ISSN 1028-334X, Doklady Earth Sciences, 2006, Vol. 411, No. 8, pp. 1267–1271. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.V. Maslov, Yu.L. Ronkin, M.V. Isherskaya, O.P. Lepikhina, 2006, published in Doklady Akademii Nauk, 2006, Vol. 410, No. 6, pp. 799–803.

GEOCHEMISTRY

# REE Systematics and Nd Model Age of Upper Vendian Argillites of the Shkapovo–Shikhan Depression

**Corresponding Member of the RAS A. V. Maslov[a], Yu. L. Ronkin[a], M. V. Isherskaya[b], and O. P. Lepikhina[a]**

Received March 6, 2006

**DOI:** 10.1134/S1028334X06080241

The Shakapovo–Shikhan Depression—one of the largest in the eastern part of the East European Platform—is filled with Upper Vendian sedimentary rocks of the Bizhbulyak Complex about 1.6–1.8 km in total thickness. The depression is framed by the Orenburg, Tatar, and Komi–Permyak arches in the southwest, west, and northwest, respectively. These arches are composed of the Archean (~80% of total area of ancient drainage basin [2]) and Paleoproterozoic crystalline rocks. According to the seismostratigraphic data [3], the Upper Vendian sedimentary rocks give way eastward to the coeval Asha Group of the Bashkir Anticlinorium. The transition occurs via a system of fold–thrust dislocations.

Different aspects of the formation of the Upper Vendian rocks in the Shkapovo–Shikhan Depression were considered by E.M. Aksenov, M.M. Aliev, M.M. Balashova, Yu.R. Bekker, T.V. Belokon, I.K. Chepikova, Z.P. Ivanova, T.V. Ivanova, A.A. Klevtsova, N.S. Lagutenkova, R.Kh. Masagutov, S.G. Morozov, L.D. Ozhiganova, I.E. Postnikova, and other researchers. According to their data, the Archean garnet and biotite–plagioclase gneisses of the Tatar Arch served as the main source of clastic material during the deposition of the Baikibashevo and Staropetrovo formations [4, 5, and others]. Furthermore, it is suggested that the Salikhovo and Karlin times were marked by the transport of clastic material from the east, where the Riphean, Lower Vendian, and initial Upper Vendian metasedimentary rocks were eroded [4, 6]. This interpretation was based on mineralogical and petrographic data.

The systematics of rare earth elements (REE) and estimation of the Nd model age for the fine-grained terrigenous rocks of the Bizhbulyak Complex allowed us to get principally new information on the composition of rocks, their relationships in the paleodrainage basin, and the contribution of the western and eastern provenances to the formation of the sedimentary sequence of the Shkapovo–Shikhan Depression in the Late Vendian.

The Bizhbulyak Complex comprises (from bottom to top) the Baikibashevo, Staropetrovo, Salikhovo, and Karlin formations [1]. The Baikibashevo Formation (10–85 m thick) is composed of sandstone, gravelstone, and fine-pebble conglomerate, as well as silty sandstone and silty argillite mainly occurring in its upper portion. The Staropetrovo Formation (85–320 m) consists largely of siltstone and argillite with a variable amount of sandy material as separate interbeds and members or dissemination. The Salikhovo Formation (100–450 m) comprises sandstone and siltstone with subordinate argillite interbeds. The Karlin Formation (0–600 m) is made up of argillite with interbeds and packets of lighter colored siltstone and sporadic sandstone. The K–Ar age of glauconite from silty sandstone of the Staropetrovo Formation is ~595 Ma. Glauconite from sandstone and siltstone of the Basa Formation was dated with the same method at 600–557 Ma [7]. In the unified stratigraphic chart of Vendian sequences in the Volga–Ural province, the Baikibashevo Formation is correlated with the Uryuk Formation; the Staropetrovo Formation, with the Basa Formation; the Salikhovo Formation, with the Kukkarauk Formation; and the Karlin Formation, with the Zigan Formation of the Bashkir Anticlinorium [1].

