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Mudstone Lithogeochemistry and Formation Conditions of Vendian Deposits in the Shkapovo–Shikhan Basin

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Abstract—Variation of geochemical modules and indices in mudstones from the Upper Vendian Kairovo and Shkapovo groups of the Shkapovo–Shikhan Basin provides the comprehensive information on changes in maturity of the fine aluminosiliciclastic material delivered in the basin, characterizes the redox environment in bottom water, and makes it possible to reconstruct the rock composition in provenance and its evolution through time. The generally moderate maturity of the fine terrigenous clastic material suggests that a nearly semiarid–semihumid climate dominated in paleodrainage area throughout the Late Vendian. It has been established that reducing environment did not exist in bottom water of the central Shkapovo–Shikhan Basin throughout the Late Vendian. Intermediate rocks prevailed in the paleodrainage area. More silicic rocks could occur only in the early Staropetrovo and late Salikhovo times. Data points of mudstones from the Kairovo and Shkapovo Groups plotted on the Cr–Ni, Co–V, Co/Hf–Ce/Cr, La–Th, and La/Sm–Sc/Th diagrams indicate that both Archean and more mature Paleoproterozoic crustal blocks existed in different proportions in the Late Vendian within source areas.

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INTRODUCTION

In the Volga–Ural region of the East European Platform, Vendian sedimentary rocks fill the Upper Kama and Shkapovo–Shikhan basins divided by the Sarapul–Krasnoufimsk Saddle (*Stratigraficheskaya*..., 2000; Belokon et al., 2001) (Fig. 1). Both Lower and Upper Vendian rocks are known in the Upper Kama Basin, but only Upper Vendian Kairovo and Shkapovo rocks occur in the Shkapovo–Shikhan Basin (*Stratotip*..., 1983; Aksenov, 1998; *Stratigrafischeskaya*..., 2000).

The objective of this work is to obtain information on variation of maturity degree of the fine aluminosiliciclastic material delivered to the sedimentary basin (indicator of climate in paleodrainage areas and redox environments in bottom water) and to reconstruct temporal compositional changes of provenance on the basis of geochemistry of the fine-grained terrigenous rocks. Such rocks prevail in the Upper Vendian sequence of the Shkapovo–Shikhan Basin and make it difficult or even impossible to estimate the aforementioned parameters based on traditional petrographic and lithological investigations.

Most of the parameters that characterize general sedimentological features in the study territory were previously known from the results of semiquantitative emission spectroscopy typical of each lithostratigraphic unit as a whole. In this work, we have used the geochemical features of mudstones based on their ICP-MS analysis. Since the mudstone samples were accurately tied up to the sections of each four formations, we could reconstruct in detail the main factors of sedimentation for almost the entire Late Vendian.

LITHOSTRATIGRAPHY AND STRUCTURAL–TEXTURAL ATTRIBUTES OF VENDIAN ROCKS IN THE SHKAPOVO–SHIKHAN BASIN

The Shkapovo–Shikhan Basin is a vast (500×250–$300\ km^2$) depression tilted to the east and southeast. It is bounded in the west and southwest by the Tatar, Komi–Permyak, and Orenburg arches (Lozin, 1994; Belokon et al., 2001). The thickness of the Vendian sequence in the basin is as much as 1.6–1.8 km. According to Belokon et al. (2001), the basin is underlain by Riphean rocks that become younger in the southeastern direction. However, the presence of pebbles of crystalline rocks in conglomerates of the Baikibashevo Formation suggests that the Vendian sequence of the Shkapovo–Shikhan Basin also overlapped the Archean–Paleoproterozoic complexes. The Vendian structural stage within the Shkapovo–Shikhan

Basin is separated from the under- and overlying rocks by regional angular unconformities. The Vendian sequence generally inherits morphology and prominent structural elements of the Riphean Kama–Belaya and Sernovodsk–Abdulino aulacogens (Lozin, 1994; Masagutov, 2002). However, the Vendian sequence differs from the underlying Riphean rocks by less intense deformation and general apronlike attitude. Although the present-day western boundary of the Vendian sequence does not fit the ancient coastline, they are rather close (Belokon et al., 2001). It is assumed that Riphean–Vendian sedimentary basins formed at the East European Platform–Urals junction in the course of the development of a rift system that dissected the Archean–Mesoproterozoic basement (Lozin, 1994).

As follows from the seismic stratigraphy (Lozin and Khasanov, 1991a, 1991b; Berzin et al., 1996; Echtler et al., 1996; *Glubinnoe…*, 2001), Upper Vendian sedimentary rocks of the Shkapovo–Shikhan Basin are replaced with the Upper Vendian Asha Group of the Bashkirian Anticlinorium along the fold–thrust dislocation system.

The Kairovo Group in the Shkapovo–Shikhan Basin comprises the Baikibashevo and Staropetrovo formations, while the Shkapovo Group consists of the Salikhovo and Karlin formations (Fig. 2).

The *Baikibashevo Formation* is composed of the greenish gray and gray sandstones with dissemination of black and pink minerals that impart a specific appearance to the rocks. Sandstones contain a variable admixture of gravel and pebbles. They also include interbeds of darker siltstones and mudstones. Inequigranular and coarse-grained poorly sorted massive sandstones with gravelstone interbeds and sporadic pebbles (up to 2–3 cm across) of reddish pink potassium feldspar, vein quartz, and crystalline rocks dominate in the lower part of the Baikibashevo Formation. Medium- and coarse-grained sandstones with numerous, relatively well-rounded mudstone plates also occur here. Low-angle, small- and medium(?)-scale unidirectional multistage cross-bedding is occasionally observed in the sandstones. Silty sandstones with numerous thin silty mudstone laminae, which emphasize the wavy, cross-wavy, fine cross-, and striated bedding, dominate in the upper part of the formation. The thickness of the Baikibashevo Formation varies from 10 to 85 m. The maximal thickness is noted in the southeastern Shkapovo–Shikhan Basin in the present-day Ural Foredeep.

The *Staropetrovo Formation* consists of greenish gray and less abundant brown silty–clayey rocks[1] with a variable admixture of psammitic material either as discrete interbeds and members or as dispersed grains. In some particular sections, the psammitic material occupies approximately one-half of the formation. Siltstones with carbonate cement and thin interbeds of silty

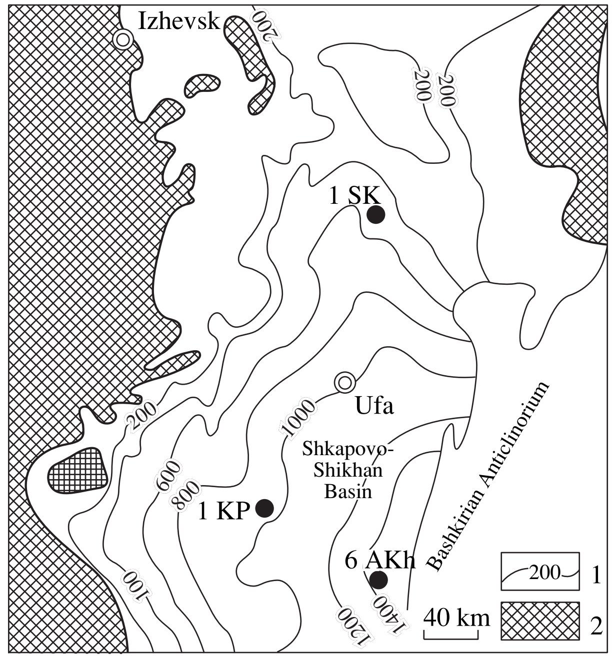

Fig. 1. Schematic structure of the Shkapovo–Shikhan Basin (after Belokon et al., 2001) and location of the studied deep boreholes. (1) Isopachs (m) of the Upper Vendian sequence; (2) regions lacking Upper Vendian rocks. Boreholes: (1 SK) Severokushkul-1, (1 KP) Kipchak-1, (6 AKh) Akhmerovo-6.

limestone appear in the Staropetrovo sections in the eastern part of the basin. The thickness of the formation increases from 85 in the western and northern areas to 320 m in the eastern and southern areas. Horizontal, low-angle wavy, wavy, trough-shaped, cross-wavy, and cross-bedding are typical of sandstones and siltstones of the Staropetrovo Formation (Lagutenkova and Chepikova, 1982; Maslov and Isherskaya, 1998, 2005). Fine unidirectional cross-bedding is occasionally combined with the cross-bedding and low-angle wavy discontinuous bedding. It is suggested that initial sediments with such combination of bedding types were deposited in the coastal environment of shallow-water marine basin and weak bottom currents (Lagutenkova and Chepikova, 1982). Rocks with the fine cross-wavy and trough-shaped bedding typical of coastal areas of the marine shoal occur at some levels. Lenticular wavy bedding associated with the fine unparallel and low-angle wavy bedding is occasionally observed in intercalating siltstones and mudstones. These sediments were probably deposited on shoals of the rough sea (Lagutenkova and Chepikova, 1982).

The *Salikhovo Formation* is composed of brown, reddish brown, and greenish gray (mainly in the lower part of the sequence) sandstones and siltstones with auxiliary interbeds of greenish gray and dark brown mudstones. In some sections, mudstones prevail over sandstones and siltstones. The thickness of the Salikhovo Formation varies from 100 to 450 m. The

[1] Actually, some of these rocks are vitric tuffs (Lagutenkova, 1963; *Stratotip…*, 1983).

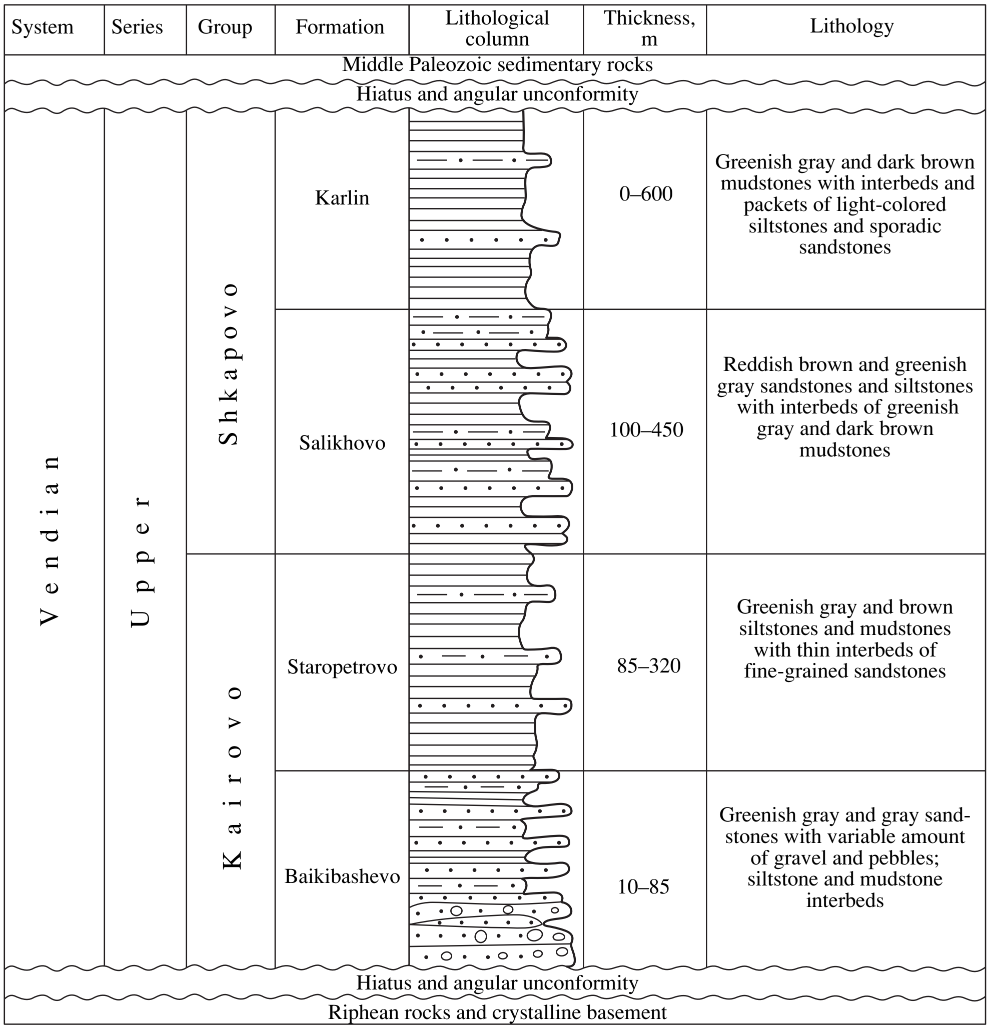

Fig. 2. Integrated lithostratigraphic column of Upper Vendian sedimentary rocks in the Shkapovo–Shikhan Basin.

