

The Lower Riphean Fine-Grained Aluminosilicate Clastic Rocks of the Bashkir Anticlinorium in the Southern Urals: Composition and Evolution of Their Provenance

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Abstract—The major and trace element geochemistry of the Burzyan fine-grained aluminosilicate clastic rocks of the Bashkir Anticlinorium was used to estimate the composition of provenance and its evolution from 1650–1640 to 1350 Ma. Total REE contents are higher than 200 ppm in all the shale samples analyzed, and approximately 3 times lower in the clayey rocks of the upper unit of the Ai Formation. The $(La/Yb)_N$ and $(Gd/Yb)_N$ in the shales of this level are also much lower. The Eu/Eu^* value of Burzyan shales is 0.6–0.7, which is typical of most post-Archean clayey rocks. The REE patterns of shales from all the lithostratigraphic levels analyzed are rather similar and close to the PAAS pattern. The evolution of the Early Riphean sedimentary basin that occupied the territory of the present-day Bashkir Anticlinorium is interpreted as follows. The beginning of the Early Riphean was characterized by (1) the formation of a shallow sedimentary basin, (2) the erosion of large blocks of the mature continental crust composed of felsic rocks impregnated by basic dikes and other minor intrusions, and (3) the predominance of proximal provenances. In late Ai time, the aforementioned blocks were completely graded; and distal sources of aluminosilicate clastic materials became prevalent. Felsic rocks were eroded in the source areas. Basic rocks contributed to the provenance in early Kusa time, but subsequently they have not been involved in erosion until the end of the Early Riphean. Clastic material was mainly removed during that time period from the west and northwest, i.e., from the eastern parts of the East European Platform. An abrupt and relatively short-term rearrangement of the migration paths of terrigenous material is supposed for late Satka time, when a great amount of magnesium was supplied to the basin. As follows from the model Nd ages of shales throughout the Burzyan section, the source of magnesium had a pre-Riphean age and was situated north or northeast of the present-day Bashkir Anticlinorium.

INTRODUCTION

Since the middle 1940s, the compositions of pebbles from conglomerates and clastic grains from sandstones have traditionally been used in the Russian geological literature for the reconstruction of provenances [1–4]; clayey rocks are much more rarely used for this purpose. At the same time, foreign authors widely use fine-grained aluminosilicate clastic rocks (shale and mudstone) as a universal tool for the unraveling of the compositions and evolution of provenances, especially in Precambrian supracrustal sequences [5–12]. The advantage of this approach is determined by the low permeability of clayey rocks for postsedimentation fluids and their much better mixing and homogenization in comparison with coarse-grained sediments [6]. The analysis of REE patterns of shales is one of the most efficient ways to estimate the compositions of rocks in source areas, because their REE distribution does not

undergo substantial epigenetic modification, and, hence, the sedimentary rocks inherit, to a considerable extent, the REE distribution of the source rocks ¹ [6–8, 15–17]. Various geochemical ratios, e.g., La/Sc , La/Cr , La/Co , Th/Sc , and Th/Co , are also informative in this respect [7, 8, 11, 12, 17].

This paper is the first of a series of publications on the geochemistry of fine-grained aluminosilicate clastic rocks of the Riphean reference stratigraphic section on the western slope of the southern Urals. We address the major and trace element geochemistry of shales from the Burzyan Group as a lower Riphean straton in order to reconstruct the evolution of their provenances from 1650–1640 to 1350 Ma.

¹ Some authors admit that the type of sediments and climatic factors exert a certain influence on the REE patterns of sedimentary rocks [13 and others], but this influence is insignificant in comparison with the compositional variations of igneous rocks [14].

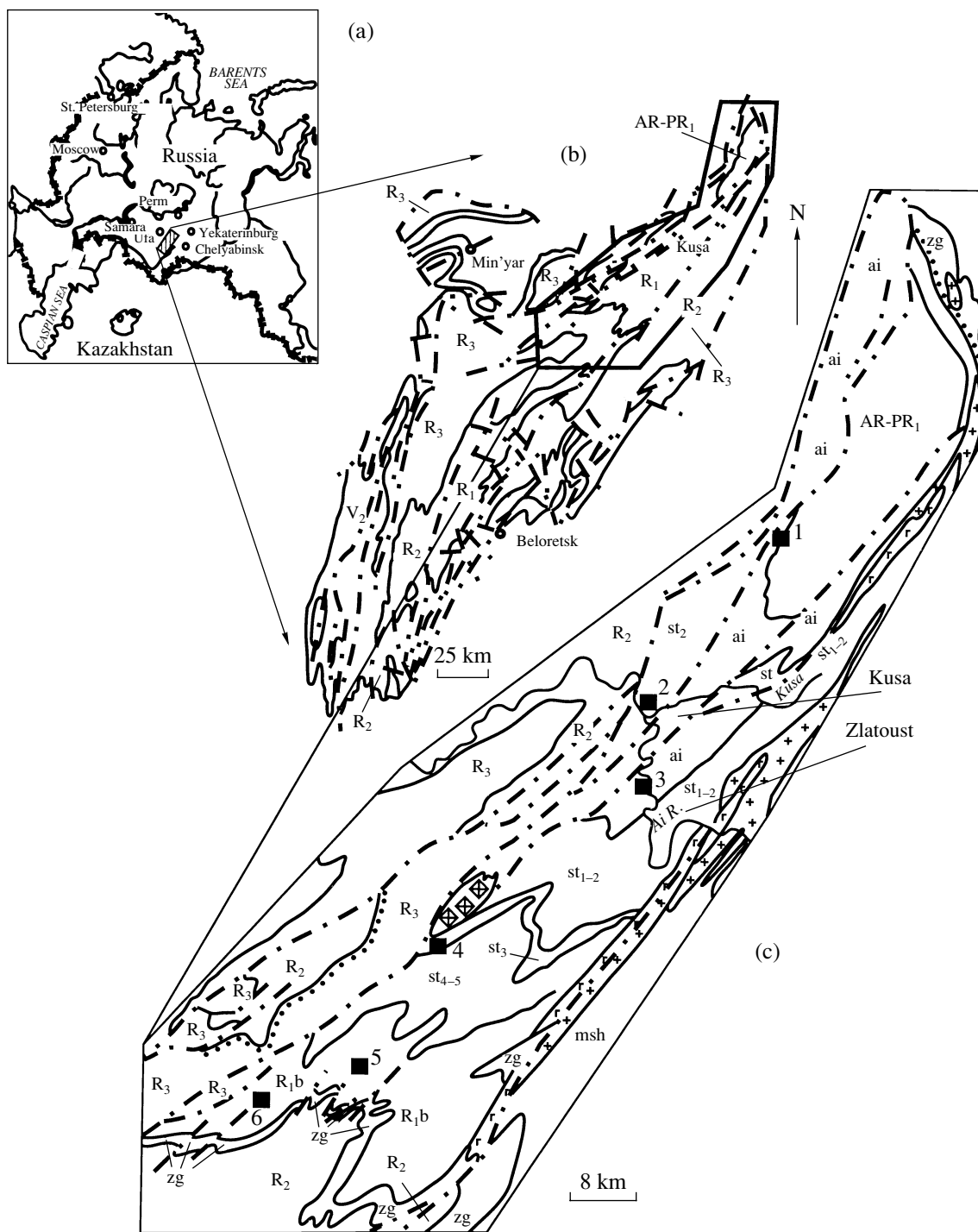


Fig. 1. (a) Index map, (b) schematic geological map of the Bashkir Anticlinorium, and (c) geological map of its northeastern portion (modified after [19]). The dashed line in (a) contours the Bashkir Anticlinorium. AR-PR₁, Archean and Paleoproterozoic rocks; R₁, Lower Riphean; R₂, Middle Riphean; R₃, Upper Riphean; V₂, Upper Vendian; ai, Ai Formation; st, Satka Formation; st₁₋₂ lower and upper Kusa subformations of the Satka Formation; st₂, upper Kusa Subformation of the Satka Formation; st₃, Polovinka Subformation of the Satka Formation; st₄₋₅, lower and upper Satka subformations of the Satka Formation; R_{1b}, Makarovskaya Subformation of the Bakal Formation; msh, Mashak Formation; zg, Zigal'ga Formation. Solid squares in Fig. 1c show sample locations: (1) Chernyi Klyuch Creek, (2) Ai River downstream from the Kusa cemetery; (3) Ai River downstream from the Medvedevka River; (4) eastern outskirts of Satka near the Rechnaya railway station; (5) near Polushkin Farm; (6) Bakal open pits.

GEOLOGIC SETTING OF THE LOWER RIPHEAN SEDIMENTARY SEQUENCES

The Burzyan Group comprises the Ai, Satka, and Bakal formations. Its sections typically crop out in the northeastern Bashkir Anticlinorium in the framing of the Archean–Paleoproterozoic Taratash Inlier (Fig. 1). These stratigraphic units are correlated in composition and phytolith complexes with the Bol'shoi Inzer, Suran, and Yusha formations of the Yamantau Anticlinorium [18–20].

The Ai Formation is subdivided into two large units [21] (Fig. 2). The lower unit overlies the deeply eroded Archean–Paleoproterozoic rocks of the Taratash Complex and consists of coarse-grained terrigenous rocks and locally developed basic volcanics. The U–Pb age of the volcanic rocks was estimated as 1615 ± 45 Ma [19]. The upper unit is composed mainly of low-carbonaceous shales.²

The Satka Formation (1700–3500 m) conformably overlies the Ai Formation and consists of dolomite and limestone with subordinate thin interlayers of siltstone and shale. The formation is subdivided into five subformations (from bottom to top): the lower and upper Kusa, Polovinka, lower and upper Satka [18, 20]. The lower Kusa Subformation (>900 m) consists of dolomite with minor limestone and shale. The upper Kusa Subformation (800–900 m) is also dominated by dolomite; shale and its low-carbonaceous varieties occur as thin interbeds. The Polovinka Subformation (160–200 m) comprises carbonaceous shale with siltstone and carbonate interlayers. The lower Satka Subformation (300–450 m) is mainly composed of dolomite with terrigenous admixture; low-carbonaceous shale and phytogenic carbonate rocks are subordinate. The upper Satka Subformation (up to 1200 m) consists in its lower part of dolomite including clayey varieties. These rocks give way upsection to dolomite with carbonaceous shale interlayers and limestone. The Satka Formation is intruded by rapakivi granite of the Berdyash pluton having a U–Pb zircon age of 1348 ± 16 Ma [23].