More than 40 argillite samples that represent all formations of the Upper Vendian were taken from cores of boreholes Kipchak-1, Akhmerovo-6, and Severokushkul-1 (Fig. 1) for isotopic and geochemical studies. After macroscopic and microscopic examination of the samples, we determined the contents of major oxides in them and omitted the samples for which the data points did not fall into the shale field in the $\log(SiO_2/Al_2O_3)$–$\log(Fe_2O_3/K_2O)$ diagram proposed by Herron [8]. In the remaining 23 samples, the REE contents were determined with acid decomposition and subsequent

[a] *Zavaritsky Institute of Geology and Geochemistry, Uralian Division, Russian Academy of Sciences, Pochtovyi per. 7, Yekaterinburg, 620151 Russia; e-mail: maslov@igg.uran.ru*

[b] *Institute of Geology, Ufa Scientific Center, Russian Academy of Sciences, ul. Karla Marksa 16/2, Ufa, 450000 Russia*

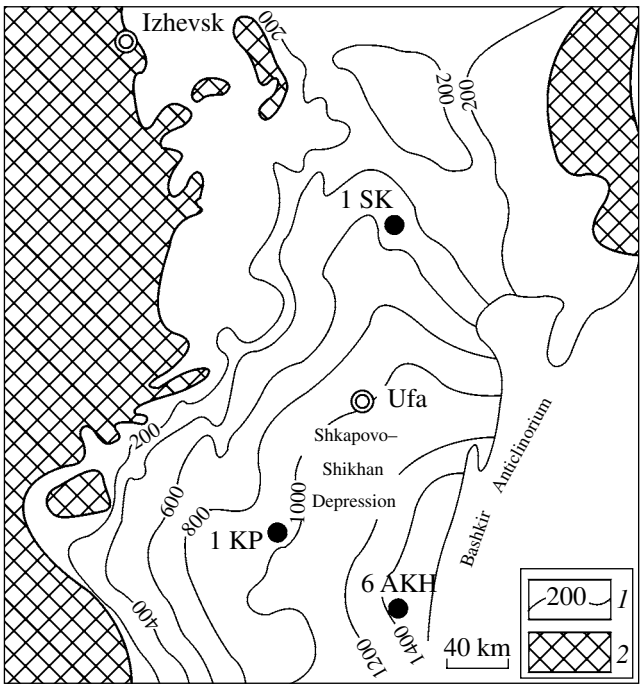


**Fig. 1.** Schematic structure of the Shkapovo–Shikhan Depression and location of the studied deep boreholes: (SK 1) Severokushkul-1, (KP 1) Kipchak-1, (AKH 6) Akhmerovo-6. (*1*) Isopachs of Upper Vendian rocks; (*2*) areas devoid of Upper Vendian rocks.

measurements on an HR ICP-MS Element2 tandem high-resolution analyzer with ionization in the induced coupled plasma [9]. The concentrations and isotopic compositions of Sm and Nd were determined in 10 samples of this series. The uncertainty of the elemental analysis was not worse than ±(3–8) rel. % if the content of an element was more than 10–20 detection limits.

According to the XRD data, argillites of the Bizhbulyak Complex consist of $2M_1$ and 1M hydromicas, mixed-layer silicate (illite–smectite), Fe–Mg chlorite, and kaolinite. The rocks contain an admixture of quartz, plagioclase, and microcline grains of a fine silt dimension.

The positive correlation between lithochemical modules TM = $TiO_2/Al_2O_3$ and FM = $(Fe_2O_3 + FeO + MnO + MgO)/SiO_2$, on the one hand, and the negative correlation between modules SPM = $(Na_2O + K_2O)/Al_2O_3$ and HM = $(Al_2O_3 + TiO_2 + Fe_2O_3 + FeO)/ SiO_2$, on the other, indicate that the rocks underwent only one sedimentation cycle [10] and that their lithogeochemical features may be used for reconstruction of the paleodrainage basin.