area of maximal thickness coincides with the central part of the Shkapovo–Shikhan Basin. The wavy and low-angle wavy bedding is combined with the fine (thickness of series is up to 1.5 cm) cross-wavy bedding typical of coastal zone of the shallow-water marine basin. Mudcracks noted by some authors on the bedding surface of sandstones and siltstones testify to an extremely shallow-water environment. In the central Shkapovo–Shikhan Basin, rocks of the Salikhovo Formation are mainly characterized by the trough-shaped, wavy, and low-angle wavy parallel bedding (Ivanova et al., 1969; Lagutenkova and Chepikova, 1982).

The *Karlin Formation* consists of the greenish gray and much less abundant dark brown mudstones that contain microinterlayers, interbeds, and packets of the lighter-colored siltstone and less frequent sandstones. The thickness of the formation varies from 0 to 600 m. Attenuation or complete absence of these sediments is related to the pre-Paleozoic erosion. The maximum thickness is observed in the southern and southeastern parts of the basin (*Stratotip…*, 1983; Isherskaya and Romanov, 1993). Horizontal, low-angle wavy, lenticular, and cross-wavy bedding, as well as uneven, often hummocky bedding surfaces with occasional ripple marks are typical. Fine variously directed (unparallel) bedding typical of shallow-water marine environment is observed in fine intercalations of siltstones and mudstones. One can also see the wavy unparallel bedding typical of the shallow-water coastal zone of rough sea (Lagutenkova and Chepikova, 1982).

The Baikibashevo Formation of the Shkapovo–Shikhan Basin correlates with the Uryuk Formation of the Asha Group in the Bashkirian Anticlinorium; the Staropetrovo Formation, with the Basa Formation; the Salikhovo Formation, with the Kukkarauk Formation; and the Karlin Formation, with the Zigan Formation (*Stratotip…*, 1983; *Stratigraficheskaya…*, 2000). The K–Ar age of glauconite from silty sandstone of the Staropetrovo Formation is ~595 Ma (Kazakov et al., 1967). The glauconite from the Uryuk and Basa formations is dated back to 582–569 Ma (*Stratotip…*, 1983) and 600–557 Ma, respectively.

RESULTS OF PREVIOUS INVESTIGATIONS

Various features of the Vendian sedimentation in the Volga–Ural region were considered by M.M. Aliev, E.M. Aksenov, Yu.V. Andreev, M.M. Balashova, T.V. Belokon, I.K. Chepikova, N.S. Gatiyatullin, Z.P. Ivanova, T.V. Ivanova, M.V. Isherskaya, A.A. Klevtsova, N.S. Lagutenkova, E.V. Lozin, R.Kh. Masagutov, S.G. Morozov, L.D. Ozhiganova, I.E. Postnikova, and other researchers. Most of the authors suppose that lower units of the Upper Vendian (Baikibashevo Formation) formed in the eastern Russian Platform during transgression from the Urals. Episodic regression at the end of the Kairovo time was replaced by transgression of a larger scale.

The Late Vendian environment was characterized by a relatively temperate or warm and humid climate (Postnikova, 1977). In contrast, Ivanova and Edrenkina (1971) and Masagutov (2002) suggested a relatively cold climate, based on the distribution of Mn, V, Cr, Ni, and Cu. According to (Aliev et al., 1977), the largely oxidizing environment and warm climate typical of the Riphean and Early Vendian was replaced by reducing conditions and relatively cold climate in the Late Vendian.

Ordered and variable types of the distribution of minor elements in Upper Vendian sedimentary rocks indicate that the sediments were deposited in marine and coastal-marine environments, respectively (Isherskaya, 1978). This statement is supported by structures of rocks (Lagutenkova and Chepikova, 1982) and the relative abundance of glauconite (Ivanova et al., 1969). Based on Ba and Cl contents in clayey rocks, Lagutenkova and Chepikova (1982) suggested that Upper Vendian sediments of the Volga–Ural region were deposited in the normal marine (occasionally, brackish) environment.

The majority of authors believe that the geochemical regime of bottom water in the basin of the Baikibashevo time changed from the oxidizing to reducing type. Both the reducing (Lagutenkova and Chepikova, 1982) and neutral (reduction-free) conditions (Ivanova and Klevtsova, 1960; Ivanova et al., 1969) existed in sediments of the Staropetrovo time. Poorly differentiated sandy and sandy–silty sediments accumulated in a slightly oxidizing environment typical of the Salikhovo time. An oxidizing environment existed in the late Salikhovo time (Ivanova and Klevtsova, 1960; Masagutov, 2002). The redox environment of the Karlin time varied from the neutral to slightly reducing type in the coastal zone and to the stable reducing type in the deep-water zone (Masagutov, 2002).

The Volga–Kama Massif composed of garnet and biotite–plagioclase gneisses, granodiorites, quartzites, mica–quartz schists, and gabbrodolerites served as the main provenance during the deposition of sediments of the Kairovo Group. Local intrabasinal uplifts delivered the recycled sedimentary material (Ivanova et al., 1969; Aliev et al., 1977). In the Shkapovo time, Riphean, Lower Vendian, and lowermost Upper Vendian metamorphic and sedimentary rocks were eroded in an eastern provenance. The mineral composition of Vendian rocks indicates that Archean and subordinate Paleoproterozoic rocks of the Volga–Kama Massif were eroded in the Kairovo time. Polymictic sandstones with fragments of volcanic rocks in the Kairovo and Shkapovo sections indicate that Early Vendian volcanics were also eroded.

In our opinion, geochemical signatures of mudstones from the Kairovo and Shkapovo groups testify to the substantial contribution of acid pyroclastic material and products of its erosion (Maslov and Isherskaya, 2004). On the basis of average values of the chemical index of alteration (CIA), chemical index of weathering (CIW), and index of composition variation (ICV) (Maslov et al., 2003a), we suggested that the Vendian rocks were formed under conditions of semiarid or semihumid climate. The average Mo/Mn, V/(V + Ni), and other ratios show that the reducing environment did not exist in bottom water during the Late Vendian. Based on the Eu/Eu* ratio, mudstones of the Staropetrovo Formation can be divided into three groups. Rocks of the first group are related to the destruction of a crust similar in composition to the average continental crust. The Archean clastic material is subordinate in mudstones of the second and third groups (Eu/Eu* = 0.69–0.72 and >0.80, respectively). This conclusion is supported by a rather high Gd_N/Yb_N ratio in some mudstone samples. Median values of La/Sc, La/Ni, Th/Cr, and Th/Sc ratios in mudstones from different Vendian lithostratigraphic units indicate the erosion of a rather high percentage of mafic and felsic igneous rocks from the Late Vendian provenance.

MATERIALS AND METHODS

Our lithogeochemical investigation is based on the analysis of core samples from the Kipchak-1, Akhmerovo-6, and Severokushkul-1 boreholes in the collection of M.V. Isherskaya (Institute of Geology, Ufa Scientific Center). We analyzed more than 40 samples of mudstones from the Baikibashevo, Staropetrovo, Salikhovo, and Karlin formations. After their macroscopic and microscopic examination, we determined the major elements with the XRF analysis on a CPM-18 spectrometer at the Zavaritsky Institute of Geology and Geochemistry (G.S. Neupokoeva, L.V. Fomina, V.P. Vlasov, and N.P. Gorbunova, analysts). The major element contents in mudstones served as an additional criterion for the subdivision of samples into silty–clayey rocks and mudstones. Samples with data points plotted on the Herron (1988) diagram beyond the shale field were omitted and 23 samples were left for the further analysis. We compiled a summary section of the

Table 1. Location of analyzed samples in the Upper Vendian section of the Shkapovo-Shikhan Basin

Formation	Borehole	Sample	Thickness measured from the formation base, m	Interval, m
Karlin	Kipchak-1	IM-12	458	2390–2393
		IM-13	385	2463–2466
		IM-14	343	2506–2509
		IM-15	317	2531–2535
		IM-16	311	2537–2541
		ISh-4	292	2557–2559
		IM-17	98	2750–2755
		IM-18	60	2790–2792
		IM-19	16	2833–2837
Salikhovo	Akhmerovo-6	IM-1	213	2285–2289
		IM-2	210	2289–2294
		IM-3	195	2304–2306
		IM-4	174	2329–2332
		IM-5	170	2333–2337
	Severokushkul-1	ISh-7	48	1977.4–1985
		IM-27	25	2071.8–2080.1
Staropetrovo		IM-28	180	2168.7–2176
		IM-29	172	2176.6–2185.6
		ISh-14	163	2185.6–2193
		IM-31	76	2272.6–2281.1
		ISh-16	68	2281.1–2285
		ISh-17	63	2285–2293.5
Baikibashevo		IM-32	20	2290.7–2299.7

Kairovo and Shkapovo groups for the examination of upsection variations in various lithogeochemical modules and indices of composition alteration (CIA and others) and ratios of minor elements. Each of the analyzed samples was tied-up strictly to the base of a certain formation (Table 1). The summary section has a thickness of 1103 m.

LITHOLOGY AND GEOCHEMISTRY OF VENDIAN MUDSTONES IN THE SHKAPOVO–SHIKHAN BASIN

As follows from the XRD results (DRON-3 diffractometer, $Cu_{k\alpha}$), mudstones from all lithostratigraphic subdivisions of the Kairovo and Shkapovo groups contain an admixture of quartz, plagioclase, and microcline. Rutile is present in some samples from the Baikibashevo, Salikhovo, and Karlin formations. Clay minerals are represented by hydromica (modifications $2M_1$ and 1M) and a mixed-layer mineral of illite–smectite type, Fe–Mg chlorite, and kaolinite[2]. Judging from the intensity of reflections 10 and 7.10–7.15 Å, contents of the hydromica and chlorite–kaolinite phases are approximately equal, although hydromica prevails in some samples. The presence of weak reflection 7.5 Å suggests that some samples contain halloysite, which is typical of mudstones of the Karlin Formation.

