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Variations of Eu/Eu* Ratio in Vendian Shales of the Volga–Ural Region and the Boundary Traced between the Redkino and Kotlin Horizons

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Abstract—Variations of Eu/Eu* ratio in shales from the upper Vendian Kairovo and Shkapovo groups of the Shkapovo–Shikhan depression, the Volga–Ural region, are considered. Shales in the lower part of the Karlin Formation are established to be similar in geochemistry to the shale member with abnormally low Eu/Eu* ratios at the base of the Upper Vendian Kotlin Horizon of the East European Platform. According to these data, the studied formation appears to be a lithostratigraphic unit of the Kotlin Horizon, while the Baikibashevo, Staropetrovo and Salikhovo formations belong to the Redkino Horizon of the upper Vendian.

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Key words: Eu/Eu* ratio, shales, Upper Vendian, the Shkapovo–Shikhan depression of the Volga–Ural region, Redkino Horizon, Kotlin Horizon.

One of the topical problems of the Late Precambrian stratigraphy in the Volga–Ural region is to trace boundaries between the Redkino, Kotlin and Rovno horizons of the Upper Vendian and to substantiate their stratigraphic ranges in eastern areas of the East European Platform based on interchangeable indications (*Stratigraphic Scheme*…, 2000). The enhanced resolution and substantiation of subdivision and correlation schemes of Upper Precambrian deposits are necessary for more efficient works aimed at assessment of oil-and-gas potential in the Riphean sedimentary sequences.

REGIONAL STRATIGRAPHY

The Upper Vendian deposits are widespread the eastern Verkhnekamsk and Shkapovo–Shikhan depressions of the East European Platform (*Stratotype of the Riphean*…, 1983; Aksenov, 1998; *Stratigraphic Scheme*…, 2000; and others).

In the Verkhnekamsk depression, Vendian deposits are divided into the Borodulino and Kudymkar groups attributed by Klevtsova (1965) to the Las'va Complex. In the Shkapovo–Shikhan depression, concurrent deposits are represented by the Kairovo and Shkapovo groups of the Bizhbulyak complex.

The Kykva and Vereshchagino formations are distinguished in the Borodulino Group; the Velva and Krasnokamsk formations in the Kudymkar Group. The Kykva Formation is composed of polymictic sandstones and siltstones with interlayers and members of conglomerates, gritstones and dark-colored shales. It is up to 111 m thick. The Vereshchagino Formation is represented by gray shales and light gray polymictic siltstones with rare sandstone interlayers. Imprints of the Ediacaran fauna were found in shale samples from some borehole sections of the Vereshchagino Formation that is up to 380 m thick. The Velva Formation 315 m thick at maximum includes dark gray to variegated shales, gray to light gray siltstones and glauconite sandstones. The Krasnokamsk Formation (about 500 m thick) is composed of red and variegated sandstone and siltstone beds of polymictic or feldspar–quartz composition and of subordinate shale intercalations.

Lagutenkova (1963) described ash tuff interlayers in upper Vendian deposits and established presence of ash admixture in silty sediments in the southern part of the Verkhnekamsk depression. By visual examination, ash tuffs are hardly distinguishable from normal sedimentary rocks, and their pyroclastic nature is established under the microscope only. Among these rocks, there are vitroclastic and crystal-lithoclastic tuffs of peculiar composition. Vitroclastic varieties consist of very fine, acute-angled or irregularly shaped fragments of volcanic glass; prismatic idiomorphic plagioclase laths occur sometimes as well. Angular fragments of quartz (5–7%) and plagioclase (up to 10%), along with calcitized and/or chloritized porphyrite fragments usually lacking clear boundaries (up to 28–29%), are dominant components of crystal-lithoclastic tuffs. The brownish green groundmass of the rocks represents, most likely,

a highly altered volcanic glass (aggregate of chlorite, zeolite or hydromica). In Lagutenkova's opinion, ash tuffs in Vendian deposits of the Verkhnekamsk depression are derivatives of andesite-basaltic volcanism. Ash tuffs are dated by the K–Ar method at about 580 Ma (*Explanatory Note*…, 2000). As is shown in an early work (Balashova and Il'inykh, 1967), pyroclastic and pyroclastic-sedimentary rocks are characteristic of upper Vendian deposits of the whole Verkhnekamsk depression.

