameter to Archean sedimentary rocks.

The magnitude of Eu anomaly in the fine-grained terrigenous rocks from the whole Vendian section of the Kvarkushsko–Kamennogorskii meganticlinorium is usually restricted to a rather narrow range. The minimum values (~0.71–0.78) are characteristic of the shales and fine-grained siltstones of the Taninskaya and Garevskaya levels (Fig. 6). The Eu/Eu* ratio increases somewhat upsection ranging from 0.59 to 0.68.

These observations suggest a certain heterogeneity of paleocatchments and changes in their composition with time. The most mature compositions (corresponding to the UCC or granite-dominated crust) of eroded areas were characteristic of the beginning of the Vendian, Taninskaya, and Butonskaya times. During Garevskaya–Koiva and Kernosskaya–Ust-Sylvitsa times, basic and ultrabasic rocks played a certain role in the provenances; their fraction was probably relatively high in the Chernokamenskaya time. Based on these observations, two distinct cycles of variations in the composition of paleocatchments can be distinguished in the Vendian section of the Kvarkushsko–Kamennogorskii meganticlinorium: Taninskaya–Koiva and Butonskaya–Ust'-Sylvitsa. The initial stages of these cycles were characterized by the abundance of rather mature crustal materials in the paleocatchments, some components of which could have an Archean age. During the final stages of cycles, both basic and felsic igneous rocks played a significant role in the eroded areas.

SYSTEMATICS OF Cr, Ni, Co, Th, Sc, AND Hf IN THE MUDSTONES OF THE SEREBRYANKA AND SYLVITSA GROUPS

The relationships of Cr, Ni, Co, Th, Sc, Hf, and some other elements in the shales and mudstones also

Table 3. Median values of some indicator trace element ratios in the shales and mudstones of the Serebryanka and Sylvitsa groups

Indicator ratio	Serebryanka Group					Sylvitsa Group				
	tn	gr	kv	bt	kr	stp	prv	chk_1	chk_2	usl
La/Th	4.66	3.31	3.04	3.43	3.4	3.21	3.02	3.03	3.76	2.71
La/Co	4.83	3.33	2.97	9.54	2.6	2.72	2.36	2.66	0.23	2.49
Th/Co	1.04	1	0.98	2.78	0.76	0.85	0.78	0.88	0.06	0.92
Sc/Th	0.86	1.27	1	1.09	1.03	1.17	1.12	1.29	2.78	0.98
La/Sc	5.44	2.6	3.04	3.16	3.3	2.75	2.7	2.34	1.35	2.77
Ni/Co	4.49	4.76	2.72	5.54	3.41	3.11	3.87	3.1	3.44	2.68
Cr/Ni	2.25	1.73	3.78	4.22	2.76	1.96	2.39	2.60	2.47	2.83
Cr/Th	10.95	9.93	11.33	8.38	12.29	6.68	9.24	8.86	136.62	8.24

Note: Formations: tn, Taninskaya; gr, Garevskaya; kv, Koiva; bt, Butonskaya; kr, Kernosskaya; stp, Staropechninskaya; prv, Perevalok; chk_1, lower subformation of the Chernokamenskaya Formation; chk_2, upper subformation of the Chernokamenskaya Formation; and usl, Ust'-Sylvitsa.

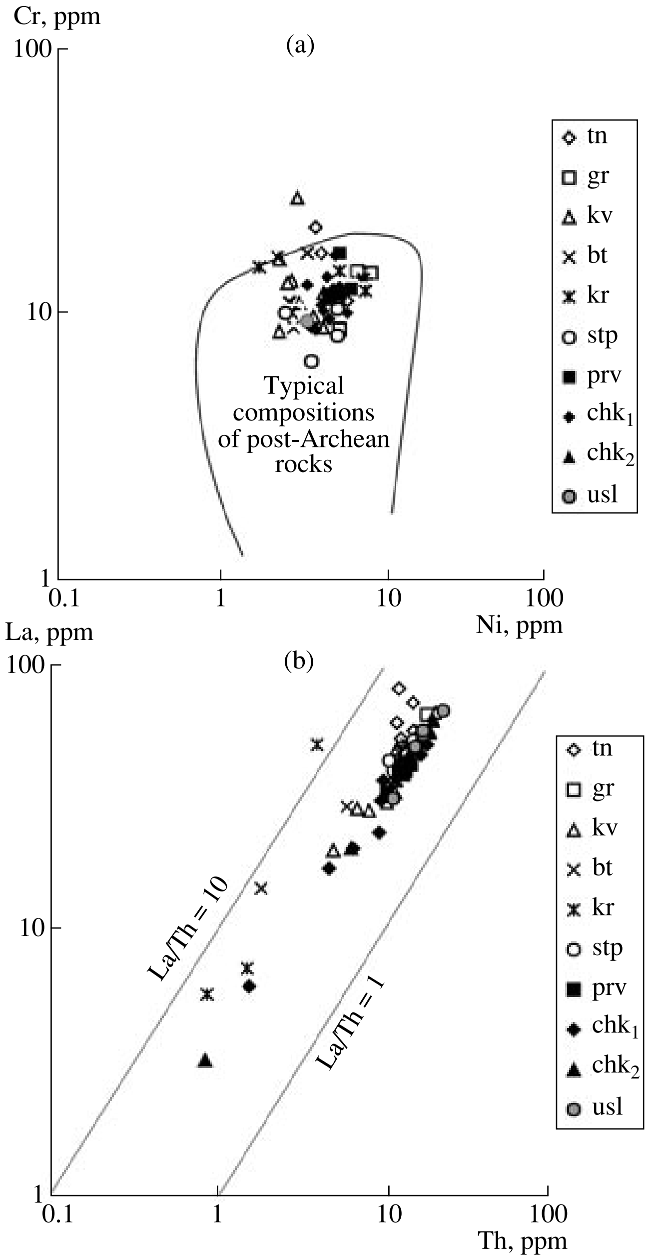

Fig. 8. Projections of the compositions of individual shale and mudstone samples from the Serebryanka and Sylvitsa groups on the (a) Cr–Ni and (b) La–Th diagrams. Symbols are the same as in Fig. 4.

support the existence of certain compositional variations in the paleocatchments during the deposition of the Serebryanka and Sylvitsa groups.

It is convenient to characterize the distribution of these elements in the fine-grained terrigenous rocks of various Vendian lithostratigraphic units by comparing with PAAS. The normalization of the median values of Cr, Ni, Co, Th, Sc, and Hf contents in mudstones and shales to the PAAS concentrations shows that the abundances of these elements in the rocks studied are similar to those of PAAS, except for Co, which is depleted in our samples, and Hf, which is enriched relative to the PAAS concentrations (Fig. 7a). If instead of the median values, particular samples from a certain level are considered, for example, from the Koiva Formation (Fig. 7b), significant variations are revealed for each of these elements. For instance, the concentrations of Sc in shale samples from the Koiva Formation are from 0.44 to 1.02 PAAS, and the La content may be both significantly lower (0.53) and higher (1.72) than that of PAAS. The same is characteristic of Hf and Th. The Cr content ranges from 0.8 to 2.55 PAAS (!!), and only the Co content is always lower than that of PAAS, which is in line with the median values.

The Cr/Ni ratio of the shales of the Serebryanka and Sylvitsa groups is from 1.73 to 4.22 (Table 3). There is either no correlation between Cr and Ni ($r = -0.74$ for the Taninskaya level, and $r = -0.21$ for the Koiva level) or a relatively poor correlation ($r = 0.17$ for the Butonskaya level, and $r = 0.28$ for the lower subformation of the Chernokamenskaya Formation); there is also no correlation between Cr and V or Ti. The highest Cr/Ni ratios were detected in the shales formed during the second half of the Serebryanka time (Koiva and Butonskaya time), whereas this parameter is approximately two times lower in the rocks of earlier and later epochs but is still higher than the critical values (~1.4–1.5 [84]). This suggests that there were no significant amounts of directly eroded ultramafic and mafic rocks in the paleocatchments of the Serebryanka and Sylvitsa times, although they were certainly present in the provenances.

In the Ni–Cr diagram, most of the Vendian shales and mudstones plot within the field of typical post-Archean compositions with relatively low Cr concentrations, and only some mudstone samples from the Koiva and Taninskaya formation have higher Cr contents (Fig. 8a).

In the Th–La diagram (Fig. 8b), the compositions of shales and mudstones of the two groups plot mostly within the field of post-Archean rocks, and only a few points of the fine-grained terrigenous rocks of the Kernosskaya and Chernokamenskaya formations fall within a field with considerably lower La and Th contents, which is typical of Archean metasedimentary rocks. However, all the compositions of shales and fine-grained mudstones of the Taninskaya level, the conglomerates of which contain mainly rock fragments from the crystalline basement of the east European platform, fall within the field of post-Archean sedimentary rocks.