The occurrence of kaolinite and a mixed-layer mineral of illite–smectite type in mudstones may indicate that Upper Vendian sedimentary rocks of the

[2] The occurrence of phase $2M_1$ (muscovite) is confirmed by a triplet of 2.98, 2.86, and 2.78 Å in addition to 10.0 and 4.48 Å reflections in the X-ray pattern. The mixed-layer mineral of illite–smectite type is identified by a broad reflection in the 10–12 Å range on X-ray patterns of oriented specimens and by asymmetry of reflection 10 Å on the low-angle side. After calcination up to 600°C, all these reflections disappear and symmetry of reflection 10 Å increases. The most significant reflections of kaolinite coincide with reflections of chlorite (7.1 and 3.56 Å) or mica (4.44 Å). Reflection 14.2 Å completely disappears after the calcination of oriented samples up to 600°C.

Table 2. Chemical composition (wt %) of representative samples of Upper Vendian mudstones from the Shkapovo–Shikhan Basin

Component	Baikibashevo Formation		Staropetrovo Formation				Salikhovo Formation			Karlin Formation				
	IM-22	IM-32	ISh-14	ISh-16	IM-29	IM-31	ISh-7	IM-27	IM-1	IM-12	IM-13	IM-16	IM-17	IM-18
SiO_2	54.94	56.12	60.66	59.72	58.79	53.58	58.10	59.31	63.13	61.03	61.73	62.70	59.58	63.55
TiO_2	0.84	0.83	0.75	0.71	0.78	0.68	0.72	0.75	0.93	0.80	0.82	0.79	0.75	0.79
Al_2O_3	16.47	17.55	16.64	17.32	16.77	18.45	16.51	16.42	15.35	16.00	15.75	15.29	17.01	15.13
Fe_2O_3 tot	8.80	6.79	8.21	6.32	8.14	9.22	6.41	7.68	7.32	8.00	6.60	6.54	6.72	6.41
MnO	0.08	0.06	0.12	0.05	0.07	0.28	0.11	0.11	0.09	0.17	0.06	0.07	0.12	0.06
MgO	4.40	3.28	2.84	2.98	2.77	2.67	3.02	2.57	2.22	2.38	2.80	2.80	2.62	2.72
CaO	0.77	1.00	0.30	0.69	0.48	1.13	2.25	0.99	0.21	0.56	0.31	0.29	0.81	0.23
K_2O	4.48	5.33	4.06	4.68	3.68	4.34	4.82	3.57	3.88	4.22	3.49	3.33	5.51	3.05
Na_2O	2.20	1.36	1.85	1.20	2.31	1.72	2.50	2.46	2.50	1.80	1.70	1.80	2.15	1.90
P_2O_5	0.15	0.08	0.12	0.09	0.12	0.47	1.37	0.15	0.10	0.19	0.08	0.09	0.11	0.10
L.O.I.	5.10	6.37	4.98	6.04	5.11	7.87	4.79	4.87	2.77	5.19	5.40	5.26	3.51	5.28
Total	98.22	98.76	100.52	99.81	99.02	100.42	100.60	98.88	98.50	100.34	98.75	98.94	98.90	99.22

Shkapovo–Shikhan Basin were deposited on coastal shoals that accumulated the slightly altered in seawater kaolinite delivered from zones of weathering.

The clay mineral composition suggests that the degree of postsedimentary alteration of Upper Vendian rocks was relatively low (initial catagenesis) and the total subsidence depth did not exceed 1–2 km.

The major oxide compositions of mudstones from the Baikibashevo, Staropetrovo, Salikhovo, and Karlin formations are presented in Table 2. In comparison with the post-Archean Australian Shale (PAAS), mudstones from the Kairovo and Shkapovo groups are depleted in Al_2O_3 and TiO_2. The PAAS-normalized total Fe content (as Fe_2O_3) varies from 0.82 to 1.42 (average 1.1). MgO and K_2O contents are 0.92–1.49 and 0.64–1.49, respectively. In general, these values show a wide scatter in both Kairovo and Shkapovo sections, and it is difficult to outline any trend (Fig. 3).

To characterize the general compositional features of Upper Vendian mudstones of the Shkapovo–Shikhan Basin, we applied the approach elaborated by Yudovich and Ketris (2000).

In the ($Na_2O + K_2O$)–HM[3] diagram, the overwhelming majority of data points of mudstones from the Kairovo and Shkapovo groups fall into the field typical of normosiallites. Much less data points are located in the fields of hypo- and supersiallites, and sporadic data points of mudstones from the Karlin Formation and data point of one mudstone sample from the Baikibashevo Formation fall into the silite field, suggesting a substantial silty or silty–sandy admixture. Two mudstone samples from the Staropetrovo and Salikhovo formations belong to hypohydrolyzates. The total ($Na_2O + K_2O$) content in the studied fine-grained terrigenous rocks varies from 4 to 8 wt %.

In the module SPM–FM diagram, the majority of mudstone data points are localized in field VI that corresponds to the pelitic (largely, hydromicaceous) rocks with a significant admixture of fine-grained feldspar fragments. According to (Yudovich et al., 1991), such rocks are typical of arid weathering zones and are most widespread in Riphean sedimentary sequences. In addition to these rocks, mudstones of type V are also known in the Vendian sequence of the Shkapovo–Shikhan Basin. They correspond to the standard three-component (chlorite–montmorillonite–hydromica) system (Yudovich and Ketris, 2000). According to these authors, such rocks are unrelated to weathered crusts.

In the TiO_2–TM diagram, approximately one-half of mudstone data points fall into the field of hydromicaceous clay, whereas the remaining data points are localized in the overlap zone of hydromica and smectite clays.

Relationships between TM, IM, SPM, and HM in mudstones of all four formations show that TM and IM reveal a positive correlation ($r = 0.30$), whereas the correlation between SPM and HM is negative ($r = -0.14$). Taking into consideration the data in (Yudovich and Ketris, 2000), one can conclude that the rocks considered above went through only one evolution

[3] The following modules are used in this paper: hydrolyzate module HM = ($Al_2O_3 + TiO_2 + Fe_2O_3 + FeO$)/ SiO_2, alumina–silica module AM = Al_2O_3/SiO_2, sodium–potassium module SPM = ($Na_2O + K_2O$)/Al_2O_3, femic module FM = (Fe_2O_3 + FeO + MnO + MgO)/SiO_2, titanium module TM = TiO_2/Al_2O_3, and iron module IM = (Fe_2O_3 + FeO + MnO)/($TiO_2 + Al_2O_3$) (Yudovich and Ketris, 2000).

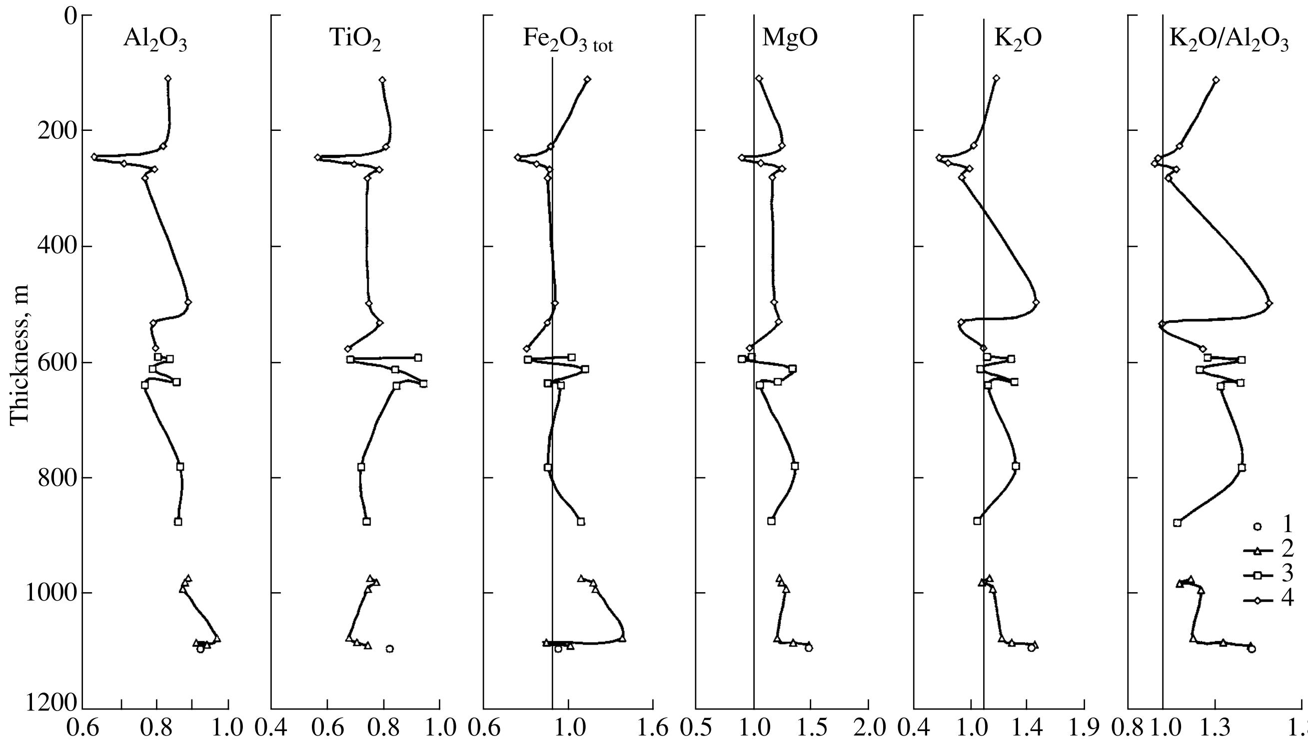

Fig. 3. PAAS-normalized variations in ratios of major oxides in the Upper Vendian section of the Shkapovo–Shikhan Basin. Formations: (1) Baikibashevo; (2) Staropetrovo; (3) Salikhovo; (4) Karlin.

cycle: weathering ⇒ transport ⇒ sedimentation ⇒ diagenesis ⇒ catagenesis. Thus, their lithogeochemical signatures can be used to reconstruct paleodrainage systems, character of weathering, and paleogeographic patterns.

Table 3 shows contents of some minor elements in the representative mudstone samples from the Staropetrovo, Salikhovo, and Karlin formations. Let us consider the distribution of representative minor elements relative to the PAAS values.

Large ion lithophile elements (Rb, Cs, Ba, Sr, Th, and U). Contents of these elements are slightly lower in mudstones from the Staropetrovo and Salikhovo formations and markedly lower in most of mudstone samples from the Karlin Formation (Fig. 4).

High-field strength elements (Zr, Nb, Hf, and Y) tend to remain in the melt during the crystallization of igneous rocks. Therefore, they are mainly concentrated in silicic rocks. Together with REE, they serve as indicators of provenance composition. In mudstones from the Staropetrovo Formation, the HFSE contents are almost similar to those in the PAAS. Relative to the PAAS, fine-grained terrigenous rocks of the Salikhovo Formation are enriched in Y and Nb and similar in terms of the Zr and Hf contents. Mudstones of the Karlin Formation are divided into three groups in terms of HFSE contents. Mudstones of the first group (samples IM-12, IM-14, IM-19, IM-15, and IM-13) mainly taken from the upper portion of the Karlin Formation are appreciably depleted in the HFSE relative to the PAAS. In mudstones of the second group (samples IM-16, ISh-4, and IM-18), the Zr, Nb, Hf, and Y contents are approximately comparable with the PAAS level. Sample IM-17 (the third group) is characterized by the maximal negative Eu anomaly (see below). Comparison of the Zr distribution in mudstones from different Upper Vendian lithostratigraphic units of the Shkapovo–Shikhan Basin did not reveal the upsection increasing trend. This is consistent with the notion of the first-cycle origin of these rocks.