The Kairovo and Shkapovo groups of the Shkapovo–Shikhan depression include the Baikibashevo and Staropetrovsk and the Salikhovo and Karlin formations respectively. The Baikibashevo Formation is represented by greenish to pinkish gray or brown inequigranular polymictic and quartz–feldspar sandstones with gravely clasts and pebbles, which are intercalated with subordinate siltstone and shale interlayers. The formation is up to 130 m thick. The Staropetrovo Formation corresponds to greenish gray shales with interlayers and microlaminae of light gray siltstone, chocolate-brown shale and, more rarely, gray polymictic fine-grained sandstone. The formation thickness varies from 80 to 300–400 m. The Salikhovo Formation comprises brown to red-brown and greenish gray (in the lower part), mainly fine-grained polymictic sandstones and siltstones with intercalated red beds of shales. The maximal thickness of the formation is up 350 m. The Karlin Formation is similar in composition to the Staropetrovo Formation. Its thickness exceeds 600 m in the most complete sections (*Stratotype of the Riphean*…, 1983; *Stratigraphic Scheme*…, 2000; and others).

The Las'va Complex of the Verkhnekamsk depression is unambiguously correlated with type sections of upper Vendian deposits in the Moscow syneclise (Aksenov et al., 1999; *Stratigraphic Scheme*…, 2000). For instance, the Kykva and Vereshchagino formations comprising tuff horizons correspond most likely to the Redkino Group (Horizon). The Velva and Krasnokamsk formations are correlated to the Lyubim and Reshma formations respectively. The lower boundary of the Kotlin Horizon, which is placed at the base of the Lyubim Formation in the Moscow syneclise, corresponds to the Velva Formation base in the Verkhnekamsk depression.

The Bizhbulyak Complex of the Shkapovo–Shikhan depression is similar in stratigraphic position, structure, and lithology to the Asha Group in the western flank of the Southern Urals. In this case, the Baikibashevo Formation is correlated with the Uryuk Formation of the Asha Group of the Bashkirian meganticlinorium, the Staropetrovo Formation with the Basa Formation, the Salikhovo Formation with the Kukkarauk Formation, and the Karlin Formation with the Zigan Formation (*Stratotype of the Riphean*…, 1983; Aksenov et al., 1999; *Stratigraphic Scheme*…, 2000). On the other hand, the Bizhbulyak Complex is also correlated well with the Las'va Complex of the Verkhnekamsk depression. In opinion of many researchers, correlation between the Baikibashevo and Kykva, Staropetrovo and Vereshchagino, Salikhovo and Krasnokamsk formations is doubtless not only because of similar lithology and position in the succession, but also owing to presence of reference tuff horizons, identical microfossil assemblages, and close isotopic ages (Aksenov et al., 1999; *Stratigraphic Scheme*…, 2000). At the same time, the Kotlin Horizon base reliably traceable in the Verkhnekamsk depression is hardly distinguishable in the Shkapovo–Shikhan depression within a thick and rather monotonous succession of alternating siltstones, shales, and fine-grained sandstones of the Staropetrovo Formation. The succession contains microfossils of the Redkino affinity at the lower levels, whereas microfossils typical of the Kotlin Horizon occur at the upper levels (*Stratigraphic Scheme*…, 2000). There are alternative viewpoints however. For instance, Klyuzhina (1990) believes that there are no analogs of the Kotlin and Rovno horizons in the Urals, and Kozlov (1990) attributed, without serious reasoning, the Kairovo Formation to the Lower Vendian and the Shkapovo Group together with the Kudymkar Formation to the Upper Vendian.

As it follows from the aforesaid, a search for additional independent evidence clarifying position of the Kotlin Horizon base in Vendian sections of the Volga–Ural region and the Urals is a timely problem.

Felitsyn and Sochava (1996) showed that the problem could be probably solved based on geochemical peculiarities of Vendian sedimentary rocks, in particular, on the europium anomalies (Eu/Eu*) characterizing fine-grained siliciclastic sediments. The use of this approach became possible recently owing to availability of the ICP-MS analytical method to research practice.