The Bakal Formation is composed of shale, siltstone, dolomite, and limestone, 1400–1600 m in thickness. Its lower part, about 650 m thick, is referred to as the Makarovskaya Subformation and consists mainly of low-carbonaceous shales. The upper part, the Malobakal'skaya Subformation comprises ten members of shale, siltstone, and carbonate rocks varying in thickness from 100–150 to 250–300 m. These rocks are cut in the Bakal ore field by the Main dike [24] having an Rb–Sr isotopic age of 1360 ± 35 Ma [25]. The age of diagenesis of the lowermost Bere-

² In the stratigraphic scheme proposed by M.I. Garan [22], the lower unit corresponds to the Navysh, Lipovye Gory, and Chudinka subformations with a total thickness of 1400–1600 m, and the upper unit is correlated with the Kisegan and Sungur subformations with a total thickness of 800–1000 m.

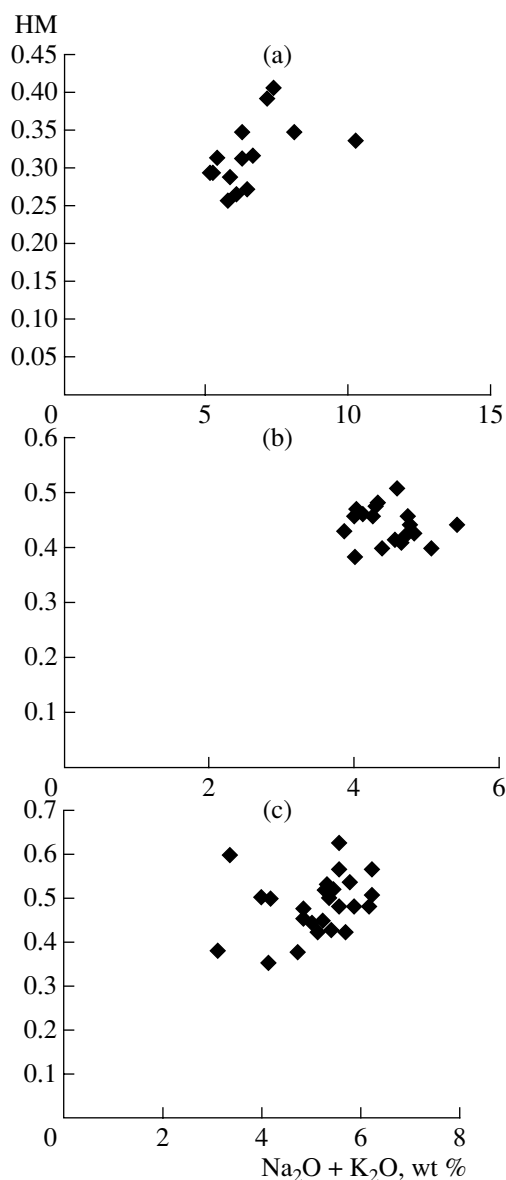


Fig. 2. Hydrolyzate module (HM) versus $\text{Na}_2\text{O} + \text{K}_2\text{O}$ for the shales of the (a) Ai Formation, (b) Makarovskaya, and (c) Malobakal'skaya subformations of the Bakal Formation; Burzyan Group of the northeastern Bashkir Anticlinorium.

zovskaya member was determined by the Pb–Pb method as 1430 ± 30 Ma [26].

PROVENANCE COMPOSITION: PREVIOUS RECONSTRUCTIONS

In the Burzyan section, conglomerates and sandstones are common only in the lower unit of the Ai Formation. The pebbles of conglomerates are composed of various quartzites, quartzite-like sandstones, phyllites, feruginous cherty rocks, iron formations, quartz porphyries, granites (microcline, biotite, two-mica, amphibole, and alaskite), plagiophyric rocks, blasto-

mylonites, metasomatic rocks, etc. [27–30]. The compositions of pebbles indicate that the metamorphic and igneous rocks of the Taratash Inlier and the eastern part of the Russian Platform (red microcline granite, rapakivi granite, etc.) were eroded in early Ai time.³ According to A.M. Sukhorukov (1973, 1975, unpublished reports), the distribution of pebble sizes in the conglomerates testifies to the very short distance of clastic material transport before its burial.⁴

The sandstones of the lower unit of the Ai Formation are mainly represented by arkose, subarkose and graywacke arkose [30]. The lithic clasts of the psammitic framework are represented by various structural types of microquartzite, granular quartz, quartz–mica rocks, felsic igneous rocks, and diabase. The accessory minerals of the sandstone are similar to those of Taratash gneisses [33]. In the $Al_2O_3/SiO_2-(CaO + N_2O + K_2O)$ and $Al_2O_3/SiO_2-(Fe_2O_3 + FeO + MgO + TiO_2 + MnO)$ diagrams proposed by Kossovskaya and Tuchkova [34], the points of sandstone from the lower unit of the Ai Formation fall into the fields of rocks derived by the erosion of rhyodacite, granite, and granodiorite with the lowest Al_2O_3/SiO_2 values.

The geochemical characteristics of the Burzyan rocks that have been obtained up to now are very limited. For example, it was shown that the REE patterns of Lower Riphean carbonate rocks are similar to those of granites making up the continental crust [35]. Parnachev [36] suggested that the Lower Riphean clayey rocks are contaminated with volcanic material, which follows from petrographic examination and the elevated REE contents. Based on major- and trace-element geochemistry, Rykus *et al.* [37] stated that the dioritic gneiss and hypersthene plagiogneiss of the Taratash Complex were mainly eroded in early Ai time.⁵ Felsic and intermediate rocks from pre-Riphean basement blocks were eroded in late Ai time. The geochemical signature of terrigenous sediments was somewhat different in Satka time: “the characteristic assemblage of terrigenous minerals (Cr-spinel, pyroxene, and sulfides) and the V–Cr–Cu association indicate a substantial role of mafic and, probably, ultramafic rocks in the source area” [37, p. 18].

According to our previous investigations, felsic rocks were predominant in the provenance throughout the Early Riphean. This was supported by the

LREE/HREE ratio of shales, in particular, $(La/Yb)_N \gg 4$ [38–40].

CONDITIONS OF FORMATION OF THE LOWER RIPHEAN SEDIMENTARY SEQUENCES

A comprehensive survey of concepts and ideas concerning the conditions of formation of the Lower Riphean sedimentary sequences in the Bashkir Anticlinorium was presented previously (see overview and references in [41, 42]). Garan' [43, 44] suggested that the sedimentation of Ai time occurred in a grabenlike trough. In his opinion, the coarse clastics of the lower unit of the Ai Formation are near-shore shallow sediments. The fine-grained terrigenous sediments of the upper unit mark a gradually increasing transgression. Shallow-water marine sediments were largely formed in the Satka and Bakal times. The major source areas were situated to the west of the present-day Bashkir Anticlinorium. V.P. Feoktistov *et al.* (1977, unpublished report) supposed that the formation of the Lower Riphean sedimentary sequence was related during the initial stages to the erosion of an emerging highland, which underwent long-term chemical weathering and was almost completely peneplaned by the end of the Burzyan.

Until the early 1980s, the Burzyan Group was regarded as a typical marine miogeosynclinal sequence, and deposition in a continental environment was assumed only for the lowermost units [27–29, 43–47]. In the late 1970s, the Ai, Satka, and Bakal formations were classified by Ivanov [48] and other authors [49–54] as riftogenic platform deposits. According to this concept, the middle and upper Burzyan sediments were deposited in marine or intracontinental lacustrine basins with a relatively rough bottom topography. It was suggested that many small basins with variously evolved evaporite sedimentation occurred within the outlines of the present-day Bashkir Anticlinorium, and the land areas that divided these basins could serve as local provenances [50].

We distinguished several stages in the evolution of the Early Riphean basin [38, 41, 55–57]. The earliest stage was related to the fragmentation of the basement of the East European Craton over a rather large territory. A roughly equant shallow sedimentation basin that covered most of the present-day Perm, Chelyabinsk, and Orenburg regions; Tatarstan; and Bashkortostan loomed in the very early Burzyan within the present-day Bashkir Anticlinorium and the adjacent Volga–Ural region [42]. Owing to the uneven movements of basement blocks inside the basin and at its margins, the sedimentary filling was characterized by a contrasting facies pattern and considerable variations in grain size, composition, and thickness of sediments. During the further subsidence of the territory and widening of the water area in late Ai time, the previously existing land

³ Olli [27, p. 332] characterized the source area and argued that the terrigenous material was supplied from the west throughout the whole time of sedimentation.

⁴ The provenance composition of the rest of the Burzyan section cannot be reconstructed by traditional petrographic methods. In order to circumvent this obstacle, we previously used the data on the Bol'shoi Inzer and Yusha formations from the Yamantau Anticlinorium [31, 32], which are conventionally correlated with the upper part of the Ai Formation and the Bakal Formation.

⁵ Rykus and his colleagues analyzed the minor elements largely by semiquantitative emission spectroscopy; some of these determinations were repeated by atomic absorption spectroscopy.