A comparison of the median values of the La/Th, La/Co, Th/Co, Sc/Th, La/Sc, and Ni/Co ratios in the shales and mudstones of the Serebryanka and Sylvitsa groups (Table 3) with these parameters in various model sources [3, 25, 74, 88, 89] (Table 4) showed that, within the whole Serebryanka and Sylvitsa period, the paleocatchments were probably dominated by granitoids and geochemically mature rocks of the upper continental crust. The "background" Cr/Th values in the mudstones and shales range from 6.68 to 12.29. This ratio is higher than 136 in one mudstone sample from

Table 4. Variations in some indicator trace-element ratios in the products of weathering of compositionally different provenances, upper and lower continental crust, and oceanic crust [3, 25, 75, 89, 90]

Provenance	La/Sc	Th/Sc	Th/Co	Cr/Th	Eu/Eu*
Granitoid-dominated provenance	4.8–55.0	0.6–32.0	~5.5	0.43–6.0	0.32–0.65
Provenance dominated by amphibolites with minor silicic rocks	0.04–0.09	0.005–0.006	–	1.1–1.15	0.9–1.08
Calc-alkaline granitoids	–	–	–	0.8–5.4	0.71–1.4
Ophiolites	0.19–0.32	0.015–0.02	0.012–0.018	260–560	0.98–1.02
Upper continental crust	2.7	1.0	1.11	3.3	0.61
Lower continental crust	0.3	0.03	0.03	222	1.07
Oceanic crust	0.1	0.006	0.005	1227	1.02

the upper subformation of the Chernokamenskaya Formation. This suggests that either basic rocks occurred in the provenances with silicic rocks or basic pyroclastic material was introduced into the basin simultaneously with the accumulation of terrigenous sediments. The latter mechanism is most probable for the sec-

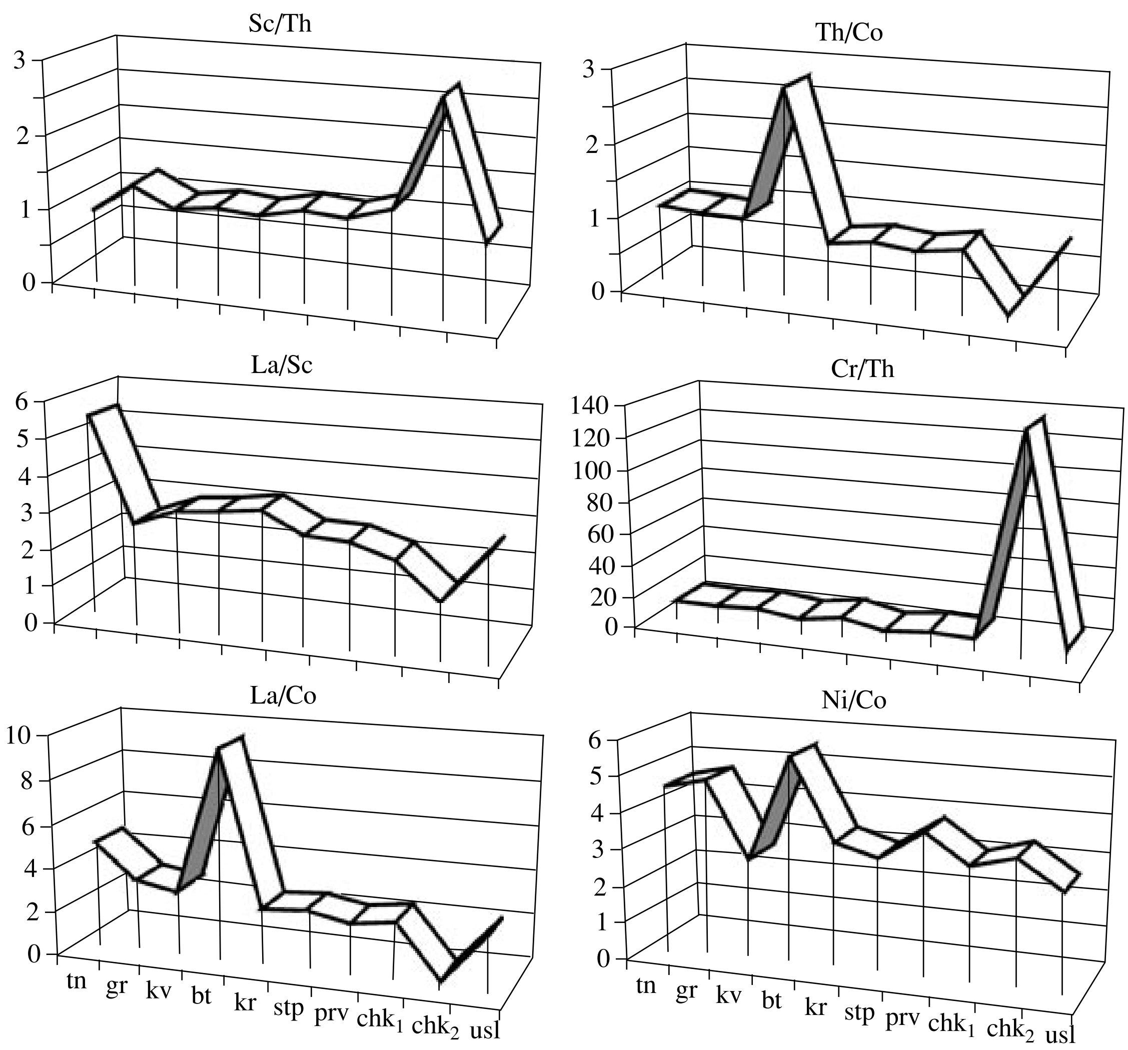

Fig. 9. Variations in the median values of Sc/Th, La/Sc, La/Co, Th/Co, Cr/Th, and Ni/Co ratios of the shales and mudstones of various lithostratigraphic units of the Serebryanka and Sylvitsa groups of the Kvarkushsko–Kamennogorskii meganticlinorium. Symbols are the same as in Fig. 4.

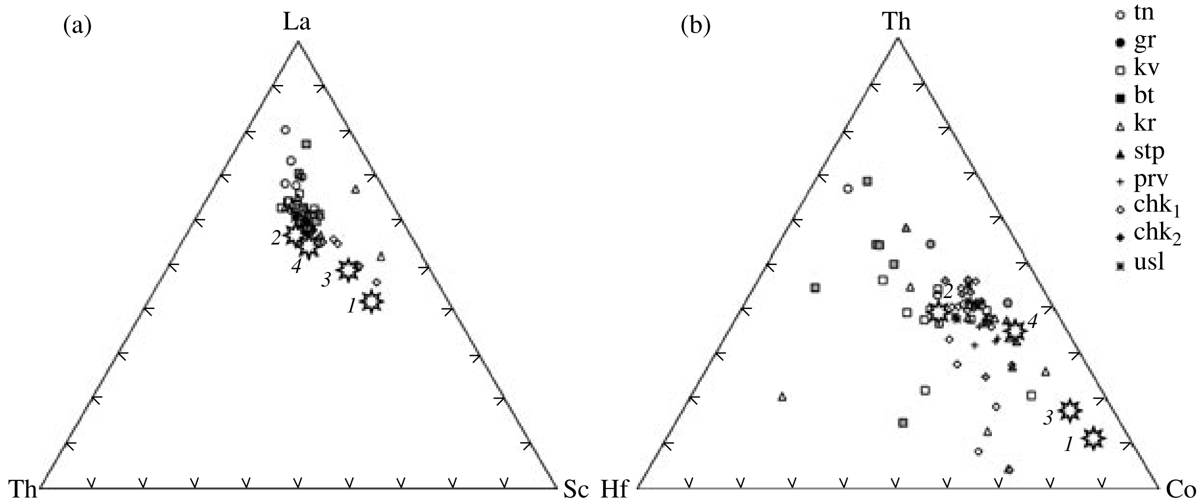

Fig. 10. Compositions of individual shale and mudstone samples from the Serebryanka and Sylvitsa groups in the (a) La–Th–Sc and (b) Th–Hf–Co diagrams. Symbols are the same as in Fig. 4. (*1*) Archean shale (mudstone) [3]; (*2*) upper continental crust (UCC) [24]; (*3*) Archean upper crust (AUC) [24]; and (*4*) post-Archean Australian shale (PAAS) [3].

tion of the Chernokamenskaya Formation, where D.V. Grazhdankin (Paleontological Institute, Russian Academy of Sciences, Moscow) discovered ash interbeds; moreover, the mudstones of this formation show much higher Sc/Th and Cr/Th and lower La/Sc and La/Co ratios compared with rocks from other levels (Fig. 9).