RESULTS AND DISCUSSION

In the mid-1990s, study of europium anomaly variations in the Upper Vendian shales of the East European Platform revealed in a series of separate sections (Rybnitsa, Kostovo, Tuchkino, and others) a peculiar shale member 20 to 30 m thick, confined to the boundary between the Kotlin and Redkino horizons. Characteristic of the member are the distinct europium anomaly (0.19–0.46) and Th/Co ratio of about 1.4 (Fig. 1) that is considerably higher (Felitsyn and Sochava, 1996) than the reference PAAS value of 0.63 accepted for the post-Archean Australian shale. Petrographic and geochemical data on the analyzed rocks show that silicic tephra is an important component of their composition. As the mentioned europium anomaly in upper Vendian shales could be interrelated in origin with a short-term volcanic event widely manifested in the East European Platform, fine-grained siliciclastic rocks displaying this geochemical feature can be used as rather powerful and

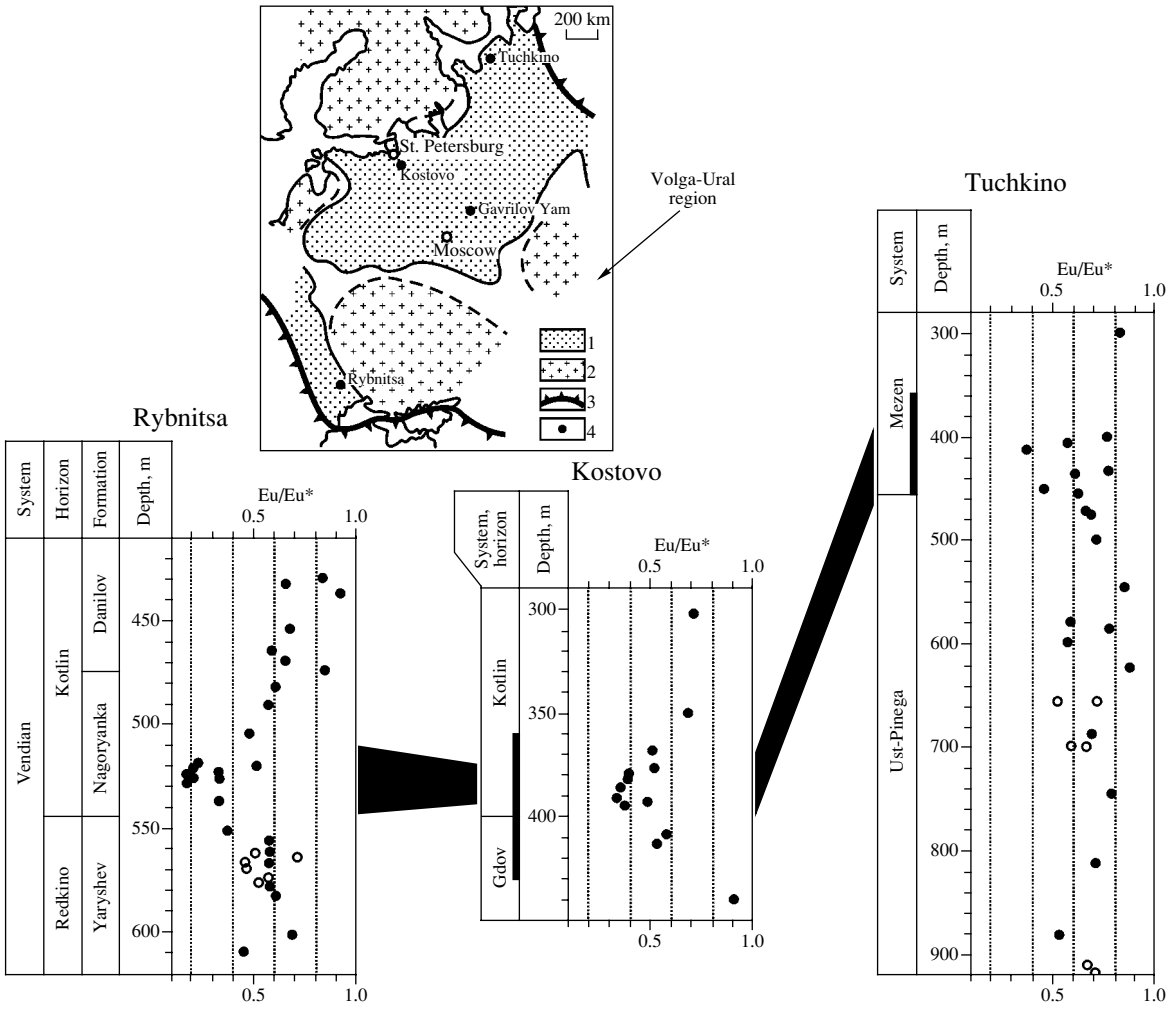

Fig. 1. Eu/Eu* ratios in shales (black circles) and silicified tuffs (open circles) from borehole sections Rybnitsa, Kostovo, and Tuchkino (after Felitsyn and Sochava, 1996, with modifications); dark bands between diagrams denote stratigraphic interval with abnormally low Eu/Eu* ratios in shale, and black vertical bar designates range of the Lower Kotlin microfossil assemblage (palynozone K_1 after Burzin et al., 1990). Symbols in the inset map: (1) Late Vendian sedimentation basins; (2) intracratonic provenances; (3) platform boundary; (4) borehole site.

attractive tool for subdivision and correlation of distant sections.