Table 1. Schematic stratigraphic column of the Lower Riphean (Burzyan Group) in the northeastern Bashkir Anticlinorium

Formation	Subformation, sequence	Thickness, m	Sample number (Nd isotope determination)	T, strat, Ma
Bakal	Malobakal'skaya	800–900	–	1430+/-30
	Makarovskaya	650	41sh	–
Satka	Upper Satka	1000–1200	–	–
	Lower Satka	300–350	–	–
	Polovinka	180–220	2835-6	–
	Upper Kusa	800–900	–	–
	Lower Kusa	900–950	–	–
Ai	Upper unit	500–800	815-10-6	–
	Lower unit	1800–2200	28n	1615+/-45

has been flooded, and the supply of clastic material ceased. A shallow-water shelf environment was predominant in the Satka and Bakal times, and sedimentation proceeded under conditions of compensated subsidence. By the end of the Bakal time, the marine basin exhibited a tendency to shoaling and closing, which eventually resulted in its transformation into a near-shore lagoonal (lacustrine?) water reservoir, where red-colored aluminosilicate sediments were deposited [24, 58].

SAMPLES AND ANALYTICAL PROCEDURES

The major-element compositions of shales from the Burzyan Group are characterized by 60 samples. Each sample was subjected to optical microscopic and XRD studies. Chemical compositions were determined at the laboratory of the Institute of Geology, Bashkir Branch, Russian Academy of Sciences; the central complex laboratory of PGO Bashkirgeologiya, in Ufa; the central laboratory of Uralgeologiya, Yekaterinburg; and the central laboratory of the Department of Natural Resources, Ural Federal Territory, Yekaterinburg.

Eighteen shale samples were analyzed for 40 trace elements (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) by ICP MS using a PlasmaQuad II spectrometer providing elemental analysis and isotopic screening. Powdered samples, 50 mg in weight, were decomposed with a 5 : 1 mixture of hydrofluoric and nitric acids at a temperature of 170°C in Teflon beakers for 24 hours. After relatively slow evaporation, the material was dissolved in 3% nitric acid with a dilution coefficient of about 10^3 and was then measured on the ICP MS analyzer. Indium was added to the dry sample before its decomposition as an internal standard. The

BCR-1 and BCR-2 (Basalt Columbia River) reference samples of USGS were used as external standards. The external standard was measured repeatedly after every five samples in order to account for gradual changes in the time-dependent characteristics of the device (e.g., detection limit and its variation as a function of mass). The relative accuracy was determined for each element and varied from 3 to 20–50%.⁶

Nd isotopic characteristics were determined for four samples (Table 1). The concentrations and isotopic compositions of Sm and Nd were measured by isotope dilution mass-spectrometry on a Finnigan MAT-262 mass spectrometer. All chemical procedures were carried out in a clean room [59] with a forced supply of filtered (HEPA filters) atmospheric air and using Teflon and quartz beakers and specially purified reagents.

The chemical preparation of samples for Sm and Nd isotopic analysis included a number of consecutive operations: sample decomposition, extraction of REE sum, and the separation of Sm and Nd. The samples were decomposed in a mixture of hydrofluoric and perchloric acids in Teflon autoclaves or Teflon beakers at atmospheric pressure depending on the composition of the sample studied. A charge with a certain amount of spike $^{150}\text{Sm} + ^{149}\text{Nd}$ (based on the optimal proportion of 0.15 g of spike per 1 µg Nd in the charge) held at a temperature of 130–180°C until complete decomposition. The reaction mixture was evaporated dry, dissolved in 10N HCl, and evaporated again. The dry residue was dissolved in 2 ml of 2.3N HCl and centrifuged. The solution was placed into the first chromatographic column with Dowex 50 × 8 200–400 mesh cationite. In this column, the REE sum was separated from the

⁶ The highest values are pertaining to the very low concentrations close to the detection limit.

major components by stepwise elution with 2.3N and 3.9N HCl. The eluate fraction containing Nd, Sm, other REE, and traces of some other elements was then evaporated and dissolved in 0.6 ml of 0.1N HCl. The final Sm and Nd separation was carried out on the second chromatographic column with polytrifluorochlorethylene (KEL-F) powder covered with di-(2-ethylhexyl) orthophosphoric acid. Gradient elution with 0.1N and 0.3N HCl was used for a more efficient separation of Nd and Sm from traces of the alkali earth elements.

Laboratory blanks were commonly below 0.3 ng Nd and 0.2 ng Sm.

The Sm and Nd isotopic compositions of $^{150}\text{Sm} + ^{149}\text{Nd}$ spike mixtures and samples were measured on a Finnigan MAT-262 multicollector mass spectrometer in static mode. Two-filament ion-source blocks with Re filaments, which were preliminary annealed in vacuum to expel impurities, were used for Sm and Nd analysis. The Nd isotopic ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The internal statistics of mass-spectrometric analysis provided a relative precision better than 0.002% for $^{143}\text{Nd}/^{144}\text{Nd}$. The reproducibility of the results was estimated from parallel measurements of the La Jolla standard. The accuracy of the Sm/Nd ratio (0.2–0.5%) was calculated from the long-term reproducibility of measurements of the BCR-1 and BCR-2 standards. The parameters of evolution diagrams were calculated using the regression programs by Ludwig [60]. The decay constant $6.54 \times 10^{-12} \text{ yr}^{-1}$ recommended by the International Commission were used for age calculation.

RESULTS OF PETROGRAPHIC AND X-RAY DIFFRACTION STUDIES

Quartz–hydromica shales with variable chlorite content are prevalent in the lower part of the Ai Formation. Hydromica 1M, 2M₁, and Fe-chlorite are the most abundant clay minerals in the shale of the western limb of the Taratash Anticlinorium; minor amounts of mixed-layer chlorite-vermiculite were also found [61]. Clastic hydrated and chloritized biotite and clastic muscovite flakes occur in thin shale laminas from the polymictic sandstone and gritstone of the Efremov Mountains and Mount Yerokhin spurs. At the southwestern margin of the Taratash Inlier, the originally clayey rocks of the upper part of the Ai Formation are represented by phyllite-like sericite–chlorite slates. The hydromica polytype 2M₁ and Fe-chlorite are most abundant in these rocks [62].

The shales of the Satka Formation and their low-carbonaceous varieties consist of fine-grained flaky aggregates of hydromica, variable amounts of Fe-chlorite, and silt-size quartz and plagioclase grains. Thin interbeds of quartz–hydromica and quartz–chlorite–hydromica shales occur within the dolomite sequence of the upper Kusa Subformation. The terrigenous admixture is composed of silt-size quartz, plagioclase, and K-feld-

spar grains. According to XRD analysis, hydromica polytypes 1M, 2M₁ and Fe-chlorite are the major clay minerals. Quartz–hydromica shale dominates the Polovinka Subformation. The relative amount of silt-size quartz and plagioclase admixture does not exceed a few volume percent. The XRD results indicate the presence of 2M₁ mica and poorly crystallized Mg–Fe chlorite. The clay phase of interlayers of dark gray phyllite-like slates of the upper Satka Subformation consists largely of distinctly crystalline Mg–Fe chlorite; mica polytype 2M₁ occurs sometimes as an admixture [61].

The low-carbonaceous shale of the Makarovskaya Subformation of the Bakal Formation consists of low-birefringent Fe-hydromica and fine-grained flaky sericite with minor chlorite. The content of clastic material is 10–15%. It is mainly composed of corroded silt-size quartz grains. Shungite-like organic material associates with flow cleavage forming slightly wavy thin films and uniform diffuse impregnations [63]. The shale of the Malobakal Subformation consists of hydromica, sericite, and Fe-chlorite; the latter accounts for 10–30% of the rock by volume. The amount of terrigenous material (commonly, silt-size quartz) is below 7–10%. Relicts of a mixed-layer swelling mineral of the montmorillonite–vermiculite series were established by XRD and microprobe analysis in shales from thick (100 m and more) monotonous terrigenous units of the Bakal Formation (e.g., Irkuskan and Makarovskaya subformations) [63, 64].

MAJOR ELEMENT COMPOSITIONS OF SHALES

Based on the boundary values of the hydrolyzate module $\text{HM} = (\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO})/\text{SiO}_2$ equal to 0.30 and 0.55, Yudovich and Ketris [65] classified clastic sedimentary rocks into three groups: silites ($\text{HM} < 0.3$), siallites and siferlites ($\text{HM} = 0.30\text{--}0.55$), and hydrolyzates ($\text{HM} > 0.55$). According to this scheme, most silty-clayey rocks are siallites, which are subdivided into hyposiallites ($\text{HM} = 0.30\text{--}0.35$), normosiallites ($\text{HM} = 0.36\text{--}0.48$), and supersiallites ($\text{HM} = 0.49\text{--}0.55$). These authors noted that, if $\text{HM} > 0.48$, the clayey sediment must contain erosion products of weathered rocks (kaolinite, chamosite, or iron hydroxides). The discrimination of sedimentary rocks into siallites and pseudosiallites ($>3\%$ MgO) also has important genetic implications. It is suggested that pseudosiallites contain a certain amount of volcanogenic (pyrogenic) material.