Transitional metals (Cr, Co, Ni, V, Sc, and Cu). Contents of these elements in mudstones of the Staropetrovo Formation are comparable with the PAAS values, except for some samples depleted in Ni. Relative to the PAAS, mudstones from the Salikhovo Formation are characterized by slightly lower contents of the majority of transitional elements. Cr and Cu contents in some samples are two times lower. In mudstones of the Karlin Formation, the contents of transitional elements (except Cr) are substantially lower in many cases (Fig. 4); and the Ni, V, and Cu contents in some samples are particularly low in comparison with the PAAS.

Rare earth elements. The REE contents in mudstones of the Staropetrovo Formation are similar to those in the PAAS. The MREE contents are elevated only in sample IM-31 taken from the upper part of the lower third of the section. In mudstones of the Salikhovo Formation, the REE contents are much

Table 3. Minor element contents (ppm) in Upper Vendian mudstones from the Shkapovo–Shikhan Basin

Element	Staropetrovo Formation				Salikhovo Formation			Karlin Formation				
	IM-29	ISh-14	IM-31	ISh-16	IM-1	ISh-7	IM-27	IM-12	IM-13	IM-16	IM-17	IM-18
Cr	142.83	77.85	100.66	174.71	33.41	44.30	89.75	69.04	91.88	167.33	109.63	176.68
Co	22.71	19.85	27.62	11.17	12.14	27.36	17.48	11.83	9.26	16.25	18.77	17.45
V	136.37	111.89	110.74	104.72	97.60	105.55	113.03	40.76	40.94	102.69	105.70	103.31
Ni	26.86	32.67	26.78	29.36	27.31	22.32	20.16	29.91	27.30	19.82	16.46	20.99
Zr	169.70	151.27	91.50	251.89	345.40	197.15	158.43	46.63	57.21	230.34	465.83	235.76
Nb	23.56	16.07	14.48	12.48	23.27	19.50	21.44	5.28	5.19	20.17	52.10	21.06
Hf	4.59	4.11	2.57	6.50	5.80	4.99	4.55	0.89	1.03	6.41	13.85	6.59
Y	27.53	25.54	35.08	23.83	39.63	120.83	28.08	8.42	6.85	27.78	78.32	29.74
Th	14.60	12.78	14.44	14.03	17.88	18.92	14.70	4.97	3.66	10.54	29.39	12.71
U	1.81	1.53	2.21	2.16	1.25	12.87	2.07	0.77	0.85	2.14	3.03	2.46
La	45.47	35.80	59.89	47.91	65.19	95.22	41.06	14.96	12.51	33.68	53.44	37.86
Ce	89.01	71.51	121.14	90.14	130.64	217.43	81.16	31.62	26.37	67.87	120.52	79.61
Pr	10.97	8.20	14.56	10.07	16.26	26.61	9.25	3.91	3.41	8.30	14.62	9.27
Nd	40.32	28.82	57.19	35.05	65.04	106.07	33.28	15.69	13.04	30.94	52.75	34.90
Sm	7.05	5.19	11.93	6.12	11.99	24.26	6.03	2.91	2.48	5.89	11.53	6.70
Eu	1.43	1.08	2.59	1.23	1.97	4.59	1.28	0.61	0.51	1.20	1.58	1.38
Gd	5.90	4.37	10.41	4.59	9.37	23.33	5.21	2.60	2.12	5.28	11.79	5.77
Tb	0.88	0.70	1.40	0.71	1.44	3.48	0.82	0.38	0.32	0.83	2.08	0.91
Dy	5.05	4.34	6.81	4.18	8.22	18.74	4.79	2.01	1.72	5.00	13.02	5.19
Ho	1.01	0.86	1.28	0.82	1.62	3.48	1.02	0.40	0.34	1.05	2.76	1.10
Er	2.85	2.48	2.86	2.33	4.67	8.42	2.82	1.02	0.90	2.89	7.16	2.98
Tm	0.43	0.38	0.38	0.34	0.69	1.16	0.42	0.15	0.13	0.44	1.03	0.46
Yb	2.79	2.54	2.32	2.17	4.29	6.93	2.76	0.91	0.79	2.93	6.64	2.99
Lu	0.43	0.38	0.34	0.32	0.65	1.01	0.45	0.14	0.11	0.42	0.99	0.48

Table 4. Coefficients of pair correlation between LREE, HREE, Cr, Ni, Sc, V and some major oxides in Upper Vendian mudstones from the Shkapovo–Shikhan Basin

	LREE	HREE	Cr	Ni	Sc	V
Karlin Formation						
Al_2O_3	0.58	0.59	–0.30	–0.28	0.51	0.47
K_2O	0.58	0.69	–0.46	–0.36	0.42	0.32
P_2O_5	–0.03	–0.02	–0.54	0.14	–0.05	–0.11
TiO_2	0.43	0.30	0.08	0.17	0.48	0.51
Salikhovo Formation						
Al_2O_3	0.33	0.42	–	–0.34	0.67	0.88
K_2O	0.44	0.73	–	0.21	0.64	0.44
P_2O_5	0.48	0.87	–	–0.44	0.52	0.08
TiO_2	0.51	–0.02	–0.57	0.70	–0.41	–0.12
Staropetrovo Formation						
Al_2O_3	0.89	0.43	0.05	0.29	–0.60	–0.42
K_2O	0.24	–0.46	0.28	0.83	–0.77	–0.58
P_2O_5	0.86	0.90	–0.32	–0.26	–0.10	–0.16
TiO_2	–0.65	–0.44	–0.06	0.07	0.73	0.76

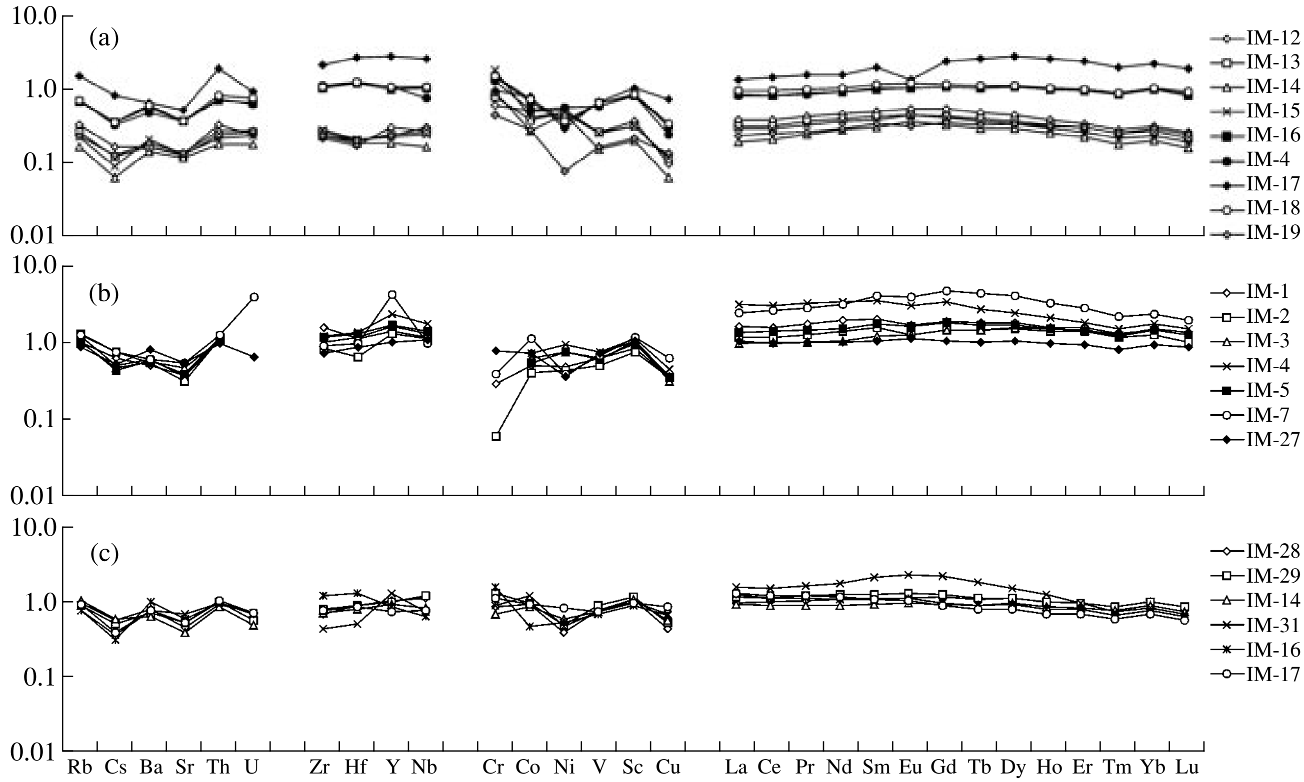

Fig. 4. PAAS-normalized ratios of minor elements in mudstones. Formations: (a) Karlin, (b) Salikhovo, and (c) Staropetrovo.

higher than in the PAAS (especially high in samples ISh-7 and IM-4). At the same time, the REE contents in sample IM-27 taken from the basal unit, the REE contents are comparable with the PAAS values. This is typical of the fine-grained terrigenous rocks that underlie the Staropetrovo Formation. Mudstones of the Karlin Formation are divided into three groups. The highest REE contents (relative to the PAAS) are typical of sample IM-17. The commensurable with the PAAS contents are characteristic of samples ISh-4, IM-18, and IM-16, whereas samples IM-12, IM-13, IM-14, IM-15, and IM-19 contain markedly less REE than the PAAS. It should be noted that the above groups are identical to those distinguished by the HFSE contents.

Coefficients of pair correlation between some major oxides (Al_2O_3, TiO_2, K_2O, and P_2O_5), on the one hand, and LREE, HREE, Yb, and some other minor elements, on the other (Table 4), indicate that LREEs in mudstones of the Staropetrovo Formation are commonly related to the clayey fraction and phosphate phase. This statement is also valid for the HREE. Other minor elements are related to the clayey fraction and, in part, Ti-bearing minerals. In mudstones of the Salikhovo Formation, the clayey fraction, phosphate phase, and Ti-bearing minerals are carriers of LREEs. HREEs are associated here with the clayey fraction and phosphate phase. Sc and V are mainly related to the clayey fraction and partially to the phosphate phase. Ni is contained mainly in Ti-bearing minerals. In mudstones of the Karlin Formation, REEs are related mainly to the clayey fraction and partly to the Ti-bearing minerals. Sc and V contents are controlled to a certain degree by the clayey fraction and partly by Ti-bearing minerals. The clayey fraction, phosphate phase, and Ti-bearing minerals do not carry Cr. A minor part of Ni is related to the phosphate phase and Ti-bearing minerals.