Several intervals of silicified tuffs and bentonitic clay occur below this member in most complete Vendian successions of the East European Platform (Felitsyn and Sochava, 1996). It is also shown that in borehole sections Kostovo (depth of 370 to 400 m), Rybnitsa (510–550 m), and Tuchkino (400–440 m), the shale member with anomalously low values of europium anomaly coincides with palynozone K_1, which characterizes lowest levels of the Kotlin Horizon (Burzin et al., 1990). Accordingly, Felitsyn and Sochava suggested that the mentioned member should be used as an independent criterion determining the boundary between the Kotlin and Redkino horizons and thus useful for correlation of distant Upper Vendian sections.

It should be noted for the sake of truth that Felitsyn and Sochava identified stratigraphic level of abnormally low Eu/Eu* values within the depth interval of 2450–2500 m, i.e., in the middle part of the Ust-Pinega Formation, as they concluded, while in the modern stratigraphic interpretation (*Stratigraphic Scheme*…, 1996) it corresponds to the Nepeitsino Formation of the Redkino Horizon. Consequently, the indicative significance of europium anomaly, Felitsyn and Sochava (1996) argued for, appears to be doubtful to some extent, requiring further substantiation and analysis of latest data on distribution of organic-walled microfossil assemblages in Upper Vendian deposits on the East European platform. Nevertheless, it seems reasonable to determine, prior to that analysis, a possible position of boundary between the Redkino and Kotlin horizons using the level with low Eu/Eu* ratios in Vendian shales of the Volga–Ural region.