The geochemical signatures of Lower Riphean shales from the northeastern Bashkir Anticlinorium were determined using the regional geochemical database of the Institute of Geology, Ufa Scientific Center, Russian Academy of Sciences, created by Gareev [66] and the data of Krupenin *et al.* [63]. The representative chemical analyses of some samples from specific lithostratigraphic units of the Burzyan Group are shown

Table 2. Chemical composition (wt %) of representative samples of Lower Riphean shales from the northeastern Bashkir Anticlinorium

Component	Ai Formation						Satka Formation						Bakal Formation					
	lower unit			upper unit			Lower Kusa Subformation			Polovinka Subformation			Makarovskaya Subformation			Malobakal'skaya Subformation		
	82-1	82-2	28n	815-10-1	815-10-4	815-10-6	83-1	83-2	83-3	2835	2835-6	2835-6a	41sh	57sh	60sh	21sh	46sh	51sh
SiO ₂	61.58	61.42	59.98	65.50	65.72	70.00	61.49	58.08	60.36	62.32	63.30	61.24	62.35	60.01	60.82	59.48	56.15	56.85
TiO ₂	0.95	0.99	0.86	0.80	0.74	0.38	0.85	0.77	0.82	0.78	0.73	0.72	0.81	0.79	0.82	0.68	0.75	0.84
Al ₂ O ₃	18.52	16.65	19.49	16.10	14.98	15.32	17.74	18.99	17.72	18.32	19.0	18.58	18.65	19.89	19.13	17.93	18.71	20.58
Fe ₂ O ₃	5.36	7.51	4.16	2.60	2.13	0.32	3.96	4.61	3.84	5.73	4.73	5.38	1.14	3.31	1.48	2.92	1.99	1.46
FeO	0.93	0.88	1.2	1.30	2.85	2.68	1.92	1.9	2.64	1.58	—	1.62	6.27	4.91	6.39	5.96	7.81	3.56
CaO	0.27	0.23	0.32	0.70	0.82	0.48	0.31	0.17	0.32	0.23	0.18	0.24	0.24	0.27	0.23	0.43	0.22	0.28
MgO	1.59	1.67	1.94	2.60	2.63	1.02	2.74	2.59	2.84	1.59	1.66	1.74	1.48	1.27	1.72	2.02	2	2.13
MnO	0.015	0.012	0.014	0.04	0.05	0.03	0.01	0.01	0.02	0.021	0.018	0.02	0.032	0.03	0.04	0.122	0.13	0.018
P ₂ O ₅	0.17	0.18	0.18	0.16	0.31	0.14	0.26	0.08	0.13	0.10	—	0.14	0.059	0.09	0.30	0.085	0.065	0.045
K ₂ O	6.95	6.16	7.84	4.62	3.34	5.62	6.15	7.90	6.91	5.54	5.6	5.84	3.23	3.63	3.34	3.84	5.26	7.65
Na ₂ O	0.13	0.12	0.14	1.71	2.08	0.48	0.34	0.74	0.87	1.21	1.11	1.91	0.88	0.72	0.93	0.61	0.2	0.11
LOI	3.34	2.93	3.62	3.35	4.07	2.94	4.18	3.29	3.48	3.48	3.68	2.48	3.84	5.18	4.50	5.35	5.45	4.4
Total	99.805	98.752	99.74	99.48	99.72	98.39	99.95	99.13	99.95	100.90	100.02	99.91	98.98	100.10	99.70	99.43	98.74	97.92

Note: Analyses were performed at the Institute of Geology, Bashkir Branch, Russian Academy of Sciences; the central complex laboratories of PGO Bashkirgeologiya, Ufa and PGO Uralsgeologiya, Yekaterinburg; and the central laboratory of the Department of Mineral Resources, Ural Federal Territory, Yekaterinburg; analysts A.M. Gabbasova, E.R. Bogdanova, L.N. Mit'kina, L.I. Zueva, L.V. Chembartseva, E.A. Gurina, and N.G. Grishenkova. Sample location: 82-1, 82-2, and 28n, east of Arshinka Village and near the Chernyi Klyuch Creek; 815-10-6, 815-10-4, and 815-10-1, the Ai River downstream from Medvedevka Village; 83-1, 83-2, and 83-3, the Ai River downstream from the cemetery of Kusa; 2835-6a, 2835, and 2835-6, the Satka River near the Rechnaya railway station; 57sh and 60sh, Polushkin Farm, 5 km east of Bakal; 41sh, the Novobakal'skii open pit; 46sh, the Petlinskii open pit, Irkuskan Member; 21sh, the Eastern open pit of the OGPU Mine (Shuida Mine), Irkuskan Member; 51sh, the Central open pit of the Irkuskan Mine, Supra-Shuida Member.

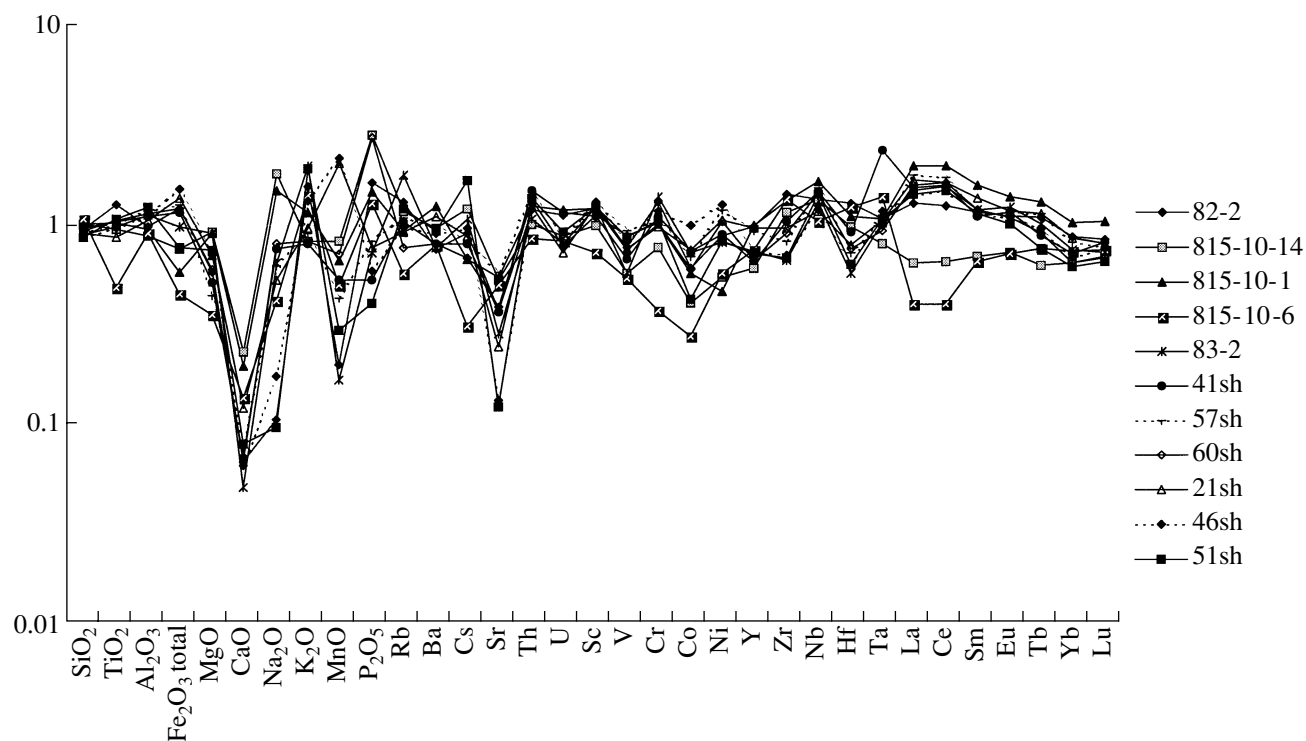


Fig. 3. Major oxide and trace element contents of the Lower Riphean shales from the northeastern Bashkir Anticlinorium normalized to NASC. See Table 2 for the stratigraphic and geographic position of samples.

in Table 2. The HM value of shales from the Ai Formation varies from 0.25 to 0.42, which allows us to classify them as miosilites, hyposiallites, and normosiallites (Fig. 2). Their $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is no higher than 8 wt % and often only slightly higher than 4 wt %. Only one of 16 samples analyzed showed an MgO content of 3 wt %. The shales of the Makarovskaya Subformation of the Bakal Formation have narrow ranges of HM and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (0.4–0.5 and 4.0–5.5 wt %, respectively). None of the 19 samples from this level contained more than 3 wt % MgO. Hence, the shales of this stratigraphic unit are mostly normosiallites without any pyrogenic admixture. On the contrary, the shales of the Malobakal Subformation are characterized by widely scattered HM values (0.35–0.60) and contain no less than 4–6 wt % $\text{Na}_2\text{O} + \text{K}_2\text{O}$ reflecting the presence of normosiallites and supersiallites, as well as hypohydrolyzates, i.e., rocks with $\text{HM} = 0.56\text{--}0.85$, in the upper unit of the Burzyan Group [65]. The hypohydrolyzates do not necessarily contain free Al or Fe oxides or hydroxides, but the presence of rocks with high HM in the upper portion of the sedimentation cycle testifies to advanced weathering in the drainage system. It is also noteworthy that none of the 25 shale samples from the Malobakal Subformation reaches the MgO content of the siallite– pseudosiallite boundary, which indicates

that there was no correlation between sedimentation and volcanic activity at this level.

VARIATIONS IN THE CONCENTRATIONS OF MAJOR OXIDES AND TRACE ELEMENTS

We compared the concentrations of major oxides and trace elements in the shales of the Burzyan Group from the northeastern Bashkir Anticlinorium with the compositions of the world standards of fine-grained aluminosilicate clastic rocks: PAAS (post-Archean Australian shale) and NASC (North American shale).⁷ Based on the comparison of the Lower Riphean shales with NASC (Fig. 3), the major oxides and trace elements may be conventionally divided into several groups. The first group (SiO_2 , TiO_2 , Al_2O_3 , Ba, and U) comprises the oxides and elements whose concentration coefficients (K_c) are close to 1 (0.80–1.24) relative to NASC. The K_c values of the second group elements are within the range 0.5–1.5 or higher. This group includes Fe_2O_3 , Na_2O , MnO, Rb, Cs, Cr, Ni, Zr, Hf, Ta (in one sample $K_c = 2.36$), Sm, Eu, and Tb. The concentration coefficients of the elements of the third group (CaO and Sr) do not exceed 0.4 in all samples; MgO, V, Co, and Y are probably close to this group. Th and Sc form a separate group: in 10 of 11 samples, the K_c of these elements are equal to or greater than one, and this

⁷ PAAS and NASC compositions were taken from [6, 7].

coefficient is lower than one in one sample. Nb, Yb, and Lu are also close to this group. Finally, the K_c of La and Ce mostly ranges from 1.24 to 1.98 and is only much lower than in two samples. The normalization of shale compositions to PAAS yields almost the same pattern. Similar results were obtained for the compositions of Burzyan shales normalized to the composition of RPSC (Russian Platform shale composition) [68].