The total REE content in particular argillite samples from the Bizhbulyak Complex varies from 43 to 590 ppm. The median value of the total REE content (ppm) for the separate formations is as follows: 210 for the Staropetrovo Formation, 280 for the Salikhovo Formation, and 77 for the Karlin Formation. The general median value of the total REE content in the Upper Vendian argillites in the Shkapovo–Shikhan Depression is 190 ppm, i.e., somewhat higher than in the post-Archean Australian Shale (PAAS).

The LREE/HREE ratio in the studied samples varies from 5.56 to 14.69 (median value for the complex as a whole is 8.91). The silty argillites of the Baikibashevo Formation are characterized by LREE/HREE = 8.13. The median values of this parameter for the fine-grained terrigenous rocks from the other three formations are 10.11, 8.41, and 7.92, respectively.

The median value of Eu/Eu* for argillites of the Bizhbulyak Complex is 0.68. The negative Eu anomaly increases upsection from 0.79 in the silty argillites of the Baikibashevo Formation to 0.68 in the fine-grained terrigenous rocks of the Karlin Formation. However, the lowest Eu/Eu* median value of 0.58 was established in the Salikhovo Formation.

The REE patterns of argillites from the Bizhbulyak Complex are characterized by their appreciable depletion in HREE and a prominent Eu minimum. The former property is typical of the Baikibashevo argillites, the major portion of argillites of the Karlin Formation, and some samples from the Salikhovo Formation (Fig. 2). The median $Gd_N/Yb_N$ value is 2.04 for rocks of the Baikibashevo Formation and varies upsection from 1.65 to 1.75. In contrast, this parameter is equal to 1.38 for the average Archean argillite and 1.36 for the PAAS [11]. Since the HREE-depleted argillites are often products of erosion of the primitive (tonalite–trondhjemite–granite) Archean rocks [11, 12], the geochemical features mentioned above suggest an abundance of HREE-depleted rocks in provenances that supplied the fine aluminosilicate clastic material to the Bizhbulyak Complex.

In the Ce/Cr–Co/Hf diagram, most data points of the Bizhbulyak argillite fall into the region located between the average Archean argillite and PAAS in terms of the Ce/Cr ratio (Fig. 3). At the same time, the argillites of the Salikhovo Formation are characterized by Ce/Cr values an order of magnitude higher. In terms of the Co–Hf ratio, the studied rocks are much closer to PAAS than to the Archean argillite. In the Sc–Th diagram, the argillites of the Bizhbulyak Complex are subdivided into two groups. The first group with Sc and Th contents lower than in the Archean argillite is composed of silty argillites of the Baikibashevo Formation and some argillites of the Karlin Formation. The Th and Sc contents in argillites of the Staropetrovo, Salikhovo, and Karlin formations, which make up the second group, are comparable to the values typical of most post-Archean clayey rocks. The Salikhovo argillite differs from its counterparts in other formations by the lowest Cr/Th ratio. In contrast, this ratio reaches ~67 in silty argillites from the Baikibashevo Formation and is comparable with the ratio in the Archean argillite [11]. In the Eu/Eu*–$Gd_N/Yb_N$ diagram, the data points of argillites are also localized in several fields.