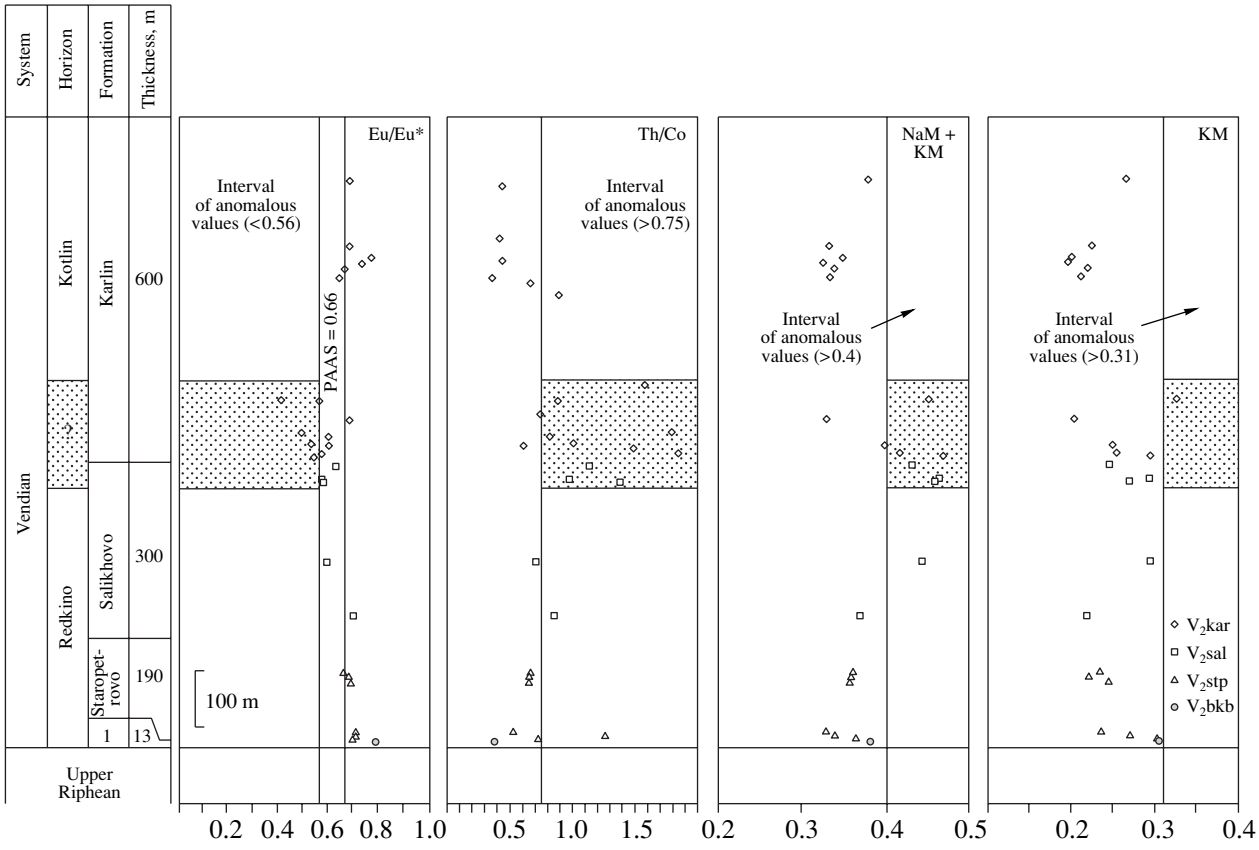

Fig. 2. Variations of Eu/Eu*, Th/Co, NaM + KM, and KM through the composite section of upper Vendian deposits in the Shkapovo–Shikhan depression, the Volga–Ural region; data points characterize samples from the Kipchak-1, Akhmerovo-6, Severokushkul-1 boreholes, and shaded interval corresponds to shales with silicic pyroclastic admixture and anomalous Eu/Eu* values: (1) Baikibashevo Formation.

We selected for analysis more than 30 samples of shales from borehole sections Kipchak-1, Akhmerovo-6, and Severokushkul-1, which penetrated through the Baikibashevo, Staropetrovo, Salikhovo and Karlin formations. The analyzed core samples are from collection of M.V. Isherskaya (Table 1).

After preliminary macro- and microscopic examination of samples, the content of petrogenic oxides was determined on spectrometer SRM-18 by the XRF method. Data on chemical composition were used to determine mudstones and shales proper among the studied samples, as is described by Herron (1988). After all the mentioned operations, concentrations of 52 trace elements, 14 REE included, were determined in 27 shale samples by the ICP-MS method on the Element 2 mass spectrometer (O.P. Lepikhina and O.Yu. Popova, Institute of Geology and Geophysics, Uralian Division RAS, performed chemical treatment of samples before trace-element analysis).

The analytical results showed that the Eu/Eu* value in shales of the Baikibashevo Formation (one sample) corresponds to 0.79 (Table 2). This value is substantially higher than that typical of the PAAS (0.66) (Taylor and McLennan, 1988) or clays of the East European Platform (0.70) (Migdisov et al., 1994). It suggests that rocks at the sampled level contain most likely some admixture of feldspar or fine aluminosilicate clastic material derived by erosion from a primitive (Archean?) substratum. The Eu/Eu* median value for fine-grained clayey rocks of the Staropetrovo Formation (six samples) is equal to 0.70. Individual Eu/Eu* values range from 0.70 to 0.71 in the lower part of the sampled interval of the Staropetrovo Formation and from 0.66 to 0.69 in the upper part (Fig. 2),[1] being rather close to the value characteristic of the PAAS.

In most shale samples from the Salikhovo Formation occupying higher interval in the section, Eu/Eu* ratios are ~0.58, although the europium anomaly is less distinct in the lowermost part of this interval of the Shkapovo Group.

One shale sample (IM-2) from the lowermost part of the Karlin Formation (~6 m from the formation base) yielded the Eu/Eu* ratio equal to 0.54. Higher in the

[1] Fig. 2 is plotted for a composite section of the Kairovo and Shkapovo groups, and position of each sample is verified relative to the formation base and the top of Upper Vendian succession as well. The total thickness of composite section is accepted to be 1103 m.