In the La–Th–Sc diagram, most of the compositions of shales from the Serebryanka and Sylvitsa groups form a compact cluster near the PAAS and UCC or have higher relative contents of La (this is especially common in the rocks of the Taninskaya and Butonskaya formations of the Serebryanka Group) (Fig. 10a). A few points (samples of the Chernokamenskaya and Kernosskaya formations) plot between the PAAS–UCC and AUC (Archean upper crust) fields; i.e., the fraction of material of the mature crust is lower in these compositions than in the rocks of other Vendian levels of the Kvarkushsko–Kamennogorskii meganticlinorium.

The Th–Hf–Co diagram exhibits much greater scatter (Fig. 10b); the samples form an extended array between the Th and Co apexes (some compositions of shales and mudstones of the Koiva, Kernosskaya, and Chernokamenskaya formations plot near the Co apex), but most compositions are located near the PAAS and UCC compositions. The compositions of mudstones from the Perevalok and Ust'-Sylvitsa formations form a compact group near the PAAS and UCC compositions. The fine-grained terrigenous rocks of the Taninskaya Formation are the most enriched in Th in this diagram; i.e., they were formed at the expense of the erosion of a rather mature upper crust.

Nd MODEL AGE OF THE MUDSTONES OF THE SEREBRYANKA AND SYLVITSA GROUPS

One of the most powerful modern tools for monitoring the composition of paleocatchments is the analysis of Nd model ages of fine-grained terrigenous rocks from relatively thick and comprehensively dated sedimentary sequences of the Late Precambrian [9, 10, 13, 90–98, etc.].

It is known that any portion of the lithosphere extracted from the mantle at some time period is characterized by certain chemical and isotopic parameters [92, 94, 95, 99, etc.]. Measurements of these parameters in whole-rock samples allow calculation of the supposed time of the differentiation of its components from the mantle. This concept is most readily applicable to juvenile plutonic rocks, i.e., rocks derived from crustal or mantle sources. It is assumed that neither Sm nor Nd are fractionated in the sedimentary process and, consequently, the analysis of the Sm–Nd isotopic system in fine-grained clastic sediments provides insight into the average model age of provenances and can be used for the construction of models of crustal evolution [10, 13, 92, 95, 98, 100]. The key parameter is the time interval during which the rare earth components of the sediments (primarily, Sm and Nd unfractionated in exogenic processes) resided in the continental crust (crustal residence age). For a particular shale or mudstone sample, this parameter averages the contributions of several sources and, consequently, it does not provide a direct estimate for the age of crust-forming processes.[5] Nonetheless, the Nd model age of a sedimentary rock provides an estimate for the average age of that part of large con-

[5] If all the crustal material formed τ years ago has remained in the crust up to the present day, its crustal residence age is τ. The erosion of this crustal segment will produce sediments with a crustal residence time of τ. However, a real geologic situation is always more complicated, and the process of erosion may involve two or more crustal segments with different ages, τ_1, τ_2, etc. If fine-grained aluminosilicate clastic materials from two sources are mixed in the proportion 1 : 1, the crustal residence age of the sediment will be $(\tau_1 + \tau_2)/2$ [90].

Table 5. Nd model ages of the shales and mudstones of the Serebryanka and Sylvitsa groups

Lithostratigraphic unit	Sample	T^{*}_{strat}, Ma	Sm	Nd	$^{147}Sm/^{144}Nd$**	$f_{Sm/Nd}$	$^{143}Nd/^{144}Nd$	±2*s* [%]	T(DM)***, Ma	±2σ, Ma
Ust'-Sylvitsa Formation	02-syl-35		4.5	23	0.11634	–0.41	0.511923	0.003	1739	24
Lower subformation of the Chernokamenskaya Formation	02-syl-21	~580	7.4	42	0.10600	–0.46	0.511799	0.002	1747	15
Perevalok Formation	5–2		7.5	40	0.11248	–0.43	0.511886	0.003	1728	23
Staropechninskaya Formation	2591		7.2	45	0.09812	–0.50	0.511736	0.004	1711	26
Kernosskaya Formation	02-syl-10	490–509 (?)	6.0	36	0.10257	–0.48	0.511791	0.003	1704	21
Butonskaya Formation	161		6.1	44	0.08374	–0.57	0.511521	0.002	1773	12
Koiva Formation	2–3	363–608 (?)	9.6	60	0.09597	–0.51	0.511510	0.002	1972	14
Garevskaya Formation	3–4		6.3	39	0.09643	–0.51	0.511607	0.003	1854	20
Taninskaya Formation	2369		7.2	45	0.09680	–0.51	0.511501	0.002	1998	14

*T_{strat} is the stratigraphic age of the sample.
**Standard error (±2σ) is not higher than 0.5%.
***T_{DM} calculated after DePaolo (1988).

tinental segments which was responsible for its formation.

There are only a few examples of such investigations of sedimentary rocks in the Russian literature. Podkovyrov et al. [11] analyzed the Sm–Nd systematics of the Riphean shales and mudstones of the Uchur–Maya region and revealed considerable variations in their Nd model ages, T_{Nd}(DM), and in ε_{Nd}(T) values. The mudstones of the Early Riphean Uchur Group show Nd model ages of 2.3–2.13 Ga and ε_{Nd}(T) values from –4.0 to –6.9. These parameters in the mudstones of the Middle Riphean Talyn Formation are 2.31–2.11 Ga and from –4.3 to –7.1, respectively. The fine-grained terrigenous deposits of the Tott Formation of the Maya plate show T_{Nd}(DM) of 1.78 Ga and ε_{Nd}(T) of +0.3. Similar rocks from the Neryuenskaya Formation of the Maya plate show T_{Nd}(DM) of 1.55 Ga and ε_{Nd}(T) of +0.4. The mudstones of the Vendian Yudoma Group show a Middle Riphean Nd model age of 1.34 Ga and ε_{Nd}(T) of about –0.3. These results suggest that the Riphean hypostratotype experienced two episodes of the influx of fresh juvenile material into the sedimentation basin, which are marked by a significant decrease in the Nd model age and a sharp increase in ε_{Nd}(T), up to positive values.

Similar variations in T_{Nd}(DM) and ε_{Nd}(T) were described in the Mesoproterozoic and Neoproterozoic fine-grained terrigenous rocks of the Yangtze block (southeastern China) [96]. The Mesoproterozoic shales of this region have Nd model ages of ~1.8 Ga. The overlying Neoproterozoic and Early Sinian rocks show much younger T_{Nd}(DM) values of about 1.3 Ga. The younger deposits that accumulated from the Late Sinian to the Permian have ancient Nd model ages of ~1.8 Ga. These differences in T_{Nd}(DM) are due to an increase in the fraction of juvenile material in the paleocatchments related to the Jingning orogeny, during which a significant amount of mantle material was added to the pre-Riphean upper crust. Considerable variations in ε_{Nd}(T) were also detected in the Late Precambrian deposits of the Yangtze block. For instance, ε_{Nd}(T) ranges from –2.6 to –5.3 in the Mesoproterozoic shales and from +0.4 to +0.6 in the phyllites of the Upper Shuangqiao Formation (Early Neoproterozoic) and remains at the same level up to 0.74 Ga.

We calculated the Nd model age of ten samples of mudstones and shales from the Serebryanka and Sylvitsa groups collected from all lithostratigraphic levels (Table 5). These calculations showed that the

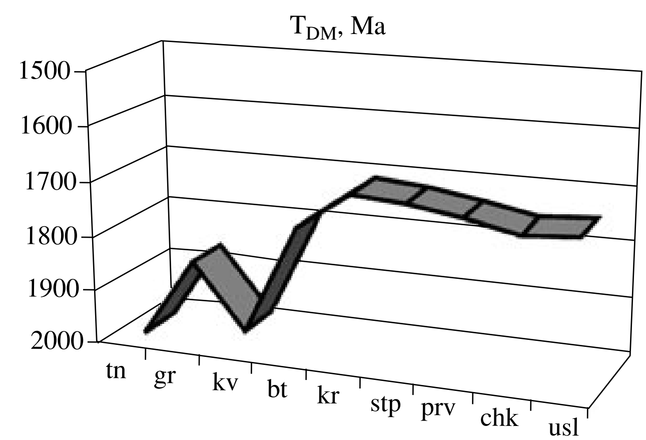

Fig. 11. Variations in the T_{DM} values of the shales and mudstones of the Serebryanka and Sylvitsa groups. Symbols are the same as in Fig. 2.