DISCUSSION

Reconstruction of **paleoclimate** from geochemical data is based on the estimation of maturity degree of the fine aluminosiliciclastic material that was delivered from the paleodrainage area to the sedimentary basin. Temporal variation of the character of weathering in source regions may be estimated from the vertical variation of hydrolyzate (HM) and alumina–silica (AM) modules, chemical index of alteration (CIA), chemical index of weathering (CIW), and index of composition variation (ICV) (Maslov et al., 2003a).

Rocks with the higher HM and AM values are composed of material subjected to intense weathering in paleodrainage areas (Yudovich, 1981; Yudovich and Ketris, 2000; *Interpretatsiya…*, 2001). It is also necessary to consider proportions of the major oxides, which behave differently in the process of chemical weathering in paleodrainage areas (Nesbitt and Young, 1982; Harnois, 1988; Visser and Young, 1990; Cox et al., 1995). The indices are calculated from the following

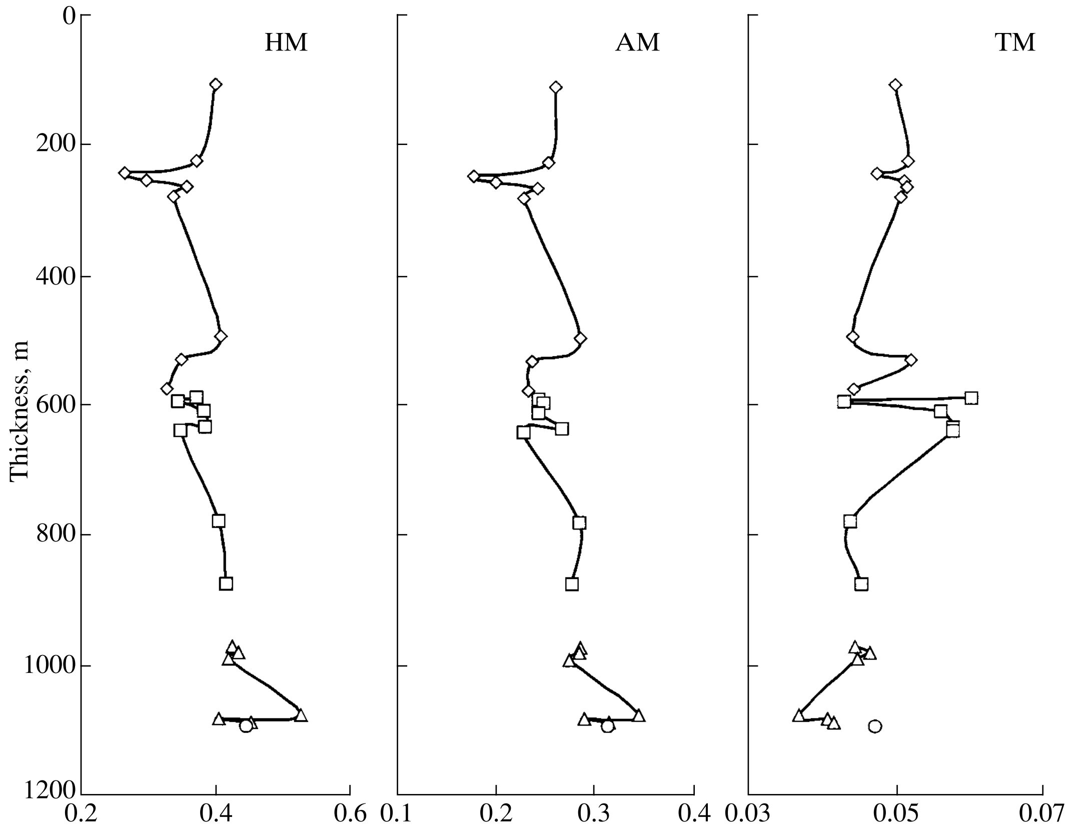

Fig. 5. Variations of hydrolyzate (HM), alumina–silica (AM), and titanium (TM) modules in Upper Vendian mudstones from the Shkapovo–Shikhan Basin. See Fig. 3 for legend.

formulas: CIA = $100 \times Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)$, CIW = $100 \times Al_2O_3/(Al_2O_3 + CaO + Na_2O)$, and ICV = $(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + TiO_2)/Al_2O_3$. Unweathered and intensely weathered rocks are characterized by CIA ~ 50 and the ~100, respectively. Boundary between deposits of humid and arid (or nival) climates is drawn at CIA =70. The CIW value positively correlates with the degree of rock decomposition in paleodrainage areas. In the slightly altered basalts and granites, CIW varies from 59 to 76 (Harnois, 1988). In weathered rocks of the same composition, CIW = 94–98. The ICV index also reflects the maturity degree of the fine aluminosiliciclastic material delivered to the sedimentary basin. Immature shales with high contents of alien silicate minerals are characterized by ICV > 1, whereas the more mature pelitic rocks have ICV < 1 (Cox et al., 1995).

Variations of HM, AM, and TM. The HM values in mudstones of the Kairovo and Shkapovo groups vary from 0.53 to 0.27. As is evident from Fig. 5, median HM values gradually decrease upsection from 0.45 (Baikibashevo Formation) to 0.35 (Karlin Formation). The trend is reversed one only in the upper third of the Karlin section (samples IM-13 and IM-12). Median values of alumina–silica module also decrease upsection from 0.45 in the Baikibashevo mudstones to 0.43 in the Staropetrovo mudstones, 0.38 in the Salikhovo mudstones, and 0.35 in rocks of the Karlin Formation. Variation in the TM value is different. In mudstones of the Staropetrovo and Salikhovo formations, this module shows a significant increase upward the section. In rocks of the Karlin Formation, this trend is much less prominent. One can see several episodes of increase and decrease of the TM value against the background of insignificant growth. All the above-mentioned modules appreciably vary at the boundary between the Salikhovo and Karlin formations.

Thus, we can note a gradual decrease in the maturity degree of the fine aluminosiliciclastic material delivered in the course of the Late Vendian evolution. This trend suggests that the intensity of weathering weakened with time, and delivery of the moderately mature clastic material, similar to that of the Baikibashevo–early Staropetrovo time, began only in the latest Karlin time. The slight increase in TM values in mudstones of the Baikibashevo–Salikhovo time indicates a weak trend of the redeposition of clastic material. However, this trend disappeared in the Karlin time.

Variations of CIA, CIW, and ICV. Variations of HM and AM values only yield qualitative characteristics of rock transformation in paleodrainage areas. In contrast, the CIA index makes it possible to distinguish

Table 5. Minor element ratios used for discrimination of zones based on redox parameters

U/Th	Authigenic U	V/Cr	Ni/Co
Anoxic zone			
1.25	12.0	4.25	7.0
Anoxic zone			
0.75	5.0	2.0	5.0
Oxic zone			

more definitely rocks deposits formed in the arid, humid, or nival climate. All of the Upper Vendian lithostratigraphic levels discussed above are characterized by the CIA value of <70 (median value 61–67) (Fig. 6). Therefore, one can suppose that the climate in paleodrainage areas was close to the semiarid type during the whole Upper Vendian. The most mature fine aluminosiliciclastic material was delivered to the sedimentation region in the Staropetrovo and early–middle Karlin times. The less weathered fine aluminosiliciclastic material is typical of the middle Salikhovo time. The Karlin Formation also includes an interval with mudstones composed of only slightly weathered material (sample IM-14).

Taking into consideration the aforementioned data, the CIW index of the Upper Vendian mudstones (55–66) indicates a relatively slight alteration of rocks in the drainage areas. Variation of the CIW index in the Baikibashevo–Salikhovo time from 64–65 to 55–56 demonstrates a clear decreasing trend of maturity degree of the fine aluminosiliciclastic material delivered to the sedimentary basin. In the uppermost part of the Salikhovo Formation, the maturity of material markedly increases (62–63), but it remains unchanged (~61) throughout the Karlin Formation. The ICV index shows approximately the same variation trend in the Kairovo and Shkapovo groups.

Redox conditions of bottom waters in sedimentary basins are usually indicated by the Mo/Mn, V/(V + Ni), and some other ratios (Kholodov and Nedumov, 1991; Hatch and Leventhal, 1992; Jones and Manning, 1994; Rachold and Brumsack, 2001; Gavrilov et al., 2002; and others). Numerous investigations carried out to date (Maslov et al., 2003b) have made it possible to outline boundary values of these ratios used for the discrimination of redox environments (Table 5). However, the application of different ratios does not always yield completely consistent results. The Mo/Mn ratio is the most informative (Kholodov and Nedumov, 1991; Gavrilov et al., 2002).

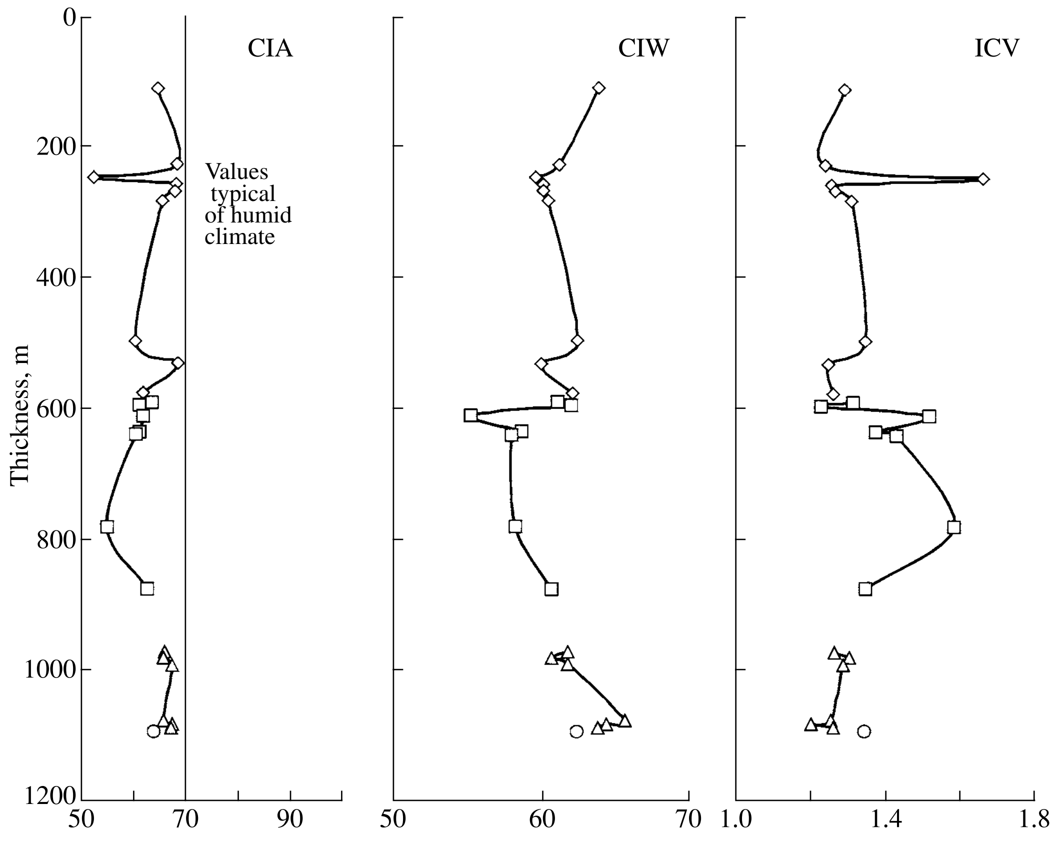

Fig. 6. Variations of CIA, CIW, and ICV indices in Upper Vendian mudstones from the Shkapovo–Shikhan Basin. See Fig. 3 for legend.