Table 1. Stratigraphic levels and brief characterization of analyzed samples

Formation	Borehole	Interval, m	Sample no.	Thickness above formation base, m	Thickness below top of Upper Vendian composite section	Brief characterization
Karlin	Kipchak-1	2374.6–2376.8	IM-12	490	110	Homogeneous dark chocolate-brown shale
		2463–2466	IM-13	375	225	Dark gray shale with thin horizontal lamination
		2506–2509	IM-14	355	245	Gray homogeneous shale with vague thin lamination
		2531–2535	IM-15	345	255	Gray fine-laminated shale with thin silt lenses
		2537–2541	IM-16	335	265	Gray shale with obscure horizontal lamination
		2557–2559	ISh-4	320	280	Greenish gray shale with horizontal and lenticular lamination
		2750–2755	IM-17	105	495	Chocolate-brown massive (homogeneous) shale
			51	104	496	
		2790–2792	IM-18	70	530	Gray homogeneous shale
		2811–2813	57	48	552	
		2818–2820	59	41	559	Greenish gray shale
		2830–2833	61	29	571	
		2833–2837	IM-19	25	575	Gray massive shale
	Akhmerovo-6	2285–2289	IM-1	11	589	Chocolate-brown shale with wavy, hummocky-cross, and flaser lamination
		2289–2294	IM-2	6	594	Chocolate-brown shale with indistinct lamination
Salikhovo		2304–2306	IM-3	293	610	Chocolate-brown shale with indistinct horizontal lamination
		2329–2332	IM-4	269	634	Massive chocolate-brown shale
		2333–2337	IM-5	263	639	Chocolate-brown shale with thin silt lenses
	Severokush-kul-1	1977.4–1985	ISh-7	124	779	Gray massive (homogeneous) shale
		2071.8–2080.1	IM-27	29	874	Greenish gray massive shale
Staro-petrovo		2168.7–2176	IM-28	122	971	Greenish gray massive shale
		2176.6–2185.6	IM-29	114	979	Dark greenish gray shale
		2185.6–2193	ISh-14	103	990	Chocolate-brown homogeneous shale
		2272.6–2281.1	IM-31	18	1075	Dark greenish gray, massive, homogeneous shale
		2281.1–2285	ISh-16	11	1082	Gray homogeneous fine-grained siltstone
		2285–2293.5	ISh-17	6	1087	
Baikiba-shevo		2294.7–2299.7	IM-32	10	1093	Dark gray shale with fine horizontal lamination

Table 2. Petrochemical and geochemical characteristics of Upper Vendian shales from the Shkapovo–Shikhan depression

Formation	Samples	NaM + KM	KM	Th/Co	Eu/Eu*
Karlin	IM-12	0.376	0.264	0.42	0.68
	IM-13	0.33	0.222	0.40	0.68
	IM-14	0.346	0.197	042	0.77
	IM-15	0.322	0.194	0.34	0.73
	IM-16	0.336	0.218	0.65	0.66
	Ish-4	0.331	0.209	0.88	0.64
	IM-17	0.450	0.324	1.57	0.41
	51	–	–	0.87	0.56
	IM-18	0.327	0.201	0.73	0.68
	57	–	–	1.78	0.49
	59	–	–	0.80	0.60
	61	–	–	0.99	0.53
	IM-19	0.398	0.247	0.60	0.60
	IM-1	0.415	0.253	1.47	0.57
	IM-2	0.467	0.292	1.82	0.54
Salikhovo	IM-3	0.430	0.244	1.12	0.63
	IM-4	0.462	0.291	0.96	0.57
	IM-5	0.458	0.267	1.36	0.58
	Ish-7	0.443	0.292	0.69	0.59
	IM-27	0.367	0.217	0.84	0.70
Staropetrovo	IM-28	0.360	0.234	0.65	0.66
	IM-29	0.357	0.22	0.64	0.68
	Ish-14	0.356	0.244	0.64	0.69
	IM-31	0.329	0.235	0.52	0.71
	Ish-16	0.339	0.270	1.26	0.71
	Ish-17	0.364	0.302	0.72	0.70
1	IM-32	0.381	0.304	0.38	0.79

Note: (1) Baikibashevo Formation; (–) module not calculated.