The behavior of Th, Sc, Cr, Ni, Zr, La, Ce, Sm, and Tb are the most interesting, because these elements display considerable variations in samples taken from various stratigraphic levels of the Lower Riphean stratotype. These elements can therefore be used as guides for the reconstruction of provenance composition.

REE PATTERNS

As was shown by Ronov *et al.* [69], Taylor and McLennan [7, 8, 70], and many other authors, the sedimentary sequences of platforms and fold belts inherit to a considerable extent the REE patterns of their provenances. Consequently, REE patterns bear information on the composition of the ancient upper crust. The LREE/HREE ratio thereby serves as a measure of the relative amounts of felsic and basic rocks in the source [71]. If $(La/Yb)_N < 4^8$ and REE patterns are flat with $(Gd/Yb)_N$ up to 1.5, a substantial contribution of basic rocks to the provenance can be supposed. If $(La/Yb)_N > 8$, one can state with much confidence that felsic igneous rocks were predominate in the source. Higher $(La/Yb)_N$ ratios (≥ 20) suggest the predominance of granitic rock in the upper crust [9].

The following main parameters were used in the interpretation of REE patterns of the Burzyan shales from the Bashkir Anticlinorium: (1) REE total; (2) $Eu/Eu^* = Eu_N \times (Sm_N \times Gd_N)^{1/2}$; (3) La_N/Yb_N characterizing the general slope of a REE spectrum and serving as indirect evidence for source rock composition; (4) Gd_N/Yb_N as an indicator of the HREE depletion and the slope of the HREE pattern.

The REE contents of the Lower Riphean (Burzyan) shales from the Bashkir Anticlinorium are presented in Table 3. The REE totals of almost all shale samples from the lower unit of the Ai Formation, lower Kusa and Polovinka subformations of the Satka Formation and Makarovskaya and Novobakal'skaya subformations of the Bakal Formation are higher than 200 ppm, and only in the upper unit of the Ai Formation is this parameter as low as 78 ppm. The La_N/Yb_N ratio changes from 3.6 in the upper part of the Ai Formation to 25.8 in the Polovinka Subformation and averages 12–16. The REE patterns of the Polovinka and Malobakal'skaya subformations show marked HREE deple-

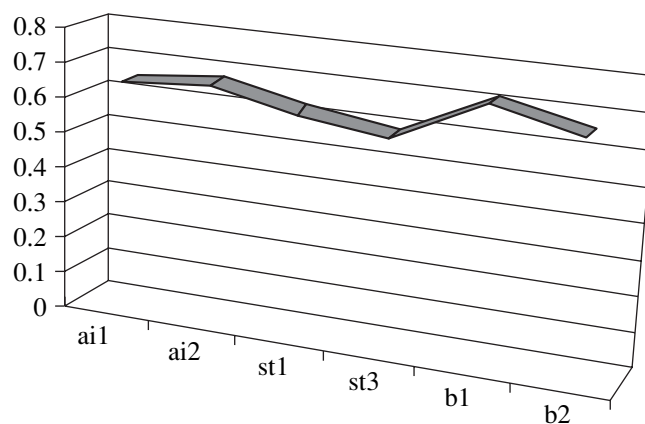


Fig. 4. Variations of Eu/Eu^* in the shales of the Burzyan Group. ai1, lower unit of the Ai Formation; ai2, upper unit of the Ai Formation; st1, lower Kusa Subformation of the Satka Formation; st3, Polovinka Subformation of the Satka Formation; b1, Makarovskaya Subformation of the Bakal Formation; b2, Malobakal'skaya Subformation of the Bakal Formation.

tion ($Gd_N/Yb_N > 2.0$). In samples from other Burzyan units, this ratio is below 2.0; the lowest value (~ 1.5) was detected in the shale from the upper unit of the Ai Formation.

The Burzyan shales and the entire Riphean section show a Eu anomaly of 0.6–0.7. The lowest Eu/Eu^* values are typical of shales from the lower Kusa and Polovinka subformations of the Satka Formation, and the highest values were detected in the fine-grained aluminosilicate clastic rocks of the Bakal level, especially of the Makarovskaya Subformation (Fig. 4).

In general, the REE spectra of all the Lower Riphean shales are similar (Fig. 5), and only the clayey rocks of the upper Ai level show flattened patterns, which probably reflects the occurrence of mafic and ultramafic rocks in their provenance.

TENDENCIES IN TRACE ELEMENT RATIOS

The approaches that are commonly used for the reconstruction of provenance composition from the geochemistry of clayey rocks were discussed in [6–12, 17, 71, 73–75] and other publications. For example, high Cr/Zr and Sc/Th ratios point to the substantial role of mafic and ultramafic rocks in the provenance, whereas high Th/Co suggests the prevalence of felsic rocks in the source area [9]. As was shown by the example of the Precambrian pelites of the Kaapvaal Craton [74], the combined use of Cr/Th, Th/Sc, and Co/Th ratios allows one to monitor the composition of provenance, because the Cr/Th ratio is probably much more sensitive to provenance composition than Eu/Eu^* , La/Yb , or Th/U. The low Cr/Th values indicate that granitoids were mainly eroded. However, the Cr con-

⁸ McLennan *et al.* [72] use the even more stringent criterion $(La/Yb)_N < 1$.

Table 3. REE contents (ppm) in Lower Riphean shales from the northeastern Bashkir Anticlinorium

Component	Ai Formation						Satka Formation						Bakal Formation					
	lower unit			upper unit			lower Kusa Subformation			Polovinka Subformation			Makarovskaya Subformation			Malobakal'skaya Subformation		
	82-1	82-2	28n	815-10-1	815-10-4	815-10-6	83-1	83-2	83-3	2835	2835-6	2835-6a	41sh	57sh	60sh	21sh	46sh	51sh
La	40.44	39.76	43.22	61.09	20.15	12.38	34.80	46.20	40.66	52.10	55.50	62.08	47.57	54.94	48.63	51.87	43.60	44.39
Ce	86.94	83.31	103.41	132.51	44.09	26.77	69.80	104.01	87.29	77.98	112.11	167.55	105.38	116.05	108.66	109.58	99.56	99.23
Pr	9.67	9.35	10.92	13.73	5.24	3.62	8.25	11.51	8.89	11.62	13.98	13.34	11.53	10.91	10.67	12.32	9.76	10.53
Nd	37.25	37.30	40.62	53.59	20.56	15.18	27.56	41.20	32.99	43.67	43.50	56.65	42.37	40.72	39.33	46.01	39.01	36.59
Sm	6.73	6.45	7.34	8.89	3.92	3.68	4.19	6.68	5.81	7.89	7.33	8.96	6.21	6.27	6.63	7.60	6.26	6.39
Eu	1.22	1.33	1.46	1.66	0.88	0.85	0.73	1.47	0.95	1.56	1.15	1.38	1.39	1.39	1.30	1.40	1.30	1.21
Gd	5.99	5.99	5.61	7.19	3.61	4.17	3.26	5.63	5.44	6.23	6.05	6.52	5.17	5.73	5.18	5.96	5.55	4.84
Tb	0.89	0.92	0.83	1.10	0.53	0.64	0.40	0.85	0.69	0.88	0.82	0.95	0.76	0.97	0.77	0.97	0.81	0.65
Dy	4.33	4.82	4.81	6.30	2.92	4.04	2.25	4.24	3.40	5.23	4.21	4.10	3.79	5.31	3.85	5.22	4.25	3.54
Ho	1.01	1.11	1.05	1.32	0.63	0.87	0.49	0.87	0.80	0.98	0.68	0.83	0.79	0.99	0.76	0.92	0.89	0.74
Er	2.55	2.85	2.72	3.35	1.81	2.47	1.47	2.30	2.01	2.57	1.75	1.90	2.25	2.66	1.93	2.88	2.17	2.03
Tm	0.38	0.46	0.37	0.50	0.30	0.38	0.22	0.33	0.33	0.36	0.25	0.28	0.33	0.42	0.29	0.44	0.35	0.28
Yb	2.50	2.71	2.55	3.19	1.99	2.30	1.51	2.33	2.02	2.41	1.56	2.06	2.21	2.56	2.01	2.64	2.13	1.93
Lu	0.34	0.39	0.37	0.48	0.32	0.34	0.26	0.34	0.28	0.34	0.27	0.29	0.38	0.36	0.32	0.37	0.35	0.30

Note: See Table 2 for sample location.

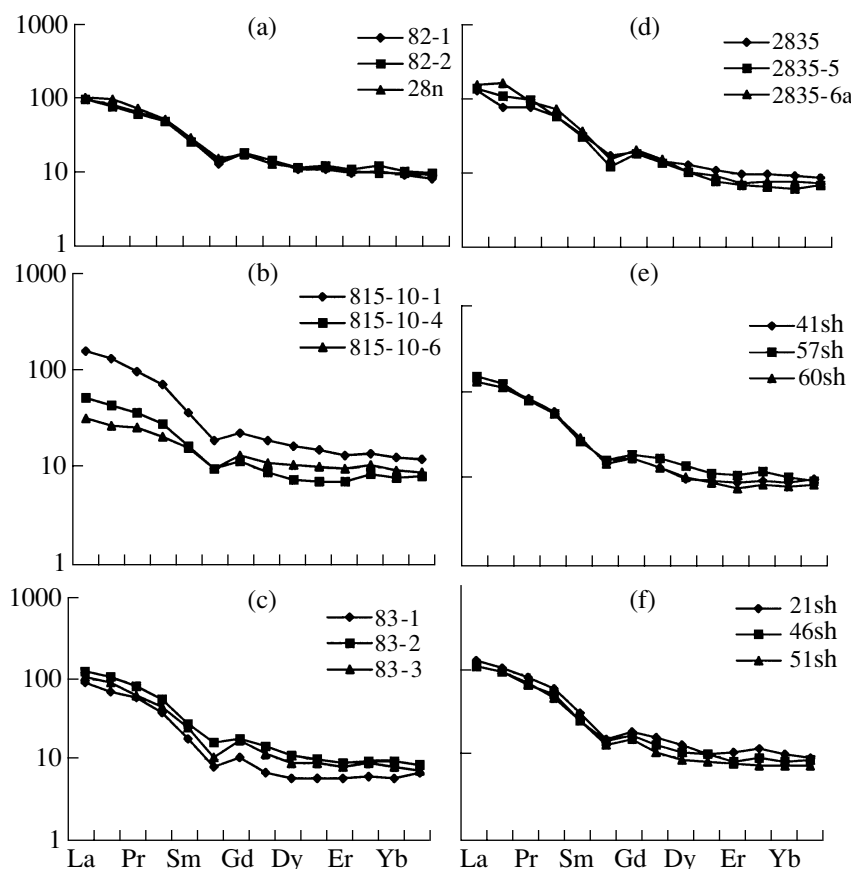


Fig. 5. REE patterns of shales from various Lower Riphean lithostratigraphic units in the northeastern Bashkir Anticlinorium. (a) Lower unit of the Ai Formation; (b) upper unit of the Ai Formation; (c) lower Kusa Subformation of the Satka Formation; (d) Polovinka Subformation of the Satka Formation; (e) Makarovskaya Subformation of the Bakal Formation; (f) Malobakal'skaya Subformation of the Bakal Formation.