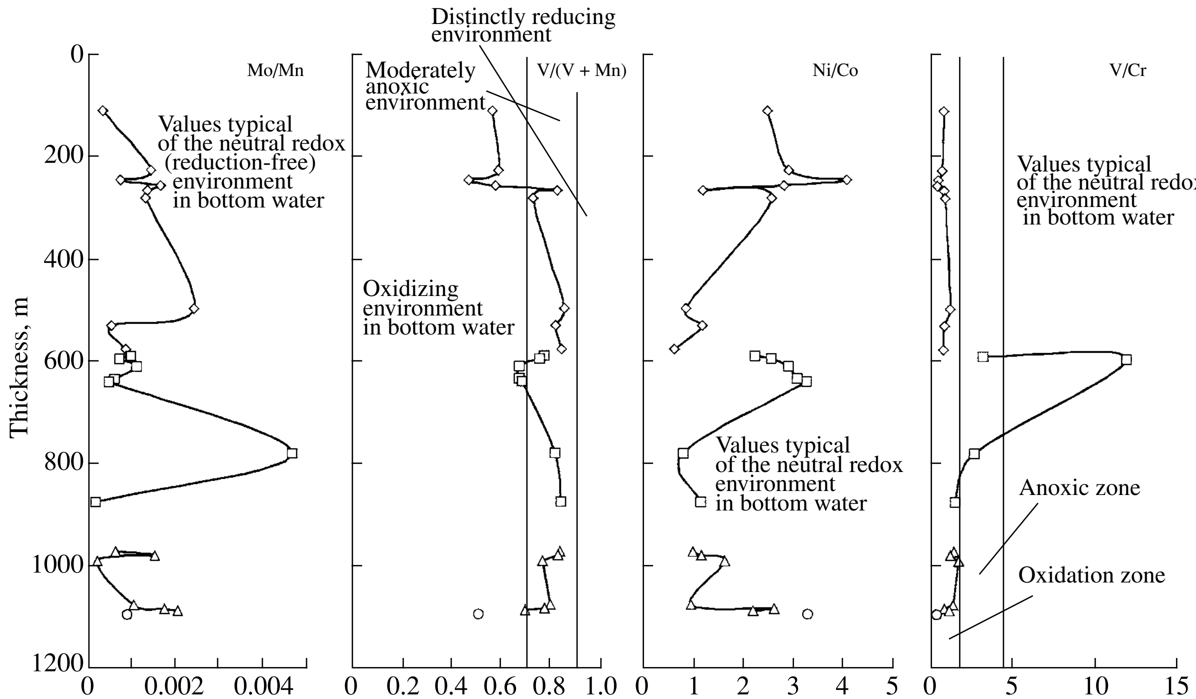

Fig. 7. Variations of minor element ratios in mudstones from the Kairovo and Shkapovo groups in the Shkapovo–Shikhan Basin as indicators of the redox environment in bottom water. See Fig. 3 for legend.

In mudstones of the Kairovo and Shkapovo groups, this ratio varies from 0.0009 to 0.0047 (Fig. 7) and definitely indicates that no stagnant bottom water existed in the Late Vendian sedimentary basin at the site of the Shkapovo–Shikhan Basin. The same conclusion may be drawn from the Ni/Co ratio. The V/(V + Ni) and V/Cr ratios show that the majority of mudstones were deposited in the oxidizing environment, and a lesser portion of mudstones was formed in the anoxic zone. However, conclusions based on these ratios are doubtful, because some samples classed with the moderately anoxic environment with respect to the V/(V + Ni) ratio may be interpreted as deposits of well-aerated basin with respect to the V/Cr ratio (e.g., samples IM-16, IM-17, and IM-18). However, it is indicative that none of the considered ratios give grounds to recognize the so-called Vendian Domanik in the Upper Vendian sequence of the Shkapovo–Shikhan Basin (*Vendskaya…*, 1985).

The (Fe + Mn)/Ti ratio is one of the indicators most frequently used to discriminate the **products of submarine hydrothermal discharge** in sediments (Strakhov, 1976). The value of this ratio in sediments of the present-day water reservoirs, where the hydrothermal activity is surely absent, ranges from 7.7 to 17. If this ratio exceeds 25, the hydrothermal (endogenic) material may be expected in sediments (Strakhov, 1976; Butuzova, 1998).

To calculate the (Fe + Mn)/Ti ratio, we used more than 60 full chemical analyses of mudstones of the Kairovo and Shkapovo groups. None of the analyzed samples yielded the value above 5.85. Thus, the Late Vendian sedimentation in the Shkapovo–Shikhan Basin was not accompanied by the hydrothermal activity.

In order to identify the **volcanic material** in the volcanic-free fine-grained terrigenous material subjected to intense catagenetic transformations (“camouflaged pyroclastic rocks”), Yudovich et al. (1984, 1986) applied the following lithochemical criteria: anomalously high (or conversely, anomalously low) values of the TM; elevated values of the IM; high contents of Na_2O (>3 wt %) and $Na_2O + K_2O$ (>5 wt %); high values of the potassium module ($PM = K_2O/Al_2O_3$), which exceeds the muscovite norm (0.31); and significant correlation between K_2O, TiO_2, and MgO. In some samples from the Staropetrovo, Salikhovo, and Karlin levels, the PM value exceeds the muscovite norm and attains 0.35 (Fig. 8), indicating the occurrence of silicic pyroclastics. This suggestion is also supported by high values of the AM index (0.37–0.38 against 0.27 of the orthoclase norm) and the (Na + K) module (>0.4) in four of 20 mudstone samples from the Karlin Formation and in 17 of 20 mudstone samples from the Staropetrovo Formation (Table 6). In contrast, the overwhelming majority of the analyzed samples show the TM and IM values typical of clayey rocks. Hence, camouflaged mafic pyroclastics are most likely absent in these samples.

Rock composition in the paleodrainage areas can be efficiently reconstructed on the basis of ratios between La, Th, Co, Sc, Cr, Ni, V, Zr, and some other minor elements, which do not change substantially in

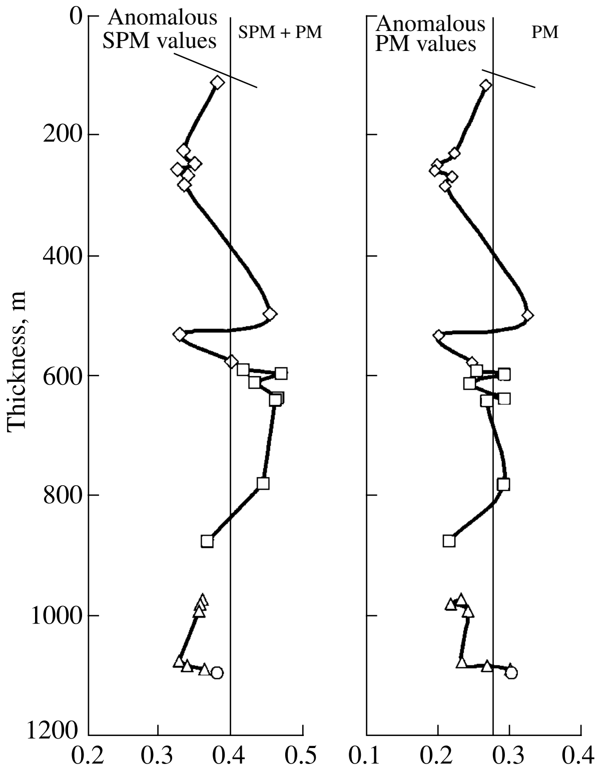

Fig. 8. Variations of SPM and PM modules in mudstones from the Kairovo and Shkapovo groups. See Fig. 3 for legend.

the course of lithogenesis and metamorphism. These elements are poorly soluble in water. Therefore, they are transported from the provenance to sedimentation regions and retained in sedimentary rocks almost without any loss (Nesbitt, 1979, Davis, 1980; Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987; McLennan, 1989; Condie and Wronkiewicz, 1990; Condie, 1993; Girty et al., 1994; Cullers, 1995; Bierlein, 1995; Jahn and Condie, 1995; Panahi and Young, 1997; Bhat and Ghosh, 2000; and others). The Th/Sc, La/Sc, La/Co, Th/Co, Th/Cr, V/Ni, and some other ratios in felsic igneous rocks (granites and granodiorites) are one to two orders of magnitude higher than in mafic rocks (*Interpretatsiya…*, 2001). Conversely, mafic igneous rocks are characterized by one to two orders of magnitude higher values of the Cr/Zr, Cr/V, and some other ratios, relative to felsic rocks. Therefore, these ratios serve as good tools for estimation of the rock composition in paleodrainage areas and its temporal variation.

As has been shown for pelitic rocks of the Kaapvaal Craton (Condie and Wronkiewicz, 1990), the Cr/Th ratio is a much more sensitive indicator of provenance composition than Eu/Eu*, La/Yb, and Th/U. However, it should be kept in mind that the Cr content in sediments may be somewhat modified as a result of weathering and redeposition, and the Cr/Th ratio actually may serve as an indicator of provenance composition only in the case of positive correlation between Cr/Th and Sc/Th. The absence of substantial variation of Cr/Th ratio during a rather long period is regarded as evidence for the stable tectonic regime that provides the efficient mixing of the fine aluminosiliciclastic material on the way of transport (Condie and Wronkiewicz, 1990).

The Cr/Ni ratio is a rather good indicator of ultramafic rocks in provenance areas (Garver et al., 1996). The value of this ratio in pelitic rocks (~1.4) testifies to the erosion of ultramafic rocks in the source area. The Cr/Ni > 2.0 suggests the substantial transformation of the fine terrigenous suspension during the transport.

Our data show that the Th/Sc, Th/Co, Cr/Zr, Cr/V, La/Sc, V/Ni, and Th/Cr ratios are most informative for the reconstruction of rock composition in provenance and its change through time (Maslov et al., 2000, 2004a–2004d).