section, within the interval of 11 to 105 m above the Karlin Formation base, both the normal (0.68) and anomalous (0.53–0.41) Eu/Eu* values are established in a series of samples (IM-1, IM-17–IM-19). The lowest value (0.41) is determined in sample IM-17 taken 105 m above the Karlin Formation base. The mentioned anomalous Eu/Eu* values nearly correspond to those reported by Felitsyn and Sochava (1996) for the shale member marking the lower level of the Kotlin Horizon in the Upper Vendian sections of the East European Platform. It is also remarkable that the Th/Co ratio in a series of shale samples from the lower part of the Karlin Formation (IM-2, 57; IM-17, and others) and from the upper part of the Salikhovo Formation (IM-3, IM-4, and IM-5) is as high as 0.76–1.8 and even higher (see Table 2). According to inference of Felitsyn and Sochava (1996), this is also indicative of a substantial content of the silicic pyroclastic material in their composition. In the Si/Al–Zr diagram (Borkhvardt and Felitsyn, 1992), a fair quantity of data points characterizing shales from the Karlinskoe and Staropetrovo formations and some rocks of the Salikhovo Formation are localized beyond the field of siliciclastic sedimentary rocks of the Redkino Horizon. Based on compositional parameters ($3 < SiO_2/Al_2O_3 < 5.5$ and $Zr < 170$ g/t), they can be regarded as rocks with some admixture of silicic (rhyolite) tephra.

For further diagnosis of the so-called cryptic silicic pyroclasts in fine-grained siliciclastic rocks, we also used a series of other petrochemical criteria (Yudovich et al., 1984, 1986), such as anomalously high (> 0.4) sodium ($NaM = Na_2O/Al_2O_3$) and potassium ($KM = K_2O/Al_2O_3$) modules, the KM values exceeding the muscovite norm (0.31), and others. The analyzed variations of NaM + KM and KM values in the Upper Vendian succession of the Shkapovo–Shikhan depression (see Fig. 2) show that the KM value exceeds the muscovite norm only in sample IM-17, which yielded (see

above) an extreme value of Eu anomaly. The sum of NM and KM values exceeds the threshold value mentioned above in most samples: ISh-7, IM-5, IM-4, IM-3 (the Salikhovo Formation) and IM-2, IM-1, IM-17 (the Karlin Formation). In the other shales studied, NaM + KM and KM values correspond to those characteristic of ordinary sedimentary rocks (Yudovich et al., 1984, 1986). This is an emphatic illustration of silicic pyroclastic admixture to shales in the lower part of the Karlin Formation and in the upper part of the Salikhovo Formation. At the same time, the Ti and Fe modules of most samples are typical of ordinary clay rocks, and hence, they are most likely lacking cryptic pyroclastic material.

Higher stratigraphic levels of the Karlin Formation are represented by shales with the Eu/Eu* value comparable with that characteristic of the post-Archean shales.

Thus, we can discriminate a shale member with varying Eu/Eu* ratios, anomalous ones included, which spans the uppermost part of the Salikhovo Formation and the lower (100–110 m) interval of the Karlin Formation in the Shkapovo–Shikhan depression. By geochemical features, shales of this member are comparable to shales marking the boundary between the Upper Vendian Redkino and Kotlin horizons in the East European Platform (Felitsyn and Sochava, 1996). An area of active explosive volcanism, which existed in the Late Vendian within the Timan orogen, was most likely the source of silicic pyroclastic material (*Vendian System*…, 1985; Aksenov, 1998; Gee and Pease, 2004; and others).

CONCLUSIONS

All the aforesaid indicates that the shale member 130–140 m thick with extremely low, anomalous Eu/Eu* values is detectable in the Upper Vendian succession of the Shkapovo–Shikhan depression of the Volga–Ural region and in Upper Vendian deposits on the East European Platform penetrated by the Rybitsa, Kostovo, and Tuchkino boreholes. The member can be regarded, with some reservations, as stratigraphic marker enabling subdivision of Upper Vendian deposits in the territory under consideration into the Redkino and Kotlin horizons. If this assumption is correct, then the Karlin Formation (and, probably, the uppermost part of the Salikhovo Formation), arbitrarily attributed before to the upper part of the Kotlin and Rovno horizons (*Stratigraphic Scheme*…, 2000), belongs to the Kotlin Horizon in the Shkapovo–Shikhan depression, whereas the Baikibashevo, Staropetrovsk, and Salikhovo (greater part) formations represent deposits of the Redkino Horizon. Since most researchers correlate reliably the Karlin Formation with the Zigan Formation of the Bashkirian meganticlinorium (*Stratotype of the Riphean*…, 1983; *Stratigraphic Schemes*…, 1993; *Stratigraphic Scheme*…, 2000; and others), the latter can also be regarded as a lithostratigraphic unit of the Upper Vendian Kotlin level. In such interpretation, the Kukkarauk and Basa formations of the Southern Urals western flank belong most likely to the Redkino Horizon.

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