Table 6. Nd model ages of the igneous rocks of the Dvoretskii complex

Rock	Sample*	Rb	Sr	$^{87}Rb/^{86}Sr$	+/–	$^{87}Sr/^{86}Sr$	+/–	ε_{Sr}
Picrobasalt	V20	1.760	147	0.0347	0.0002	0.704285	0.000016	2.50
Trachyandesite	V7	28.300	1284	0.0638	0.0002	0.704668	0.000016	4.50
Trachyandesite	V13	5.800	661	0.0254	0.0001	0.703710	0.000015	–4.60
Trachyandesite	V3	30.400	755	0.1165	0.0003	0.704547	0.000017	–3.30
Rock	Sample*	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	+/–	ε_{Nd}	T_{DM}, Ma
Picrobasalt	V20	7.84	39.00	0.12142	0.512620	0.000011	5.18	707
Trachyandesite	V7	12.10	62.40	0.11713	0.512567	0.000007	4.46	757
Trachyandesite	V13	10.50	54.20	0.11713	0.512523	0.000007	3.60	824
Trachyandesite	V3	11.40	64.40	0.10734	0.512490	0.000007	3.67	797

* Samples for the calculation of Nd model age are after [101].

T_{Nd}(DM) values of the shales and mudstones range from 2.0 to 1.74 Ga and show some regular variations (Fig. 11). For instance, the Nd model age of shales from the lower part of the Serebryanka Group (Taninskaya and Koiva levels) is 1.97–1.99 Ga and is about 140 Myr younger (1.85 Ga) for the shales of the Garevskaya Formation. However, already the shales of the Butonskaya Formation, as well as all the younger units of the Vendian of the Kvarkushsko–Kamennogorskii meganticlinorium, show T_{Nd}(DM) values from 1.77 to 1.73 Ga, which is approximately 220–250 Myr younger than the Nd model ages of the fine-grained terrigenous rocks of the lower Serebryanka Group. This is consistent with the results of the petrographic investigation of pebbles from the conglomerates (see above) and indicates that the provenances of the Taninskaya and Koiva time periods were dominated by Early Proterozoic complexes, and those eroded areas were located in the eastern part of the eastern European platform. During the Garevskaya and Butonskaya–Kernosskaya time periods, a certain amount of juvenile mantle material was added to these rocks, which resulted in a significant shift of the Nd model ages toward younger values. However, the available data do not allow us to reliably determine if this material was derived from the basement complexes or had a Ural origin.

The established features of T_{Nd}(DM) variations are in adequate agreement with variations of LREE/HREE, La_N/Yb_N, Cr/Ni, Th/Co, and La/Co in the sections of the Serebryanka and Sylvitsa groups.

DISCUSSION

As was noted at the beginning of this paper, the mineralogical and petrographic investigations from 1970–1980 demonstrated that the genesis of the Vendian terrigenous sedimentary sequences of the Serebryanka Group of the Kvarkushsko–Kamennogorskii meganticlinorium was connected mainly with the rocks of the Archean–Early Proterozoic basement of the eastern European platform, whereas the erosion processes of Sylvitsa time involved both the base rocks and the Riphean and Vendian sedimentary and igneous complexes [36, 46, 47, etc.]. On the other hand, the inherently phenomenological petrographic investigations of conglomerates and sandstones gave only a qualitative portrait, whereas isotopic and geochemical data (LREE/HREE, La_N/Yb_N, other trace-element ratios, Nd model age, etc.) provide an opportunity to compare quantitatively a number of similar but independent compositional parameters of paleocatchments. Consequently, the most adequate description of compositional changes in paleocatchment areas can be obtained by the synthesis of data from petrographic and isotope geochemical investigations.

As was shown above, variations in the LREE/HREE ratio through the section of the Serebryanka and Sylvitsa groups display two maxima (at about 13.5–15.0) corresponding to the Taninskaya and Butonskaya levels, whereas this ratio is significantly lower (8–11) in the terrigenous rocks of other Vendian units. The La_N/Yb_N ratio varies sympathetically with LREE/HREE: the maximum values were found in the shales of the Taninskaya and Butonskaya formations, and the shales of all other units show much lower values. These variations can be interpreted as results of two episodes (in Garevskaya and Butonskaya–Kernosskaya times) of the appearance of basic magmatic complexes in the paleocatchments, which were made up in Taninskaya time by rather mature pre-Riphean continental crustal complexes.[6] This suggestion is additionally supported by the geochemical data on lower ΣREE values in the fine-grained clastic aluminosilicate rocks of the Koiva–early Chernokamenskaya level compared with the pelitic rocks of the Taninskaya and Ust'-Sylvitsa levels and a sharp increase in the Cr/Ni ratio in the shales of the Koiva and Butonskaya formations.

[6] As was mentioned above, it was previously supposed that there were three rifting events [61].

According to the results of recent geological mapping in the western part of the Kvarkushsko–Kamennogorskii meganticlinorium, there is only one level of alkaline basic and ultrabasic magmatism and volcanism corresponding to the upper part of the Kernosskaya Formation (Blagodat', Dvoretskii, Shpalorezovskii, and other complexes) [43]. Thus, it can be supposed that the Garevskaya minimum in the LREE/HREE, La_N/Yb_N, and ΣREE values and the departure of some indicator trace-element ratios from the typical values of felsic rocks suggest that basic magmatic complexes occurring in the eastern part of the eastern European platform were eroded during the Garevskaya time. The low values of these ratios and the younger Nd model ages of the Vendian pelitic rocks of the Kernosskaya–Ust'-Sylvitsa interval of the Kvarkushsko–Kamennogorskii meganticlinorium were related to other factors.

Nd model ages of 707–824 Ma were calculated by us using the data of [101] for the picrobasalts, trachybasalts, and trachyandesites of the Dvoretskii complex, which is situated among the deposits of the Kernosskaya Formation (Table 6). It can be concluded that the emplacement of the Dvoretskii and other compositionally similar magmatic complexes into the upper crust of the present western slope of the central Urals and the subsequent erosion of these rocks were responsible for a significant shift in Nd model ages toward younger values in the Butonskaya (?), Kernosskaya, and subsequent periods of the Late Vendian. A near constant value of this parameter in the fine-grained clastic aluminosilicate sediments of the upper portion of the Serebryanka and the whole Sylvitsa Group (about 1.77–1.71 Ga) suggests the existence of two sources of material during the formation of these deposits: basement rocks and basic–ultrabasic igneous complexes.

As was noted above, most authors correlate the appearance of basic and ultrabasic magmatic complexes among the Vendian sedimentary sequences of the Kvarkushsko–Kamennogorskii meganticlinorium with Early Vendian rifting processes. It was supposed [57] that the development of the Early Vendian rift occurred in several stages, marked by three volcanic–carbonate–terrigenous sequences. However, recent data [43] demonstrated the existence of only one (Kernosskaya) level of the occurrence of alkaline basic magmatism in the Vendian section, which conflicts with this model. Our new isotopic and geochemical data on the composition of sedimentary sequences of the Serebryanka and Sylvitsa groups allowed us to suppose that there was only one major rift-forming event in the area during the Butonskaya (?) and Kernosskaya time. This suggestion is in agreement with the results obtained by Karpukhina et al. [101], who showed that the isotope geochemical characteristics of mafic–ultramafic associations from the Kvarkushsko–Kamennogorskii meganticlinorium indicate their connection to a mantle plume, which probably initiated the formation of the Vendian rift structure.

Thus, only the development of the Dvoretskii and comagmatic volcanic associations in the Kernosskaya time resulted in a stable change in the composition of the Vendian fine-grained terrigenous rocks and a significant decrease in their Nd model age. The Taninskaya–Koiva epoch was characterized by a different style of the formation of sedimentary sequences. During its whole duration, the geochemically mature metamorphic and granite–metamorphic complexes of the base of the east European platform were mainly eroded, whereas basic and ultrabasic magmatic complexes, which are indicative of rift-forming processes, played a minor role.

In our opinion, the above considerations have fundamental stratigraphic consequences. It is well known that during the past few years, the most important stratigraphic boundaries have been correlated in the Russian literature on Precambrian stratigraphy with the beginning of major stages of geologic history marked by basic volcanism and formation of new structural patterns [102–104]. However, as was pointed out by Semikhatov [105], the limited methodical basis results in that these boundaries are still drawn along unconformity surfaces. In the western slope of the Urals, the Riphean–Vendian boundary is usually correlated with the discontinuity surface at the base of the Serebryanka Group [e.g., 38, 106], which rests upon the eroded surface of the underlying Riphean deposits and contains thick basal conglomerate sequences (Taninskaya level) with abundant fragments of crystalline and sedimentary rocks. Some authors correlated the conglomerates of the Taninskaya Formation or the deposits of the Taninskaya, Koiva, and Staropechninskaya formations on the whole[7] with the Lapland glacial horizon [e.g., 107, 108], although there is an opinion that the base of the Vendian is marked in the central Urals by pebble-poor conglomerates of the Staropechninskaya Formation only (see reviews in [108, 109]). Our isotopic and geochemical results show that a stable connection between rift-related mafic–ultramafic volcanism and magmatism and sedimentation processes can be established in the sections of the Serebryanka and Sylvitsa groups only starting from the Butonskaya–Kernosskaya level. However, there was no significant change in the structural patterns of this area in the pre-Butonskaya or pre-Kernosskaya time periods compared with the Taninskaya–Koiva epoch [e.g., 36]. Thus, the available isotopic and geochemical data alone are insufficient to define the lower boundary of the Vendian in the western slope of the middle Urals; nevertheless, it can be concluded with confidence that one of the most important Neoproterozoic events in this area was a single-stage (in the Butonskaya?–Kernosskaya epoch) formation of numerous rift-related magmatic complexes, which have subsequently greatly influenced the formation of sedimentary sequences.