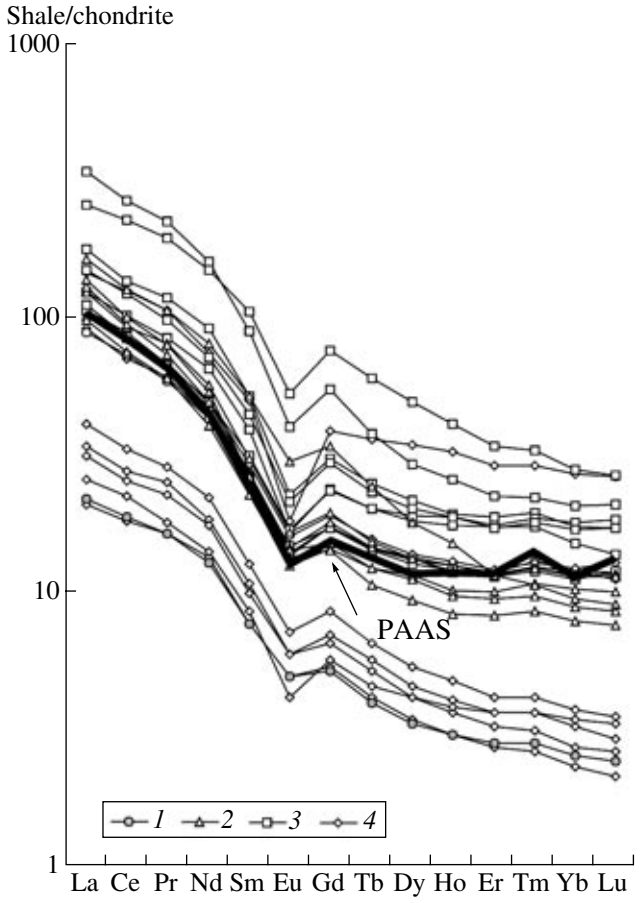


**Fig. 2.** Chondrite [11]-normalized REE patterns of argillites of the Bizhbulyak Complex. Formations (here and in Figs. 3, 4): (*1*) Baikabashevo, (*2*) Staropetrovo, (*3*) Salikhovo, (*4*) Karlin.

Thus, the facts presented above indicate that the blocks of both relatively primitive and more mature upper crustal rocks existed in provenances during deposition of the Upper Vendian sediments of the Shkapovo–Shikhan Depression. As follows from the upsection variation of the Nd model age of fine-grained terrigenous sediments of the Bizhbulyak Complex (table), the proportions of these blocks changed with time. The Nd model age is estimated at 2.0–2.3 Ga for the argillites and silty argillites of the Baikibashevo and Staropetrovo formations and 1.9–2.3 Ga for the argillites of the Karlin Formation. This implies that in the beginning and at the end of the Late Vendian, Paleoproterozoic crystalline rocks dominated in the paleodrainage systems situated to the west, southwest, and northwest of the Shkapovo–Shikhan Depression. This suggestion is supported by distinct negative Eu anomalies in all samples analyzed and the median values of $Gd_N/Yb_N = 1.71$ and $La_N/Yb_N = 9.29$ typical of the Paleoproterozoic crust [14]. The Archean rocks, probably, also occurred in provenances as indicated by a low Ce/Cr ratio (median value is 0.47) in some silty argillites and argillites at the Naikibashevo, Staropetrovo,