tent of sediments may be changed during sedimentation and weathering. Therefore, only a positive correlation between Cr/Th and Sc/Th allows one to use Cr/Th as an indicator of source area composition. The low Cr/Th and Co/Th ratios suggest that felsic rocks were mainly eroded in the provenance, whereas high or variable ratios indicate a marked contribution of mafic and ultramafic rocks. It should be noted that the lack of any appreciable variations in the Cr/Th ratio over long time periods is regarded as an indicator of a stable tectonic regime providing efficient mixing and homogenization of fine aluminosilicate clastic materials along the paths of their transfer [74]. In order to minimize the effect of mineral sorting, the La/Th, La/Sc, and Th/Sc ratios should be used for the reconstruction of provenance compositions [6]. Low Th/Sc and La/Sc values indicate the prevalence of mafic and ultramafic rocks in the source areas. The same is suggested by high Ni/Co, Cr/V, and Ni/V ratios [6, 17]. Nevertheless, it was supposed that the Ni and Cr contents in Archean and post-Archean upper crustal rocks differed from those of recent rocks [73], and these elements cannot therefore be used as reliable indicators of the upper crust compo-

sition. McLennan [8] supposed that the Th/Sc ratio is a more sensitive indicator of the average composition of provenance than La/Th. The Th–Hf–Co and La–Th–Sc diagrams are also believed to be efficient tools for the discrimination of source areas [6–8, 11, 75]. The shift of shale compositions toward the Th, Hf, and La apices point to the prevalence of felsic igneous rocks in the provenance. On the contrary, the elevated concentrations of Co and Sc testify to the predominance of mafic and ultramafic rocks.

Trace element contents and some geochemical ratios in the Lower Riphean shales of the Bashkir Anticlinorium are given in Table 4. Their analysis allowed us to draw the following conclusions.

The La/Sc, La/Co, La/Cr, La/Ni, Th/Sc, Th/Co, Th/Cr, and Th/Ni ratios are most informative for the estimation of source rock compositions [6–10, 12, 15, 17]. Their variations in the shales from various lithostratigraphic units of the Burzyan Group (Fig. 6) are considered below.

The La/Sc value of shales from the lower part of the Ai Formation is 2.2. It slightly decreases in the upper unit of the Ai Formation (1.96) and then grows upsec-

Table 4. Trace element contents (ppm) and ratios in Lower Riphean shales from the northeastern Bashkir Anticlinorium

Component	Ai Formation						Satka Formation						Bakal Formation					
	lower unit			upper unit			lower Kusa Subformation			Polovinka Subformation			Makarovskaya Subformation			Malobakal'skaya Subformation		
	82-1	82-2	28n	815-10-1	815-10-4	815-10-6	83-1	83-2	83-3	2835	2835-6	2835-6a	41sh	57sh	60sh	21sh	46sh	51sh
Li	13.87	5.54	6.38	41.76	35.68	24.01	18.94	15.50	151.26	39.35	30.56	35.03	53.26	52.68	51.63	34.93	23.02	28.86
Be	1.97	2.15	2.84	1.29	2.29	1.42	3.49	3.83	3.97	2.74	2.31	2.28	2.99	3.17	2.69	4.03	3.45	3.71
Ca	4767.66	3465.48	3977.82	7345.20	5741.13	5635.13	5153.36	3801.94	5766.10	3755.72	2944.74	3068.97	3821.52	2647.15	2235.28	5318.03	3507.71	3435.85
Sc	18.15	18.04	19.80	18.03	14.91	10.96	17.70	18.47	18.59	18.16	30.60	19.66	16.58	19.61	16.80	18.87	19.58	18.29
Ti	4479.79	3297.76	5070.38	4858.90	3997.33	3507.41	3997.69	3910.70	4990.74	4226.12	3346.85	4085.74	4119.83	4053.58	4072.36	4103.76	4176.62	3737.41
V	92.76	101.04	143.52	97.21	74.13	69.99	75.15	74.95	80.98	112.97	104.47	100.40	88.09	121.52	114.10	98.27	107.11	112.97
Cr	216.05	163.58	178.98	127.02	96.30	46.90	214.04	171.51	145.18	127.55	70.38	114.35	138.42	131.55	128.82	121.94	145.85	132.58
Mn	75.15	65.24	72.69	381.43	213.46	243.51	45.23	51.49	33.61	360.33	125.67	144.63	196.39	138.27	252.86	852.83	849.26	115.07
Co	17.70	15.75	19.91	14.94	10.62	7.23	13.41	18.80	11.66	12.96	22.97	21.68	19.28	18.04	15.49	19.59	25.80	11.05
Ni	60.32	51.35	69.82	26.99	31.93	33.14	43.13	47.60	44.78	50.76	42.78	45.07	51.85	69.27	59.90	61.67	72.89	48.31
Cu	9.82	5.68	9.64	33.05	28.97	9.25	4.99	5.52	22.28	18.31	52.05	43.81	31.97	40.50	35.57	41.74	50.45	34.76
Zn	45.15	38.18	45.41	101.81	70.14	83.42	32.09	41.58	41.24	67.15	69.89	76.26	69.41	101.70	84.46	39.69	35.37	30.05
Ga	21.62	20.90	24.54	23.78	18.49	15.66	27.09	27.63	25.45	27.41	25.59	25.11	27.06	28.66	26.02	24.24	25.38	26.04
Rb	157.09	161.52	134.97	118.00	145.45	71.29	218.11	220.71	216.63	128.75	97.68	118.39	130.60	135.80	96.40	115.75	123.08	150.01
Sr	47.37	52.64	57.95	78.14	75.78	71.64	30.88	40.54	57.99	44.71	36.12	39.05	52.17	82.65	55.20	34.70	18.77	17.33
Y	31.44	34.19	29.47	34.59	21.25	26.31	15.41	25.67	22.64	31.96	20.56	21.86	22.89	32.78	23.16	34.05	25.73	25.21
Zr	191.72	282.85	180.73	264.27	231.68	268.99	142.89	133.83	145.79	151.00	196.69	183.88	209.34	167.43	181.52	194.08	142.20	136.62
Nb	17.80	17.37	19.31	21.54	17.47	13.45	16.83	16.80	15.71	17.66	15.92	16.70	19.02	19.94	18.81	15.30	15.46	18.48
Mo	0.23	0.18	0.27	0.38	0.23	0.05	0.08	0.10	0.20	0.40	0.23	0.30	1.11	1.25	1.32	0.78	1.40	0.66
Cs	3.99	4.75	4.56	3.52	6.27	1.63	5.35	5.59	5.47	3.29	6.31	6.78	4.18	4.36	3.57	4.59	5.04	8.68
Ba	555.62	483.54	482.38	787.54	615.03	506.86	494.39	492.82	584.94	505.56	372.37	412.98	516.50	634.26	511.69	706.90	579.22	598.02
Hf	5.40	8.06	5.35	6.91	6.15	7.77	3.51	3.59	3.43	4.20	4.86	4.39	5.79	4.60	4.80	4.98	4.03	3.99

Table 4. (Contd.)