[7] The Kernosskaya Formation is sometimes also combined with these units.

CONCLUSIONS

The following conclusions were drawn from our investigations.

The systematics of REE in the fine-grained aluminosilicate clastic deposits of the Serebryanka and Sylvitsa groups provide evidence for changes in the composition of paleocatchments during the Vendian. The eroded areas were characterized by the most mature compositions approaching that of a granite-dominated crust in the very beginning of the Serebryanka time. Since the second half of Serebryanka time, basic and ultrabasic rocks have played a significant role in paleocatchments. Their fraction in the provenances was probably rather high in the Chernokamenskaya time.

The change in the composition of provenances during the deposition of the Serebryanka and Sylvitsa groups is also indicated by the distribution of Cr, Ni, Co, Th, Sc, and Hf in shales and mudstones.

The lowest values of the Cr/Ni ratio, which may be indicative under certain conditions of a direct input of eroded ultramafic rocks into the sedimentation basin, were observed in the pelitic rocks of the Koiva and Butonskaya formations. The Cr/Ni ratio of shales and mudstones from other Vendian units of the Kvarkushsko–Kamennogorskii meganticlinorium does not reach the level associating with the direct erosion of ultramafic rocks; nonetheless, this parameter suggests that such rocks were present in the paleocatchments and their amounts were much higher than in the Taninskaya–Koiva epoch. The same inference can be drawn from a comparison of the median values of La/Th, La/Co, Th/Co, Sc/Th, La/Sc, and Ni/Co ratios in the shales of the two groups and in model sources (granitoids, including calc-alkaline ones, amphibolites with minor silicic rocks, ophiolites, upper and lower continental crust, etc.).

It is conceivable that basic or intermediate pyroclastic material had a significant effect on the composition of fine-grained terrigenous aluminosilicate clastic rocks. The presence of such materials is indicated by the occurrence of ash layers in the sections of the Staropechninskaya and Chernokamenskaya formations.

Pelitic rocks with $Gd_N/Yb_N > 2.0$ were found in various lithostratigraphic units of the Serebryanka and Sylvitsa groups. This fact may be indicative of a contribution of the Archean component into the composition of fine-grained aluminosilicate clastic rocks. This suggestion is also supported by the degree of heavy REE depletion in the mudstones of the Taninskaya and Ust'-Sylvitsa formations, which is similar to the level of typical Archean sedimentary complexes. The proportions of La, Th, and Sc in some mudstone samples from the Chernokamenskaya and Kernosskaya formations can also be interpreted as indicative of the presence of the products of AUC erosion in their composition.

The $T_{Nd}(DM)$ value of the fine-grained terrigenous rocks of the Taninskaya and Koiva formations is ~2.0 Ga, whereas pelitic rocks with $T_{Nd}(DM) \cong 1.77$–1.73 Ga are predominant in the upper part of the Serebryanka Group and in the whole section of the Sylvitsa Group. This suggests that starting from Butonskaya (?)–Kernosskaya time, in addition to the rocks of the crystalline basement of the eastern European platform, a certain amount of juvenile mantle material was involved in the erosion. This resulted in a decrease in the Nd model age of pelitic rocks by 220–250 Ma. This conclusion is in agreement with the results of the petrographic investigations of pebbles from the conglomerates and the geochemical characteristics of fine-grained clastic aluminosilicate rocks.

Thus, summing up the results obtained here on the REE systematics, variations in LREE/HREE, La_N/Yb_N, ΣREE, a number of indicator trace element ratios, and $T_{Nd}(DM)$ of the Vendian pelitic rocks of the western slope of the central Urals, it can be concluded that approximately from the middle of Serebryanka time, the formation of the Vendian sedimentary rocks of the Kvarkushsko–Kamennogorskii meganticlinorium was significantly affected not only by the basement complexes of the eastern European platform but by basic and ultrabasic igneous rocks (Dvoretskii, Kus'inskii, Vil'vinskii, and others) also, which were emplaced in the field Vendian sedimentary sequences in the western slope of the central Urals. The data of geological mapping, isotope geochemical characteristics of the mafic–ultramafic magmatic complexes, and our new isotopic and geochemical data on the Vendian sedimentary rocks of the Kvarkushsko–Kamennogorskii meganticlinorium allow us to conclude that the history of formation of the Early Vendian rift in the western slope of the central Urals included one rift-forming event, which was responsible for the majority of specific features of fine-grained aluminosilicate clastic rocks described in this paper.

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project no. 03-05-64121), Program for the Support of Leading Scientific Schools (grant no. NSh-85.2003.5), Program no. 7 of the Division of Earth Sciences, Russian Academy of Sciences, "Isotopic Geology: Geochronology and Sources of Matter," and Program no. 25 of the Presidium of the Russian Academy of Sciences "Origin and Evolution of the Biosphere."

REFERENCES

1. A. A. Migdisov, "Titanium and Aluminum Relationships in Sedimentary Rocks," Geokhimiya, No. 2, 149–163 (1960).
2. A. B. Ronov, Yu. A. Balashov, Yu. P. Girin, et al., "Regularities in the Distribution of Rare Earth Elements in

the Sedimentary Shell and the Earth's Crust," Geokhimiya, No. 12, 1483–1513 (1972).