The Th/Cr ratio in the overwhelming majority of mudstone samples from the Kairovo and Shkapovo groups is typical of the intermediate and acid igneous rocks, such as diorite, granodiorite, and others (Fig. 9). Only in sample IM-2 taken from the upper part of the Salikhovo Formation, this ratio is 2.53, indicating a substantial contribution of granitic or other felsic rocks. At the same time, like in sample IM-1, the Cr/Ni ratio is low (0.28–1.22) in this sample and probably testifies

Table 6. Variation ranges of various modules in mudstones of the Vendian Kairovo and Shkapovo groups in the Shkapovo–Shikhan Basin

Module	Formation			
	Baikibashevo	Staropetrovo	Salikhovo	Karlin
AM	0.20–0.31	0.21–0.38	0.21–0.37	0.20–0.31
TM	0.046–0.051	0.037–0.053	0.043–0.060	0.041–0.059
IM	0.37–0.51	0.39–0.54	0.34–0.57	0.36–0.53
HM	0.29–0.48	0.33–0.59	0.32–0.62	0.26–0.41
PM	0.20–0.30	0.14–0.30	0.21–0.33	0.19–0.32
SPM	0.36–0.41	0.25–0.41	0.37–0.47	0.32–0.45

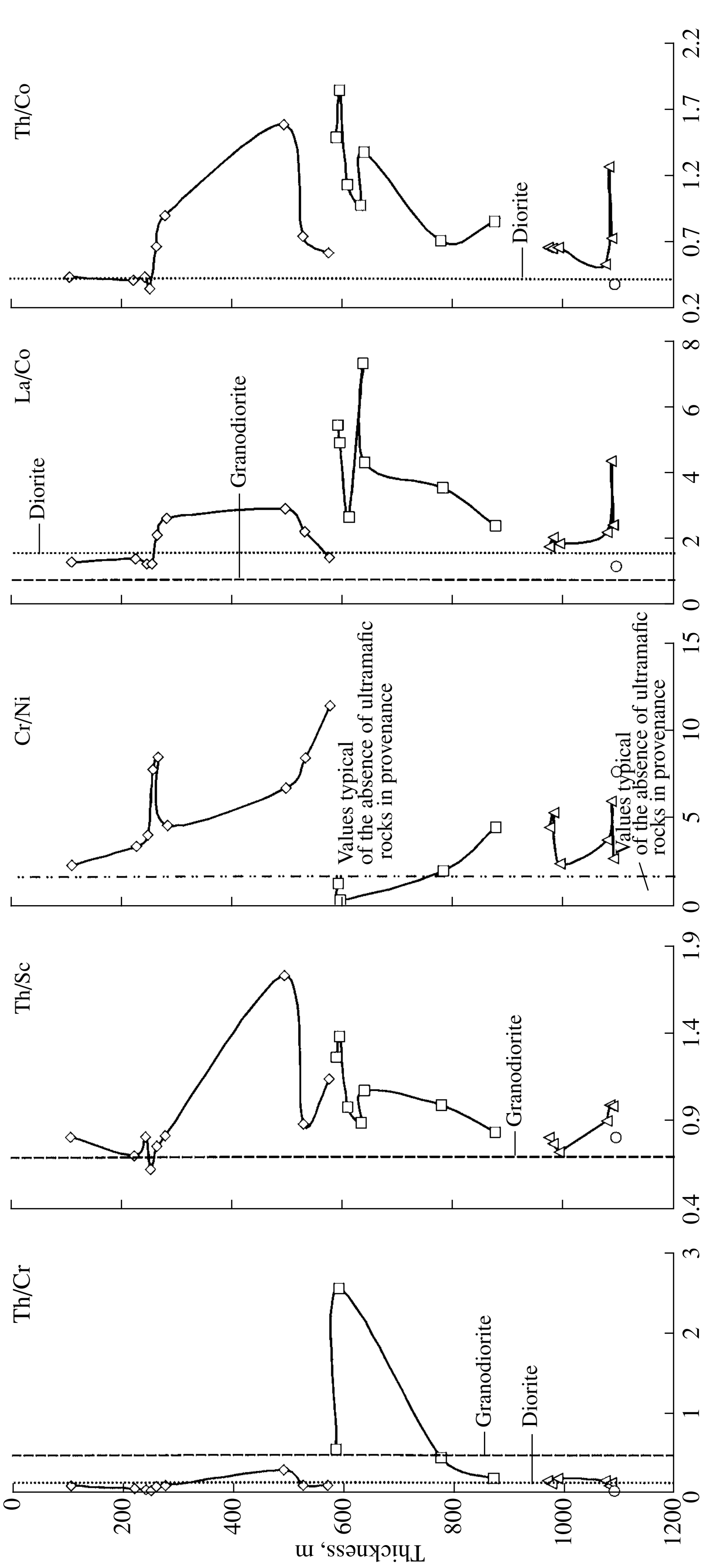

Fig. 9. Variations of ratios of some minor elements and rock compositions in mudstones of the Kairovo and Shkapovo groups in the Shkapovo–Shikhan Basin in paleodrainage areas. See Fig. 3 for legend.

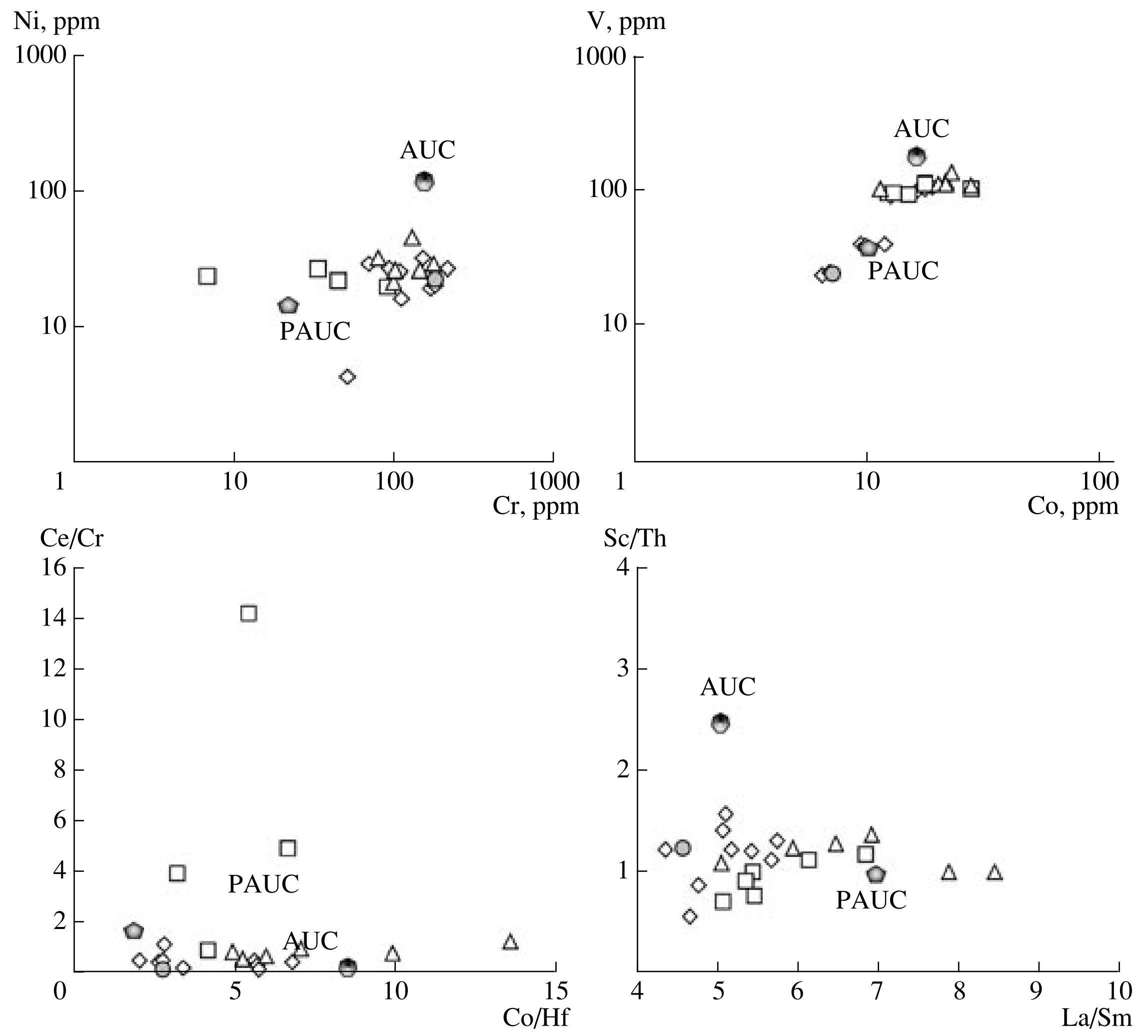

Fig. 10. Compositions of mudstones from the Kairovo and Shkapovo groups plotted on the Cr–Ni, Co–V, Co/Hf–Ce/Cr, and La/Sm–Sc/Th diagrams (Taylor and McLennan, 1985; Dobson et al., 2001). (AUC) Archean upper continental crust; (PAUC) post-Archean upper continental crust. See Fig. 3 for legend.

to erosion of ultramafic rocks in the paleodrainage area in the latest Salikhovo time.

With respect to the Th/Sc ratio, the mudstones occupy a transitional position between the products of erosion of acid and intermediate igneous rocks (Fig. 9). The highest Th/Sc ratio (1.72) was noted in sample IM-17. In general, the Th/Sc ratio in rocks slightly grows from the Baikibashevo and Staropetrovo time (0.72–0.80) to the Salikhovo time, attains 1.26–1.37 by the end of the Salikhovo time, and falls to 0.63–0.81 at the roof of the Karlin Formation.

The Cr/Ni ratio varies from 7.6 to 2.38 in mudstones of the Baikibashevo and Staropetrovo formations. Mudstones from the upper part of the Staropetrovo Formation and the lower part of the Salikhovo Formation are similar in the Cr/Ni ratio (4.48 and 4.45, respectively), whereas this ratio in the Salikhovo Formation decreases upsection to the values typical of products of the erosion of ultramafic rocks. At the base of the overlying Karlin Formation, the Cr/Ni ratio in mudstones is an order of magnitude higher. As in the case of the Salikhovo Formation, this ratio markedly drops upsection, but it remains within the limits typical of the substantial transformation of the fine terrigenous ultramafic suspension on the pathway of transport (Fig. 9).

Finally, the La/Co and Th/Co ratios in Upper Vendian mudstones of the Shkapovo–Shikhan Basin are slightly higher than those in diorites. The highest values of these ratios (7.0–7.5 and 1.7, respectively) are confined to the middle part of the section, i.e., to the upper third of the Salikhovo Formation and the lower third of the Karlin Formation. In the upper third of the Karlin Formation, these ratios are somewhat lower than in diorites.