Component	Ai Formation						Satka Formation						Bakal Formation					
	lower unit			upper unit			lower Kusa Subformation			Polovinka Subformation			Makarovskaya Subformation			Malobakal'skaya Subformation		
82-1	82-2	28n	815-10-1	815-10-4	815-10-6	83-1	83-2	83-3	2835	2835-6	2835-6a	41sh	57sh	60sh	21sh	46sh	51sh	
Ta	1.19	1.18	1.16	1.18	0.89	1.53	1.18	1.13	1.11	1.10	0.91	1.16	2.59	1.08	1.03	1.17	1.28	1.18
W	1.35	1.22	1.70	1.72	7.43	0.69	1.21	1.09	0.99	1.08	0.68	0.73	1.71	1.67	2.17	1.54	2.26	1.48
Tl	0.98	0.96	0.84	0.54	0.82	0.24	0.95	0.99	0.98	0.68	0.58	0.56	0.52	0.78	0.78	0.84	1.10	0.98
Pb	6.04	8.32	4.23	7.31	5.70	8.28	3.43	6.50	4.28	9.89	36.44	36.79	21.72	10.36	13.36	3.91	6.71	3.41
Bi	0.10	0.18	0.15	0.01	0.09	0.03	0.11	0.14	0.11	0.14	0.22	0.41	0.13	0.11	0.23	0.12	0.24	0.15
Th	13.92	14.27	13.46	14.85	12.15	10.36	13.60	12.89	14.15	16.81	12.06	14.35	17.80	17.65	16.09	14.88	15.45	16.41
U	3.04	3.03	4.06	3.24	2.40	2.25	1.86	2.19	1.76	2.01	1.75	2.09	3.10	2.28	2.13	1.96	2.16	2.51
Cr/Th	15.5	11.5	13.3	8.6	7.9	4.5	15.7	13.3	10.3	7.6	5.8	8.0	7.8	7.5	8.0	8.2	9.4	8.1
Th/Sc	0.77	0.79	0.68	0.82	0.81	0.95	0.77	0.70	0.76	0.93	0.39	0.73	1.07	0.90	0.96	0.79	0.79	0.90
Co/Th	1.27	1.10	1.48	1.01	0.87	0.70	0.99	1.46	0.82	0.77	1.91	1.51	1.08	1.02	0.96	1.32	1.67	0.67
Sc/Th	1.30	1.26	1.47	1.21	1.23	1.06	1.30	1.43	1.31	1.08	2.54	1.37	0.93	1.11	1.04	1.27	1.27	1.11
La/Sc	2.23	2.20	2.18	3.39	1.35	1.13	1.97	2.50	2.19	2.87	1.81	3.16	2.87	2.80	2.89	2.75	2.23	2.43
La/Th	2.90	2.79	3.21	4.11	1.66	1.19	2.56	3.58	2.87	3.10	4.60	4.33	2.67	3.11	3.02	3.49	2.82	2.71
La/Cr	0.19	0.24	0.24	0.48	0.21	0.26	0.16	0.27	0.28	0.41	0.79	0.54	0.34	0.42	0.38	0.43	0.30	0.33
La/Co	2.28	2.52	2.17	4.09	1.90	1.71	2.59	2.46	3.49	4.02	2.42	2.86	2.47	3.04	3.14	2.65	1.69	4.02
Th/Cr	0.06	0.09	0.08	0.12	0.13	0.22	0.06	0.08	0.10	0.13	0.17	0.13	0.13	0.13	0.12	0.12	0.11	0.12
Cr/V	2.33	1.62	1.25	1.31	1.30	0.67	2.85	2.29	1.79	1.13	0.67	1.14	1.57	1.08	1.13	1.24	1.36	1.17
V/Ni	1.54	1.97	2.06	3.60	2.32	2.11	1.74	1.57	1.81	2.23	2.44	2.23	1.70	1.75	1.90	1.59	1.47	2.34
Cr/Zr	1.13	0.58	0.99	0.48	0.42	0.17	1.50	1.28	1.00	0.84	0.36	0.62	0.66	0.79	0.71	0.63	1.03	0.97
Cr/Ni	3.58	3.19	2.56	4.71	3.02	1.42	4.96	3.60	3.24	2.51	1.65	2.54	2.67	1.90	2.15	1.98	2.00	2.74
Th/Co	0.79	0.91	0.68	0.99	1.14	1.43	1.01	0.69	1.21	1.30	0.52	0.66	0.92	0.98	1.04	0.76	0.60	1.49
Hf/Co	0.30	0.51	0.27	0.46	0.58	1.07	0.26	0.19	0.29	0.32	0.21	0.20	0.30	0.26	0.31	0.25	0.16	0.36

Note: See Table 2 for sample location.

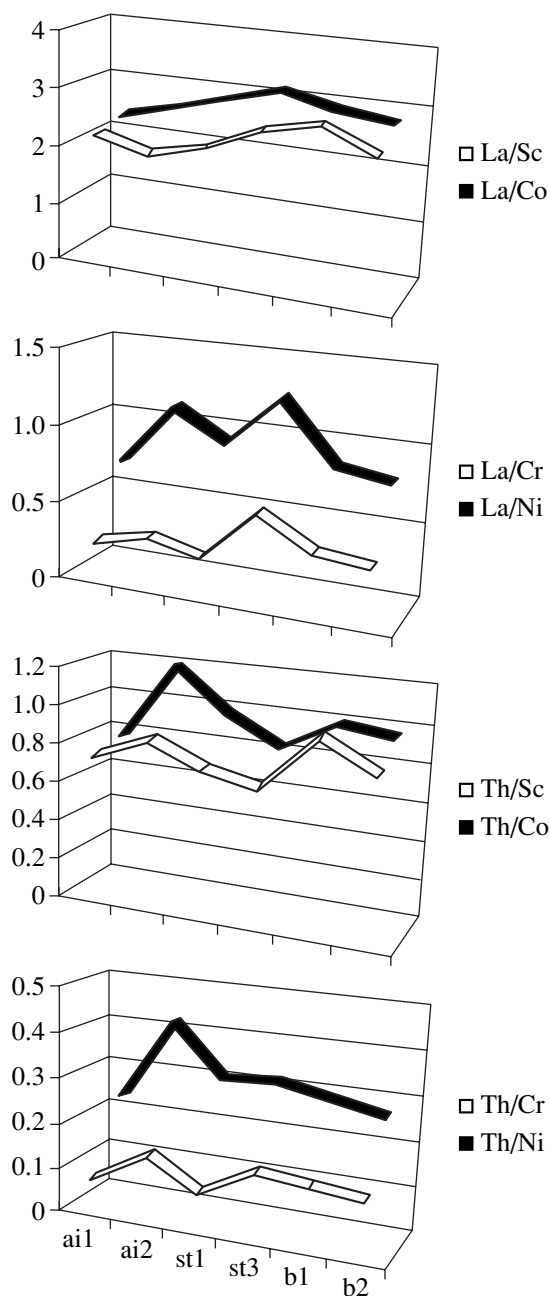


Fig. 6. Variations of La/Sc, La/Co, La/Cr, La/Ni, Th/Sc, Th/Co, Th/Cr, and Th/Ni in shales from various Lower Riphean lithostratigraphic units of the northeastern Bashkir Anticlinorium. See Fig. 5 for symbol explanation.

tion reaching 2.85 in the shales of the Makarovskaya Subformation of the Bakal Formation. The La/Sc ratio of the Malobakal'skaya shales is somewhat lower but remains higher than that of the lower levels of the Burzyan Group. This implies that the fraction of mafic and ultramafic rocks in the provenance probably increased by the end of Ai time.

The La/Co ratio of fine-grained aluminosilicate clastic rocks varies insignificantly throughout the Burzyan section. The maximum value (3.10) is

observed in the Polovinka level, whereas it ranges from 2.33 to 2.88 in other parts of the section.

The La/Cr ratio varies differently throughout the section. At the Ai and lower Kusa level, this ratio lies within a range of 0.22–0.32, and the highest value is characteristic of the upper Ai level. In the shales of the Polovinka level, this ratio is twice as high (!) as that of the underlying rocks. This indicates unequivocally that felsic rocks were predominant at that time in the provenance. Further, the La/Cr ratio becomes somewhat lower but exceeds the values established for the lower portion of the Burzyan Group section.

The clayey rocks of most of the Burzyan Group units analyzed show considerable La/Ni variations. The shape of the curve resembles the La/Cr curve but displays two distinct peaks at the upper Ai and Polovinka levels. This implies that felsic rocks were prevalent in the provenance in the late Ai and middle Satka time, whereas basic rocks could be also eroded during other time intervals.

The Th/Sc ratio is below 0.7 in the shales of the lower Ai, lower Kusa, and Polovinka levels and higher than 0.9 in the shales of the upper Ai and Polovinka levels. With a fair degree of confidence, it may be supposed that the contribution of felsic igneous rocks to the provenance in late Ai time was higher than at the very beginning of the Early Riphean. The same conclusion can be drawn comparing the shales of the Satka and Bakal formations.

The highest Th/Co ratio was established in shales from the upper Ai level, and the lowest value, from the lower Ai and Polovinka levels; the shales of the Bakal Formation and the lower Kusa level show intermediate Th/Co ratios. Two cycles are outlined from variations in the Th/Sc and Th/Co ratios through the Burzyan Group section: early Ai time \Rightarrow middle Satka time and middle Satka time \Rightarrow late Bakal time.

Variations in the Th/Cr ratio are also described by a curve with two humps. The highest ratios are typical of the shales of the upper Ai and Polovinka levels, whereas the lowest values characterize the lower Ai and lower Kusa levels; intermediate values are detected in the shales of the Bakal Formation.

Finally, the Th/Ni ratio ranges from 0.23 to 0.41 at the Ai level and is below 0.25–0.30 for all higher levels of the Burzyan Group.

Thus, except for the La/Sc and La/Co ratios, all other pairs of indicator ratios show similar distribution curves, e.g., La/Cr and La/Ni, Th/Sc and Th/Co, and Th/Cr and Th/Ni. In general, La/Cr, La/Ni, Th/Cr, and Th/Ni are the least variable ratios, although elevated values were observed in the upper Ai and Polovinka levels. The La/Sc, La/Co, Th/Sc, and Th/Co ratios are the most variable. However, while the first two ratios progressively increase from the lower Ai toward the Polovinka and Makarovskii levels and then decrease slightly, the Th/Sc and Th/Co ratios have two distinct peaks at the upper Ai and Makarovskii levels. In sum-

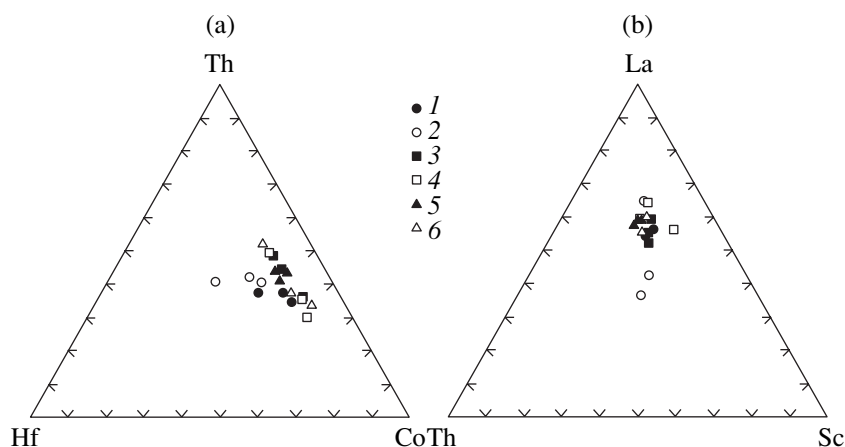


Fig. 7. Th–Hf–Co and La–Th–Sc diagrams for the Early Riphean shales (Burzyan Group) of the Bashkir Anticlinorium. (1) Lower unit of the Ai Formation; (2) upper unit of the Ai Formation; (3) lower Kusa Subformation of the Satka Formation; (4) Polovinka Subformation of the Satka Formation; (5) Makarovskaya Subformation of the Bakal Formation; (6) Malobakal'skaya Subformation of the Bakal Formation.

mary, it can be suggested that felsic rocks were mainly eroded in the provenance.