3. S. R. Taylor and S. M. McLennan, *The Continental Crust: Its Composition and Evolution* (Blackwell, Oxford, 1985; Mir, Moscow, 1988).
4. V. N. Kholodov and R. I. Nedumov, "Geochemical Criteria of the Occurrence of Hydrogen Sulfide Contamination in Ancient Basins," Izv. Akad. Nauk SSSR, Ser. Geol., No. 12, 74–82 (1991).
5. B. G. Pokrovskii, E. F. Letnikova, and S. G. Samygin, "Isotopic Stratigraphy of the Bokson Group, Vendian–Cambrian of the Sayan Mountains," Stratigr. Geol. Korrelyatsiya **7** (3), 23–41 (1999) [Stratigr. Geol. Correlation **7**, 229–246 (1999)].
6. Ya. E. Yudovich and M. P. Ketris, *Principles of Lithochemistry* (Nauka, St. Petersburg, 2000) [in Russian].
7. *Interpretation of Geochemical Data*, Ed. by E. V. Sklyarov (Intermet Inzhiniring, Moscow, 2001) [in Russian].
8. A. V. Maslov, Yu. R. Ronkin, M. T. Krupenin, and E. Z. Gareev, "Riphean Sedimentation Basins of the Southern Urals (Paleogeography, Paleoclimate, Provenances, and Paleosalinity)," in *Sedimentary Basins of the Urals and Adjacent Regions: Regularities in Their Structure and Metallogeny* (Inst. Geol. Geokhim. URO RAS, Yekaterinburg, 2000), pp. 28–52 [in Russian].
9. A. V. Maslov, Yu. L. Ronkin, M. T. Krupenin, et al., "Provenances of Riphean Sedimentary Basins at the Russian Platform–Southern Urals Junction: Evidence from Petrographic, Petrochemical, and Geochemical Data," Dokl. Akad. Nauk **389**, 219–222 (2003) [Dokl. Earth Sci. **389**, 180–183 (2003)].
10. V. N. Podkovyrov, Extended Abstract of Doctoral Dissertation in Geology and Mineralogy (IGGD RAN, St. Petersburg, 2001).
11. V. N. Podkovyrov, V. P. Kovach, and L. N. Kotova, "Mudrocks from the Siberian Hypostratotype of the Riphean and Vendian: Chemistry, Sm–Nd Isotope Systematics of Sources, and Formation Stages," Litol. Polezn. Iskop., No. 4, 397–418 (2002) [Lithol. Mineral. Resour. **37**, 344–363 (2002)].
12. Yu. O. Gavrilov, E. V. Shchepetova, E. Yu. Baraboshkin, and E. A. Shcherbinina, "The Early Cretaceous Anoxic Basin of the Russian Plate: Sedimentology and Geochemistry," Litol. Polezn. Iskop., No. 4, 359–380 (2002) [Lithol. Mineral. Resour. **37**, 310–329 (2002)].
13. A. B. Kotov, Extended Abstract of Doctoral Dissertation in Geology and Mineralogy (IGGD RAN, St. Petersburg, 2003) [in Russian].
14. R. L. Cullers, S. Chaudhuri, B. Arnold, et al., "Rare Earth Distributions in Clay Minerals and in the Clay-Sized Fractions of the Lower Permian Havensville and Eskridge Shales of Kansas and Oklahoma," Geochim. Cosmochim. Acta **39**, 1691–1703 (1975).
15. H. W. Nesbitt and G. M. Young, "Early Proterozoic Climates and Plate Motions Inferred from Major Element Chemistry of Lutites," Nature **299**, 715–717 (1982).
16. D. J. Wronkiewicz and K. C. Condie, "Geochemistry of Archean Shales from the Witwatersrand Supergroup, South Africa: Source-Area Weathering and Provenance," Geochim. Cosmochim. Acta **51**, 2401–2416 (1987).
17. L. Harnois, "The CIW Index: A New Chemical Index of Weathering," Sediment. Geol. **55**, 319–322 (1988).
18. S. M. McLennan, "Rare Earth Elements in Sedimentary Rocks: Influence of Provenance and Sedimentary Processes," in *Geochemistry and Mineralogy of Rare Earth Elements*, Ed. by B. R. Lipin and G. A. McKay, Rev. Mineral. **21**, 169–200 (1989).
19. R. V. Tyson and T. H. Pearson, "Modern and Ancient Continental Shelf Anoxia: An Overview," in *Modern and Ancient Continental Shelf Anoxia*, Ed. by R. V. Tyson and T. H. Pearson, Geol. Soc. Spec. Publ. (London) **58**, 1–24 (1991).
20. K. C. Condie, "Chemical Composition and Evolution of the Upper Continental Crust: Contrasting Results from Surface Samples and Shales," Chem. Geol. **104**, 1–37 (1993).
21. K. C. Condie, *Plate Tectonics and Crustal Evolution*, (Butterworth–Heinemann, Oxford, 1997).
22. B. Jones and D. A. C. Manning, "Comparison of Geochemical Indices Used for the Interpretation of Palaeoredox Conditions in Ancient Mudstones," Chem. Geol. **111**, 111–129 (1994).
23. R. Cox, D. R. Lowe, and R. L. Cullers, "The Influence of Sediment Recycling and Basement Composition on Evolution of Mudrock Chemistry in Southwestern United States," Geochim. Cosmochim. Acta **59**, 2919–2940 (1995).
24. S. R. Taylor and S. M. McLennan, "The Chemical Evolution of the Continental Crust," Rev. Geophys. **33**, 241–265 (1995).
25. G. Mongelli, R. L. Cullers, and S. Muelheisen, "Geochemistry of Late Cretaceous–Oligocenic Shales from the Varicolori Formation, Southern Apennines, Italy: Implications for Mineralogical, Grain-Size Control and Provenance," Eur. J. Mineral. **8**, 733–754 (1996).
26. C. M. Fedo, G. M. Young, and H. W. Nesbitt, "Paleoclimatic Control on the Composition of the Paleoproterozoic Serpent Formation, Huronian Supergroup, Canada: A Greenhouse to Icehouse Transition," Precambrian Res. **86**, 201–223 (1997).
27. S. Hassan, H. Ishiga, B. P. Roser, et al., "Geochemistry of Permian–Triassic Shales in the Salt Range, Pakistan: Implications for Provenance and Tectonism at the Gondwana Margin," Chem. Geol. **158**, 293–314 (1999).
28. B. Bauluz, M. J. Mayayo, C. Fernandez-Nieto, and J. M. G. Lopez, "Geochemistry of Precambrian and Paleozoic Siliciclastic Rocks from the Iberian Range (NE Spain): Implications for Source-Area Weathering, Sorting, Provenance, and Tectonic Setting," Chem. Geol. **168**, 135–150 (2000).
29. M. I. Bhat and S. K. Ghosh, "Geochemistry of the 2.51 Ga Old Rampur Pelites, Western Himalayas: Implications for Their Provenance and Weathering," Precambrian Res. **108**, 1–16 (2001).
30. V. Rachold and H.-J. Brumsack, "Inorganic Geochemistry of Albian Sediments from the Lower Saxony Basin NW Germany: Palaeoenvironmental Constraints and Orbital Cycles," Palaeogeogr. Palaeoclimat. Palaeoecol. **174**, 121–143 (2001).
31. Y. I. Lee, "Provenance Derived from the Geochemistry of Late Paleozoic–Early Mesozoic Mudrocks of the

Pyeongan Supergroup, Korea," Sediment. Geol. **149**, 219–235 (2002).

32. A. V. Maslov, E. Z. Gareev, M. T. Krupenin, et al., "Application of Petro- and Geochemical Information for the Reconstruction of Sedimentary Rock Setting as Exemplified by the Riphean Type Section," in *Proceedings of Conference on Terrigenous Sedimentary Sequences of the Urals and Adjacent Territories: Sedimento- and Lithogenesis, and Minerageny, Yekaterinburg, Russia, 2002* (Inst. Geol. Geokhim. UrO RAS, Yekaterinburg, 2002), pp. 143–154 [in Russian].
33. A. V. Maslov, E. Z. Gareev, M. T. Krupenin, and Yu. L. Ronkin, "The Cr/Th Ratio in the Riphean Shales of the Bashkirian Meganticlinorium as an Indicator of the Tectonic Evolution of Provenances," in *Proceedings of 36th Conference on the Tectonics and Geodynamics of the Continental Lithosphere, Moscow, Russia, 2003* (GEOS, Moscow, 2003), Vol. 2, pp. 36–40 [in Russian].
34. A. V. Maslov, M. T. Krupenin, Yu. L. Ronkin, et al., "REE, Cr, Th, and Sc in Shales from the Riphean Type Section as Indicators of the Composition and Evolution of Provenances," Litosfera, No. 1, 70–112 (2004).
35. A. V. Maslov, Yu. L. Ronkin, M. T. Krupenin, et al., "The Lower Riphean Fine-Grained Aluminosilicate Clastic Rocks of the Bashkir Anticlinorium in the Southern Urals: Composition and Evolution of Their Provenance," Geokhimiya, No. 6, 648–669 (2004) [Geochem. Int. **42**, 561–578 (2004)].
36. B. D. Ablizin, M. L. Klyuzhina, F. A. Kurbatskaya, and A. M. Kurbatskii, *Upper Riphean and Vendian of the Western Slope of the Central Urals* (Nauka, Moscow, 1982) [in Russian].
37. M. L. Klyuzhina, *Vendian System of the Urals* (Inst. Geol. Geokhim. UrO AN SSSR, Sverdlovsk, 1991) [in Russian].
38. *Stratigraphic Schemes of the Urals (Precambrian and Paleozoic)* (Roskomnedra, IGG UrO RAN, Yekaterinburg, 1993) [in Russian].
39. N. A. Rumyantseva, "Alkaline Volcanism of the Western Slope of the Urals," in *Pre-Ordovician History of the Urals* (UNTs AN SSSR, Sverdlovsk, 1980), pp. 3–29 [in Russian].
40. Yu. D. Smirnov, L. I. Luk'yanova, and N. A. Rumyantseva, "Magmatic Rocks of the Western Slope of the Urals and Timan and Their Relations with Kimberlites," in *Proceedings of Conference on the Geology and Mineral Resources of the Northeastern Part of the USSR and Northern Urals, Syktyvkar, USSR, 1973* (Inst. Geol. Komi Fil. AN SSSR, Syktyvkar, 1973), Vol. 2, pp. 319–324 [in Russian].
41. S. B. Suslov, V. N. Zorin, A. N. Kinev, et al., *State Geological Map of the Russian Federation. Scale 1 : 200 000. Second Edition. Permian Series. Sheet O-40-XVII. Explanatory Notes* (Geokarta, Perm, 2002) [in Russian].
42. E. V. Karpukhina, V. A. Pervov, D. Z. Zhuravlev, and V. A. Lebedev, "The Age of Mafic–Ultramafic Magmatism on the Western Slope of the Urals: First Sm–Nd and Rb–Sr Data," Dokl. Akad. Nauk **369**, 809–811 (1999) [Dokl. Earth Sci. **369A**, 1384–1386 (1999)].
43. E. V. Karpukhina, V. A. Pervov, and D. Z. Zhuravlev, "Mafic–Ultramafic Magmatism on the Western Slope of the Urals: Vendian–Cambrian Intraplate Magmatism," in *Proceedings of the 33rd Conference on General Tectonic Problems, Moscow, Russia, 2000* (GEOS, Moscow, 2000), pp. 194–197 [in Russian].
44. D. V. Grazhdankin, A. V. Maslov, T. M. R. Mastill, and M. T. Krupenin, "The Ediacaran White Sea Biota in the Central Urals," Dokl. Akad. Nauk **401**, 784–788 (2005) [Dokl. Earth Sci. **401A**, 382–386 (2005)].
45. A. A. Kukharenko, "Lithology and Formation Conditions of the Asha Group, Western Slope of the Central Urals," Vopr. Litol. Paleogeogr. Uch. Zapiski Leningr. Gos. Univ. Ser. Geol., No. 310, 245–274 (1962).
46. F. A. Kurbatskaya, Extended Abstract of Candidate's Dissertation in Geology and Mineralogy (Permsk. Gos. Univ., Perm, 1968).
47. F. A. Kurbatskaya and B. D. Ablizin, "Paleogeography of the Upper Precambrian Terrigenous Sequences of the Western Slope of the Central Urals (Western Subzone of the Vishera–Chusovaya Anticlinorium)," in *Geology and Petrography of the Western Urals* (Permsk. Gos. Univ., Perm, 1970), pp. 109–126 [in Russian].
48. V. I. Kozlov, A. A. Krasnobaev, Yu. L. Ronkin, and V. M. Gorozhanin, "Main Problems in the Vendian Geology and Geochronology of the South and Central Urals," in *Proceedings of Conference on the Stratigraphy of the Upper Proterozoic of the USSR (Riphean and Vendian) Ufa, USSR, 1990* (IG BNTs UrO AN SSSR, Ufa, 1990), pp. 66–68 [in Russian].
49. *Precambrian Geology of the USSR*, Ed. by V. Ya. Khil'tova, A. B. Vrevskii, S. B. Lobach-Zhuchenko, et al. (Nauka, Leningrad, 1988) [in Russian].
50. V. E. Khain and N. A. Bozhko, *Historical Geotectonics of the Precambrian* (Nedra, Moscow, 1988) [in Russian].
51. V. A. Koroteev, A. A. Krasnobaev, and V. M. Necheukhin, "Problems of Geochronology and Paleogeodynamics of the Vendian–Early Paleozoic Period in the Earth Evolution," in *Paleogeography of the Vendian–Early Paleozoic of Northern Eurasia* (Inst. Geol. Geokhim. UrO RAS, Yekaterinburg, 1998), pp. 4–8 [in Russian].
52. V. M. Necheukhin, "Metallogeny of Vendian–Early Paleozoic Geodynamic Associations," in *Paleogeography of the Vendian–Early Paleozoic of Northern Eurasia* (Inst. Geol. Geokhim. UrO RAN, Yekaterinburg, 1998), pp. 25–30 [in Russian].
53. V. N. Puchkov, "Tectonics of the Urals: Modern Concepts," Geotektonika, No. 4, 42–61 (1997) [Geotectonics **31**, 294–312 (1997)].
54. V. N. Puchkov, *Paleogeodynamics of the Southern and Central Urals* (Dauriya, Ufa, 2000) [in Russian].
55. V. V. Bochkarev and R. G. Yazeva, *Subalkaline Magmatism of the Urals* (Ural. Otd. Ross. Akad. Nauk, Yekaterinburg, 2000) [in Russian].
56. F. A. Kurbatskaya, "Structure and Evolution of the Junction Zone between the Urals and East European Platform," in *Precambrian Volcanosedimentary Complexes of the Urals* (UNTs RAN, Sverdlovsk, 1986), pp. 50–59 [in Russian].
57. F. A. Kurbatskaya, "Magmatism, Metamorphism, and Metallogeny of the Early Vendian Intracratonic Rift in the Urals," in *Proceedings of the First All-Russia Petro-*