The average rock composition in paleodrainage areas eroded in the Late Vendian may be estimated from the contents of pairs of minor elements, such as Cr–Ni and Co–V in mudstones (Taylor and McLennan, 1985), as well as from Co/Hf, Ce/Cr, La/Sm, and Sc/Th ratios (Dobson et al., 2001). In the Cr–Ni diagram (Fig. 10),

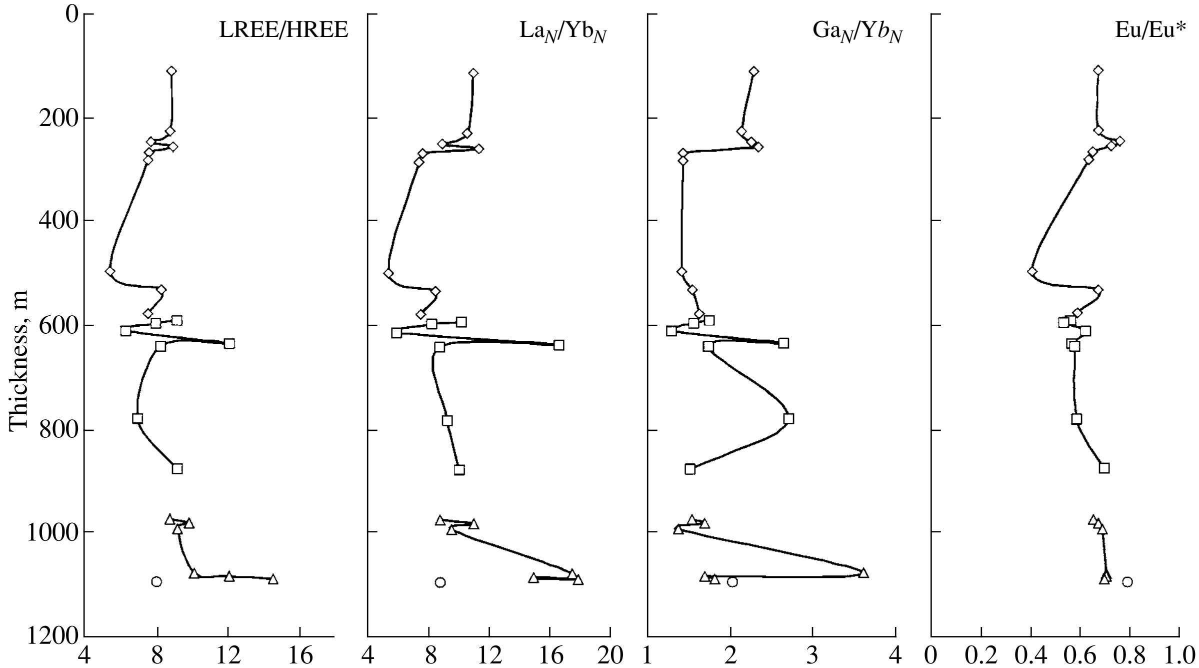

Fig. 11. Variations of LREE/HREE, La_N/Yb_N, Gd_N/Yb_N, and Eu/Eu* ratios in Upper Vendian mudstones of the Shkapovo–Shikhan Basin. See Fig. 3 for legend.

most of the data points of mudstone compositions are localized between the composition of the Archean upper crust (AUC) and the post-Archean upper crust (PAUC). The proportions of Cr and Ni in mudstones of the Salikhovo Formation are closer to the PAUC. Similar arrangement is also typical of the data points of mudstones of the Kairovo and Shkapovo groups in other diagrams shown in Fig. 10. This disposition of the data points shows that the provenances included both blocks dominated by Archean rocks and blocks composed of substantially more mature Paleoproterozoic complexes formed as a result of large-scale granitization of the continental crust of the East European Platform 1.8–1.7 Ga ago (Bogdanova, 1986).

The **rock composition of provenance and type of the eroded upper continental crust** control to a certain extent the diversity of REE patterns in the post-Archean sedimentary rocks (McLennan et al., 1990). Mafic igneous rocks are characterized by low LREE/HREE values and absence of a prominent negative Eu anomaly, whereas high LREE/HREE ratio and distinct negative Eu anomaly (Eu/Eu* < 0.9) are typical of felsic rocks (Taylor and McLennan, 1985; McLennan and Taylor, 1991). The La_N/Yb_N value of <4 and a gently sloping chondrite-normalized REE curve (Gd_N/Yb_N up to 1.5)[4] indicate that mafic igneous rocks dominated in the provenance, whereas $La_N/Yb_N > 8$ and steep slope of the curve suggest that felsic igneous rocks were predominant. High La_N/Yb_N values (≥20) testify to the predominance of granitic rocks in the paleodrainage area (Wronkiewicz and Condie, 1990). According to (Condie, 1991), the average composition of the Archean crust is characterized by the following parameters: La_N/Yb_N = 15.68, Gd_N/Yb_N = 2.04, and Eu/Eu* = 0.83[5]. For the Paleoproterozoic crust, the respective values are 11.50, 1.78, and 0.72.

In our case, the median LREE/HREE ratio for all 23 analyzed samples is 8.9 and this ratio slightly decreases upsection from 14.7 (mudstone sample ISh-17 from the base of the Staropetrovo Formation)[6] to 7.72–7.78 at the base of the upper third of the Karlin Formation (samples ISh-4 and IM-16) (Fig. 11). The La_N/Yb_N ratio varies in mudstones virtually in the same way. The median value of this ratio throughout the section is ~9.3, i.e., close to the estimate of this parameter for the Paleoproterozoic crust (Condie, 1991). The maximum values of both ratios mentioned above are characteristic of the lowermost levels of the Staropetrovo Formation (samples ISh-17 and ISh-18) and mudstone sample IM-4 from the upper third of the Salikhovo Formation. Hence, evolution of the entire Upper Vendian succession of the Shkapovo–Shikhan Basin included the erosion of rocks of the granitoid type in paleodrainage areas only at the earliest Staropetrovo and the latest Salikhovo times. Intermediate rocks were predominant in the provenance over most of the Late Vendian. The

4 The Gd_N/Yb_N ratio, an indicator of the degree of depletion in HREE, governs the slope of the curve in the HREE region.

5 However, according to (Taylor and McLennan, 1995), these parameters are equal to 6.76, 1.38, and 0.99, respectively.

6 The LREE/HREE ratio increases to ~9.3 in the Staropetrovo mudstone located 80–85 m upward the section (sample ISh-14).

Table 7. General features of variation in environmental parameters affecting the Late Vendian sedimentation

General character of fine aluminosiliciclastics	Degree of maturity of fine aluminosiliciclastics	Climatic conditions of sedimentation	Redox conditions of bottom water in the basin
Predominance of the petrogenic (first-cycle) fine aluminosiliciclastics	Gradual decrease of the maturity degree of the fine terrigenous suspension delivered to the basin in the mid-Karlin time and slight increase of the maturity by the end of the Karlin time	Predominance of semiarid and semihumid climate; relatively weak alteration of rocks in paleodrainage areas	Predominance of oxidizing conditions in bottom water throughout the Late Vendian

Influence of submarine exhalations on sedimentation	Effect of camouflaged pyroclastics on sedimentation	Composition of rocks in paleodrainage areas
Absence of the material of submarine volcanic exhalations in sediments	Absence of indications of camouflaged pyroclastics except for several levels in the Staropetrovo, upper Salikhovo, and lower Karlin formations	Predominance of rocks similar in composition with the Paleoproterozoic crust. Presence of both blocks of the Archean primitive crust and more mature Paleoproterozoic complexes in provenances. Appearance of considerable granitic bodies and probably ultramafic rocks at the end of the Salikhovo time

distinct negative Eu anomaly recorded in mudstones throughout the section suggests that these rocks underwent substantial transformation in the crust.

General trends of the alteration of the major parameters of medium, which influenced sedimentation in the Late Vendian basin, are summarized in Table 7.

CONCLUSIONS

Variations of a number of lithochemical modules, indices of compositional variations (CIA, CIW, and ICV), and ratios of several minor elements in mudstones of the Kairovo and Shkapovo groups in the Shkapovo–Shikhan Basin of the Volga–Ural region bear the most complete information on the variation of maturity degree of the aluminosiliciclastic sequence of the basin. They also provide insights into the character of redox environments in the bottom water, the rock composition in provenances, and its temporal evolution. Previously, some of these parameters were mainly based on results of the semiquantitative emission spectroscopy that characterized each lithostratigraphic unit as a whole. Now, the application of the precise ICP-MS and other techniques has made it possible to reconstruct the details of variation of the main sedimentation parameters in the course of the virtually entire Late Vendian evolution.

For example, we have shown that the maturity degree of the fine terrigenous clastic material delivered to the basin gradually decreased during the Baikibashevo–Salikhovo time and did not undergo any significant change in the Karlin time. As follows from the CIA, CIW, and ICV indices, maturity degree of the clastic material was generally moderate, suggesting that the climate in paleodrainage areas was close to the semiarid–semihumid type over the entire Late Vendian.

Based on study of the Upper Vendian sequence of the Belomorian–Kuloi Plateau, we established that the immature clastic material delivered from regions of arid climate is replaced by a more mature aluminosiliciclastic material derived from the areas of mild humid climate (Grazhdankin et al., 2005). As was shown in (Maslov et al., 2004a), the general rock compositions in provenances that served as sources of the fine aluminosiliciclastic material in both the northwestern Mezen Syneclise and the Shkapovo–Shikhan Basin were more or less similar. Hence, the differences mentioned above are most likely caused by the location of these regions in different climatic belts.

We have clearly demonstrated that the Late Vendian sedimentary basin was rather well aerated, and the Domanik or Domanik-type environment did not exist therein. Rocks close in composition to diorite or granodiorite prevailed in paleodrainage areas that surrounded the Shkapovo–Shikhan Basin in the northwest, west, and southwest. Judging from high LREE/HREE and La_N/Yb_N ratios in several mudstone samples, the more silicic rocks could only occur in provenance areas at the initial Staropetrovo and terminal Salikhovo times. The high Gd_N/Yb_N ratio (>2.0) in these samples probably indicates the Archean age of the silicic rocks (Taylor and McLennan, 1985). In contrast, the elevated Gd_N/Yb_N value in the upper third of the Karlin Formation does not correlate with LREE/HREE and La_N/Yb_N. At the same time, the low Cr/Ni ratio in mudstones from the uppermost levels of the Salikhovo Formation probably testifies to a short-term (?) appearance of ultramafic rocks in the source area.

The Eu anomaly in mudstones of the Upper Vendian sequence varies from 0.54 to 0.79. This is typical of the majority of post-Archean shales (Taylor and McLennan, 1985). The Eu minimum is distinct only in mudstones located ~50 m above the base of the Karlin Formation[7].

Localization of data points of mudstones from the Kairovo and Shkapovo groups in the Cr–Ni, Co–V, Co/Hf–Ce/Cr, and La/Sm–Sc/Th plots allows us to suggest that both the Archean and more mature Paleoproterozoic crustal blocks existed in provenances during Late Vendian. Relationships between these blocks changed with time. This is especially evident from the Gd_N/Yb_N, La/Co, and Th/Co ratios distribution in the Karlin Formation. Mudstones from the upper third of this lithostratigraphic unit are characterized by high Gd_N/Yb_N values and, conversely, by relatively low La/Co and Th/Co ratios. In our opinion, these relationships may be interpreted as evidence for predominance of the Archean crust in paleodrainage areas at the end of the Karlin time, whereas the contribution of the Archean crustal blocks was appreciably less at the beginning and middle episodes of the Karlin time. Very low Th and La contents in mudstones from the upper third of the Karlin Formation (samples IM-12, IM-13, IM-14, and IM-15) serve as evidence in favor of this suggestion.

Variation patterns of curves of the majority of lithogeochemical indicators (Figs. 5–9, 11) indicate the existence of both the poorly and highly contrasting segments. They include the uppermost Salikhovo Formation and the base of the upper third of the Karlin Formation. The latter highly contrasting segment is clearly recognized in the Th/Sc, La_N/Yb_N, LREE/HREE, Mo/Mn, Ni/Co, and V/(V + Ni) plots. However, this segment is not expressed in the Th/Cr, V/Cr, and some other plots. Distinct variations of CIW and ICV indices in the uppermost Salikhovo Formation are not correlated with the CIA index. To date, we have only analyzed a relatively small number of samples. Moreover, some intervals in the middle parts of the Staropetrovo, Salikhovo, and Karlin formations have not been sampled. Therefore, it is difficult to decide whether the contrasting variation of geochemical indicators is characteristic of the entire Upper Vendian sequence in the Shkapovo–Shikhan Basin or it is only typical of separate fragments. If the first scenario will turn out to be correct, the conclusions drawn in this work will be less valuable. The second scenario has a higher correlation potential. Hence, the study in this direction must be continued.

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[7] This intriguing phenomenon will be a subject of special publication.

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