The data points of the Burzyan shales do not form distinct trends on the Th–Hf–Co and La–Th–Sc diagrams. On the former diagram, two thirds of samples from the lower Ai, Polovinka, and Malobakal'skii levels are shifted toward the Co apex, and one third of the samples are displaced toward the Hf–Th side (Fig. 7a). All the data points plot within the central portion of the La–Th–Sc diagram (Fig. 7b). The distribution of data points does not allow us to draw any unambiguous conclusion on the composition of provenances. It should be noted that the shales of the Lakhanda Group, which were presumably derived by erosion of a granodiorite source [12], occupy the same field on the La–Th–Sc diagram.

ND ISOTOPIC COMPOSITION

In order to estimate the model ages of probable provenances, Nd isotopic characteristics were determined in four shale samples from the lower and upper units of the Ai Formation, Polovinka Subformation of the Satka Formation, and the Makarovskaya Subformation of the Bakal Formation. The $\epsilon_{Nd}(T)$ values of these samples vary from -6.4 to -8.0 and the model Nd age decreases monotonously from 2.54 to 2.27 Ga (Table 5). This indicates that Paleoproterozoic mantle-derived materials were mainly eroded during the deposition of the Lower Riphean sedimentary rocks of the Bashkir Anticlinorium.

CONCLUSIONS

The following general conclusions can be made. Based on the petrography and major-element composi-

Table 5. $\epsilon_{Nd}(T)$ and (T_{DM}) values for the Lower Riphean shales of the northeastern Bashkir Anticlinorium

Stratigraphic level	Sample number	T_{st} , Ma	Sm	Nd	$^{147}\text{Sm}/^{144}\text{Nd}^*$	$f_{\text{Sm}/\text{Nd}}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2\sigma$	$\epsilon_{Nd}(0)$	$\epsilon_{Nd}(T)$	t_{DM} , Ma
R ₁ b ₁	41sh	1430	6.05	37.9	0.09660	–0.51	0.511287	0.000016	–26.3	–8	2275
R ₁ st ₃	2835-6	~1500	7.62	45.5	0.10127	–0.49	0.511323	0.000012	–25.6	–7.3	2322
R ₁ ai ₂	815-10-6	~1615	3.31	16.6	0.12077	–0.39	0.511504	0.000010	–22.1	–6.4	2518
R ₁ ai ₁	28n	1635	7.09	35.4	0.12128	–0.38	0.511499	0.000009	–22.2	–6.4	2541

* Uncertainty is below 0.2% (2σ); T_{st} is stratigraphic age. The parameters of the model reservoir (CHUR): 0.1967 and 0.512636. R₁ai₁—lower unit of the Ai Formation; R₁ai₂—upper unit of the Ai Formation; R₁st₃—Polovinka Subformation of the Satka Formation; R₁b₁—Makarovskaya Subformation of the Bakal Formation. Analyses were performed at the Institute of Geology and Geochemistry, Uralian Division, Russian Academy of Sciences, analyst O.P. Lepikhina.

tions of psammities from the Lower Riphean Burzyan Group in the Bashkir Anticlinorium [30–32], we previously established a distinct tendency of the maturation of clastic material supplied into the Early Riphean sedimentation basin. In the very beginning of the Early Riphean, the source was largely composed of felsic igneous and metamorphic rocks with some addition of sedimentary (metasedimentary) rocks. The petrochemical parameters of sandstones from the lower unit of the Ai Formation testify to the insignificant alteration of clastic material during its transport into the basin.

At the same time, the data obtained in the middle 1990s from the study of sandstones and conglomerates could not be extrapolated to the entire Lower Riphean (Burzyan) section comprising more than 75–80% clayey and carbonate rocks. The analysis of shale compositions performed in this work allowed us to fill this gap and expand our knowledge on the composition and evolution of provenances throughout the entire Early Riphean.

The chemical compositions of the originally clayey rocks of the Burzyan Group correspond largely to sialites. Normosialites, supersialites, and hypohydrolyzates occur only in its uppermost portion (Malobakal'skaya subformation of the Bakal Formation). This indicates the rather advanced weathering of source rocks, which is consistent with previously published data. It was also established that the clayey rocks of the Burzyan Group do not contain a pyrogenic admixture, as was suggested formerly [36], and, consequently, volcanic activity did not affect the formation of the Burzyan sedimentary sequences in the territory studied.

Rather wide variations in the Cs, Th, Sc, Cr, Ni, Zr, Hf, La, Ce, Sm, Eu, and Tb contents and ratios in the Lower Riphean shales of the Bashkir Anticlinorium in comparison with NASC and PAAS allow us to use indicative element ratios for the estimation of provenance composition.

It was established that REE totals in the shales from the lower unit of the Ai Formation, the lower Kusa and Polovinka subformations of the Satka Formation, and the Makarovskaya and Malobakal'skaya subformations of the Bakal Formation exceed 200 ppm. The REE totals of the clayey rocks from the upper unit of the Ai Formation are three times lower. The La_N/Yb_N ratio of shales from this level is 3.6 in contrast to 12–16 elsewhere; the Gd_N/Yb_N ratio is also relatively low.

The Eu anomaly of Burzyan shales is 0.6–0.7, which is typical of most post-Archean clayey rocks [7, 8, 10] derived from erosion of the sialic upper crust [7].

The REE distribution patterns of the Lower Riphean shales are fairly similar for all the levels analyzed. Only the REE pattern of clayey rocks from the upper unit of the Ai Formation is more gently sloping, which is suggestive of the occurrence of mafic and ultramafic rocks in the source area.

Variations in the La/Sc, La/Cr, La/Co, Th/Sc, Th/Co, and Th/Cr ratios lead to the same conclusion. In the late

Ai, Polovinka, and early Bakal times, when psephitic and psammitic clastic material was not supplied into the basin, felsic rocks of presumably granodiorite composition were predominant in the provenance. The same can be said about the late Bakal time. In the early Ai and, probably, Polovinka time, basic rocks were also involved in erosion. This statement does not directly follow from the petrographic evidence but is supported by variations in many indicator ratios, first of all, Th/Sc and Th/Co.

Thus, the evolution of the sedimentation basin that existed in the Early Riphean in the place of the present-day Bashkir Anticlinorium may be interpreted as follows. A shallow sedimentation basin started to subside at the beginning of the Early Riphean (early Ai time) under conditions of dispersed rifting [55–57]. The subsidence was accompanied by the erosion of large blocks of the mature continental crust penetrated by basic dikes and other minor intrusions. The model Nd age of provenance corresponds to the early Paleoproterozoic ($T_{DM} \sim 2541$ Ma; $T_{strat} \sim 1635$ Ma). Local source areas were predominant. In late Ai time (sagging stage) the basement blocks were completely smoothed, and the erosion of local sources was changed by the distal supply of aluminosilicate clastic material. Felsic igneous rocks were mainly eroded at that time. Satka–Bakal time was characterized by the relatively quiet, quasi-stationary (in terms of Podkovyrov [76]) evolution of the shallow-water epicratonic basin. In early Kusa time, some participation of basic rocks in the provenance is supposed, however, the erosion of felsic rocks subsequently resumed. The main volume of aluminosilicate clastic material was supplied into the basin from distal sources [41, 42]. Judging from the Nd isotopic compositions of shales from the Makarovskaya Subformation of the Bakal Formation ($T_{DM} \sim 2275$ Ma; T_{strat} is slightly older than 1430 Ma), the model Nd age of provenance remained Paleoproterozoic during the entire Early Riphean. The Archean upper crustal component, e.g., the granulite-facies rocks of the Taratash Inlier [77], probably did not play any significant role.

The results obtained do not confirm the suggestion [37] of the predominance of mafic and ultramafic source rocks during the whole Satka time. Therefore, the source of magnesium fixed in the dolomite and crystalline magnesite of the Satka level still remains unknown. According to the recent geological and geochemical data, the deposition of the dolomite and magnesite was controlled by a complex combination of sedimentation and epigenetic processes [78]. It was supposed that the accumulation of magnesium hydrocarbonates at shallow-water platforms was crucial among these processes. The epigenetic transformation of hydrocarbonates into magnesite was accompanied by metasomatic alteration in contact with the host dolomites and appreciable (occasionally intense) recrystallization. By the example of economic magnesite deposits of the Paleogene, Neogene, and Recent ages [79], it was demonstrated that a steady supply of magnesium

into the sedimentation basin is possible only when Mg-rich rocks occur in the source provinces. The most favorable are ultramafic rocks weathered under conditions of a humid climate. The majority of Early and Middle Riphean deposits and occurrences of crystalline magnesite in the Bashkir Anticlinorium are localized in its northeastern part [78]. Assuming that the Mg source was a major control on their distribution, it may be suggested that magnesium was supplied from the north or northeast of the territory. The occurrence of olivine, chromite, and pyroxene in the heavy fractions of the sandstones and siltstones of the Bakal Formation [33] provides indirect evidence for this interpretation. Hence, in addition to the predominant erosion of felsic rocks during almost the whole Early Riphean and the supply of fine-grained aluminosilicate clastic material from the East European Platform, it is necessary to assume that a source of Mg existed in the Satka time. This source provided the formation of the more than 3500-m-thick dolomite sequence with large deposits of sparry magnesite. Judging from the Nd model age of Burzyan shales, this source had a Paleoproterozoic age and was situated to the north or northeast of the present-day Bashkir Anticlinorium.

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