graphic Conference, Ufa, Russia, 1995 (UNTs RAN, Ufa, 1995), Vol. 1, pp. 116–117 [in Russian].

58. F. A. Kurbatskaya, "On the Riphean–Vendian Boundary in the Central Urals," in *Proceedings of Conference on General Problems of the Riphean Stratigraphy and Geological History of Northern Eurasia, Yekaterinburg, 1995* (Ural. Otd. Ross. Akad. Nauk, Yekaterinburg, 1995), pp. 53–54 [in Russian].
59. R. G. Iblaminov, F. A. Kurbatskaya, G. V. Lebedev, et al., "Metallogeny of the Riphean and Vendian of the Western Slope of the Northern and Central Urals," in *Proceedings of Conference on the Geology and Minerageny of the Precambrian of the Northeastern European Platform and Northern Urals, Syktyvkar, Russia, 1996* (Geoprint, Syktyvkar, 1996), pp. 76–77 [in Russian].
60. A. V. Maslov, "Some Specific Features of Early Vendian Sedimentation in the Southern and Middle Urals," Litol. Polezn. Iskop., No. 6, 624–639 (2000) [Lithol. Miner. Resour. **35**, 556–570 (2000)].
61. F. A. Kurbatskaya, "On Boundary of the Vendian Serebryanka Group and Facies–Paleotectonic Zoning of Its Sections in the Urals," in *Proceedings of Conference on the Upper Proterozoic (Riphean and Vendian) Stratigraphy of the USSR, Ufa, Russia, 1990* (IG BNTs UrO AN SSSR, Ufa, 1990), pp. 74–76 [in Russian].
62. F. A. Kurbatskaya and O. V. Kuchina, "Vendian Phosphate-Bearing Rocks of the Central Urals," in *Proceedings of Conference on Problems of Mineralogy, Petrography, and Metallogeny* (Permsk. Gos. Univ., 2000), pp. 61–65 [in Russian].
63. N. M. Chumakov, "Tillites and Tilloids of the Western Slope of the Central Urals," in *Proceedings of All-Russia Conference on the Paleogeography of the Vendian–Early Paleozoic, Upper Riphean, Vendian, and Lower Paleozoic Sections of the Central and Southern Urals. Guidebook of Geological Excursions, Yekaterinburg, Russia, 1996* (Inst. Geol. Geokhim., Yekaterinburg, 1996), pp. 74–82 [in Russian].
64. A. V. Maslov, D. V. Grazhdankin, and M. T. Krupenin, "Sedimentation Features and Settings of Sedimentary Successions from the Lower Subformation of the Vendian Chernyi Kamen Formation in the Sylvitsa River Basin," in *Yearbook-2002* (Inst. Geol. Geokhim., Yekaterinburg, 2003), pp. 70–82 [in Russian].
65. A. V. Maslov, D. V. Grazhdankin, and M. T. Krupenin, "Chernyi Kamen Formation of the Us'va River Basin in the Middle Urals (Structure, Sedimentology, and Formation Conditions," in *Yearbook-2003* (Inst. Geol. Geokhim., Yekaterinburg, 2004), pp. 65–86 [in Russian].
66. M. L. Klyuzhina, Candidate's Dissertation in Geology and Mineralogy (IGG UFAN SSSR, Sverdlovsk, 1969).
67. A. V. Maslov, "Structural Features of the Rocks of the Upper Vendian Ust-Syl'vitsa Formation in the Type Section: Evidence for the Interpretation of Formation Conditions," in *Ezhegodnik-2002* (Inst. Geol. Geokhim., Yekaterinburg, 2003), pp. 65–69 [in Russian].
68. H. W. Nesbitt, "Mobility and Fractionation of Rare Elements during Weathering of a Granodiorite," Nature **279**, 206–210 (1979).
69. B. E. Davis, *Applied Soil Trace Elements* (Wiley & Sons, New York, 1980).
70. D. J. Wronkiewicz and K. C. Condie, "Geochemistry and Mineralogy of Sediments from the Ventersdorp and Transvaal Supergroups, South Africa: Cratonic Evolution during the Early Proterozoic," Geochim. Cosmochim. Acta **54**, 343–354 (1990).
71. S. M. McLennan, S. R. Hemming, D. K. McDaniel, and G. N. Hanson, "Geochemical Approaches to Sedimentation, Provenance and Tectonics," in *Processes Controlling the Composition of Clastic Sediments*, Ed. by M. J. Johnsson and A. Basu, Geol. Soc. Am. Spec. Pap. **284**, 21–40 (1993).
72. G. H. Girty, A. D. Hanson, C. Knaack, and D. Johnson, "Provenance Determined by REE, Th, Sc Analyses of Metasedimentary Rocks, Boyden Cave Roof Pendant, Central Sierra Nevada, California," J. Sed. Res. **B64**, 68–73 (1994).
73. F. P. Bierlein, "Rare-Earth Element Geochemistry of Clastic and Chemical Metasedimentary Rocks Associated with Hydrothermal Sulphide Mineralisation in the Olary Block, South Australia," Chem. Geol. **122**, 77–98 (1995).
74. R. L. Cullers, "The Control on the Major- and Trace-Element Evolution of Shales, Siltstones and Sandstones of Ordovician to Tertiary Age in the Wet Mountains Region, Colorado, U.S.A," Chem. Geol. **123**, 107–131 (1995).
75. S. M. McLennan, S. R. Taylor, M. T. McCulloch, and J. B. Maynard, "Geochemical and Nd–Sr Isotopic Composition of Deep-Sea Turbidites: Crustal Evolution and Plate Tectonic Associations," Geochim. Cosmochim. Acta **54**, 2015–2050 (1990).
76. R. L. Cullers and J. Graf, "Rare Earth Elements in Igneous Rocks of the Continental Crust: Intermediate and Silicic Rocks, Ore Petrogenesis," in *Rare-Earth Geochemistry*, Ed. by P. Hendersen (Elseiver, Amsterdam, 1983), pp. 275–312.
77. S. M. McLennan and S. R. Taylor, "Sedimentary Rocks and Crustal Evolution: Tectonic Setting and Secular Trends," J. Geol. **99**, 1–21 (1991).
78. A. K. Gibbs, C. W. Montgomery, P. A. O'Day, et al., "The Archean–Proterozoic Transition: Evidence from the Geochemistry of Metasedimentary Rocks of Guyana and Montana," Geochim. Cosmochim. Acta **50**, 2125–2141 (1986).
79. D. J. Wronkiewicz and K. C. Condie, "Geochemistry and Mineralogy of Sediments from the Ventersdorp and Transvaal Supergroups, South Africa: Cratonic Evolution during the Early Proterozoic," Geochim. Cosmochim. Acta **54**, 343–354 (1990).
80. K. C. Condie and D. A. Wronkiewicz, "The Cr/Th Ratio in Precambrian Pelites from the Kaapvaal Craton as an Index of Craton Evolution," Earth Planet. Sci. Lett. **97**, 256–267 (1990).
81. B.-M. Jahn and K. C. Condie, "Evolution of the Kaapvaal Craton as Viewed from Geochemical and Sm–Nd Isotopic Analyses of Intracratonic Pelites," Geochim. Cosmochim. Acta **59**, 22–39 (1995).
82. R. L. Cullers and V. N. Podkovyrov, "Geochemistry of the Mesoproterozoic Lakhanda Shales in Southeastern Yakutia, Russia: Implications for Mineralogical and

Provenance Control, and Recycling," Precambrian Res. **104**, 77–93 (2000).

83. S. M. McLennan and S. Hemming, "Samarium/Neodymium Elemental and Isotopic Systematics in Sedimentary Rocks," Geochim. Cosmochim. Acta **56**, 997–998 (1992).
84. J. I. Garver, P. R. Royce, and T. A. Smick, "Chromium and Nickel in Shale of the Tacinic Foreland: A Case Study for the Provenance of Fine-Grained Sediments with an Ultramafic Source," J. Sed. Res. **66**, 100–106 (1996).
85. M. M. Herron, "Geochemical Classification of Terrigenous Sands and Shales from Core or Log Data," J. Sed. Petrol. **58**, 820–829 (1988).
86. K. R. Ludwig, "ISOPLOT—A Plotting and Regression Program for Radiogenic-Isotope Data, Version 2.57," U.S. Geol. Surv. Open-File Rept. 91-445 (1992).
87. N. M. Rock, J. A. Webb, N. J. McNaughton, et al., "Nonparametric Estimation of Averages and Errors for Small Datasets in Isotope Geoscience: A Proposal," Chem. Geol. **66**, 163–177 (1987).
88. A. Rottura, G. M. Bargossi, V. Caironi, et al., "Petrology, Geochemistry and Sr, Nd Isotopes of Contrasting Hercynian Granitoids from the Southern Calabrian Arc (South Italy)," Miner. Petrogr. Acta **32**, 1–36 (1989).
89. P. Spadea, L. Tortorici, and G. Lanzafame, "Ophiolites of the Tyrrhenian Coastal Chain," in *6th Ophiolite Field Conference. Field Excursion. Guidebook. Florence, Italy, 1980* (Florence, 1980), pp. 19–27.
90. R. K. O'Nions, P. J. Hamilton, and P. J. Hooker, "A Nd Isotope Investigation of Sediments Related to Crustal Development in the British Isles," Earth Planet. Sci. Lett. **63**, 229–240 (1983).
91. C. D. Frost and R. K. O'Nions, "Nd Evidence for Proterozoic Crustal Development in the Belt-Purcell Supergroup," Nature **312**, 53–56 (1984).
92. R. G. Miller and R. K. O'Nions, "The Provenance and Crustal Residence Ages of British Sediments in Relation to Palaeogeographic Reconstructions," Earth. Planet. Sci. Lett. **68**, 459–470 (1984).
93. R. G. Miller and R. K. O'Nions, "Source of Precambrian Chemical and Clastic Sediments," Nature **314**, 325–330 (1985).
94. R. A. Burwash, P. A. Cavell, and E. J. Burwash, "Source Terranes for Proterozoic Sedimentary Rocks in Southern British Columbia: Nd Isotopic and Petrographic Evidence," Can. J. Earth Sci. **25**, 824–832 (1988).
95. A. Dia, B. Dupre, C. Gariepy, and C. J. Allegre, "Sm–Nd and Trace-Element Characterization of Shales from the Abitibi Belt, Labrador Trough, and Appalachian Belt: Consequences for Crustal Evolution through Time," Can. J. Earth Sci. **27**, 758–766 (1990).
96. X. Li and M. T. McCulloch, "Secular Variation in the Nd Isotopic Composition of Neoproterozoic Sediments from the Southern Margin of the Yangtze Block: Evidence for a Proterozoic Continental Collision in Southeast China," Precambrian Res. **76**, 67–76 (1996).
97. V. P. Kovach, A. B. Kotov, and V. I. Berezkin, "Age Limits of High-Grade Metamorphic Supracrustal Complexes in the Central Aldan Shield: Sm–Nd Isotopic Data," Stratigr. Geol. Korrelyatsiya **7**, 3–17 (1999) [Stratigr. Geol. Correlation **7**, 1–14 (1999)].
98. V. P. Kovach, A. B. Kotov, A. P. Smelov, et al., "Evolutionary Stages of the Continental Crust in the Buried Basement of the Eastern Siberian Platform: Sm–Nd Isotopic Data," Petrologiya **8**, 394–408 (2000) [Petrology **8**, 353–365 (2000)].
99. R. G. Miller, R. K. O'Nions, P. J. Hamilton, and E. Welin, "Crustal Residence Ages of Clastic Sediments, Orogeny and Continental Evolution," Chem. Geol. **57**, 87–99 (1986).
100. V. I. Kovalenko, V. V. Yarmolyuk, V. P. Kovach, et al., "Magmatism as Factor of Crust Evolution in the Central Asian Foldbelt: Sm–Nd Isotopic Data," Geotektonika, No. 3, 21–41 (1999) [Geotectonics **33**, 191–208 (1999)].
101. E. V. Karpukhina, V. A. Pervov, and D. Z. Zhuravlev, "Petrology of the Subalkaline Volcanism in the Western Slope of the Ural Mountains—An Indicator of the Late Vendian Rifting," Petrologiya **9**, 480–503 (2001) [Petrology **9**, 415–436 (2001)].
102. E. V. Bibikova, S. B. Lobach-Zhuchenko, M. A. Semikhatov, et al., "Precambrian Time Scale for the East European Platform and Its Framing," Izv. Akad. Nauk SSSR, Ser. Geol., No. 4, 8–22 (1989).
103. M. A. Semikhatov, "General Subdivision of the Precambrian: Conceptual Analysis," in *Proceedings of the Second USSR Conference on General Problems of Precambrian Subdivision of the USSR, Ufa, Russia, 1990* (BNTs UrO AN SSSR, Ufa, 1990), pp. 35–49 [in Russian].
104. M. A. Semikhatov, K. A. Shurkin, E. M. Aksenov, et al., "New Precambrian Stratigraphic Scale of the USSR," Izv. Akad. Nauk SSSR, Ser. Geol., No. 4, 3–16 (1991).
105. M. A. Semikhatov, "Recent Concepts of the General Subdivision of the Precambrian: An Analysis," Izv. Akad. Nauk SSSR, Ser. Geol., No. 8, 3–13 (1991).
106. *Unified and Correlation Stratigraphic Schemes of the Urals* (UNTs AN SSSR, Uralgeologiya, Sverdlovsk, 1980) [in Russian].
107. N. M. Chumakov, *Precambrian Tillites and Tilloids* (Nauka, Moscow, 1978) [in Russian].
108. *Climate during Large Biospheric Rearrangements*, Ed. by M. A. Semikhatov and N. M. Chumakov (Nauka, Moscow, 2004) [in Russian].
109. *Vendian System. Historical-Geological and Paleontological Background*, Ed. by B. S. Sokolov and M. A. Fedonkin (Nauka, Moscow, 1985), Vol. 2 [in Russian].