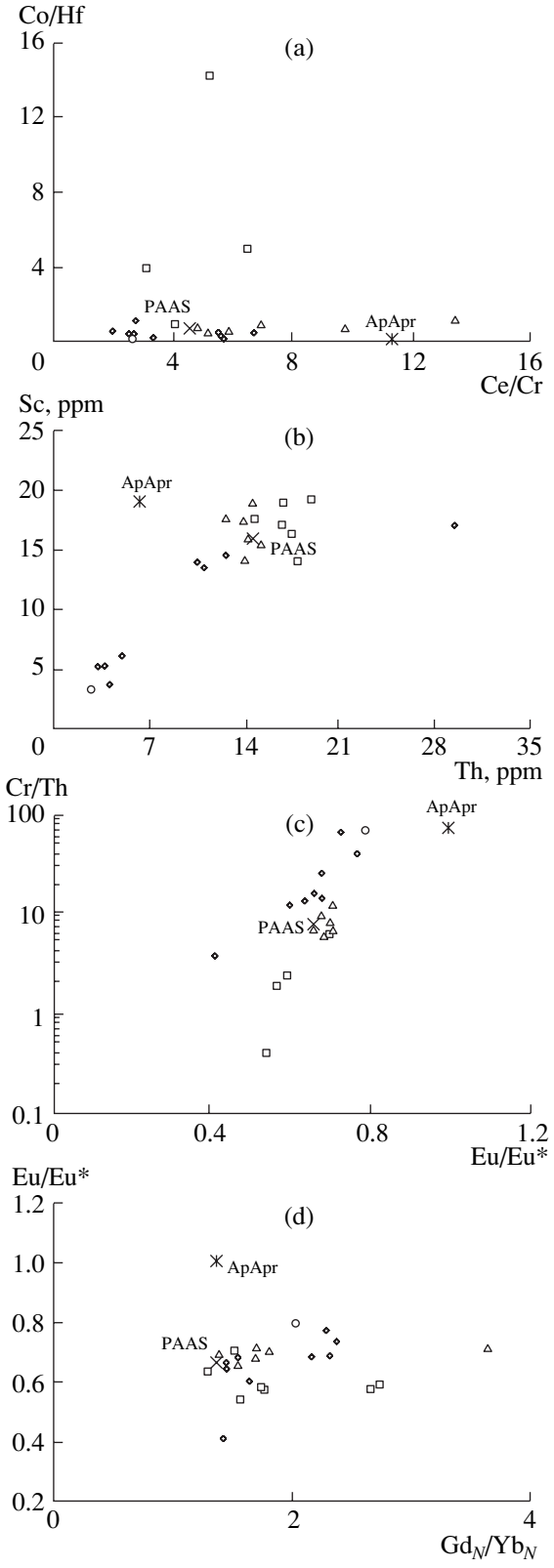


**Fig. 3.** Data points of argillites of the Bizhbulyak Complex plotted on the diagrams: (a) Ce/Cr–Co/Hf, (b) Sc–Th, (c) Cr/Th–Eu/Eu*, (d) Eu/Eu*–$Gd_N/Yb_N$. (AAG) average Archean argillite, (PAAS) average post-Archean Australian Shale, after [11].

Nd model age of the Upper Vendian argillites from the Shkapovo–Shikhan Depression

| Sample | Stratigraphic level | $t^*_{strat}$, Ma | Sm, ppm | Nd, ppm | $^{147}Sm/^{144}Nd$** | $^{143}Nd/^{144}Nd$ | ±2σ, % | $\varepsilon_{Nd}(t)$ | $t_{DM}$, Ma [13] | ±2σ, Ma |
|---|---|---|---|---|---|---|---|---|---|---|
| IM-12 | $V_2$kar | 550 | 2.80 | 16.0 | 0.1056 | 0.51164 | 0.006 | –13.0 | 1965 | 42 |
| IM-14 | | 550 | 2.08 | 9.40 | 0.1335 | 0.51198 | 0.005 | –8.4 | 2005 | 44 |
| ISH-17 | | 550 | 6.46 | 40.2 | 0.0971 | 0.51129 | 0.003 | –19.3 | 2281 | 19 |
| IM-19 | | 550 | 1.91 | 10.5 | 0.1099 | 0.51173 | 0.005 | –11.6 | 1914 | 34 |
| IM-1 | $V_2$sal | 560 | 11.9 | 64.2 | 0.1119 | 0.51198 | 0.003 | –6.7 | 1579 | 23 |
| IM-5 | | 560 | 10.1 | 49.4 | 0.1232 | 0.51209 | 0.003 | –5.4 | 1591 | 25 |
| IM-27 | | 560 | 5.45 | 35.3 | 0.0933 | 0.51177 | 0.005 | –9.5 | 1600 | 31 |
| IM-29 | $V_2$stp | 580 | 7.67 | 39.8 | 0.1166 | 0.51157 | 0.004 | –14.9 | 2302 | 28 |
| IM-17 | | 580 | 12.1 | 51.8 | 0.1408 | 0.51209 | 0.006 | –6.5 | 1976 | 59 |
| IM-32 | $V_2$bkb | 590 | 4.92 | 30.7 | 0.0969 | 0.51129 | 0.004 | –18.8 | 2277 | 27 |

Note: Formations: ($V_2$bkb) Baikabashevo, ($V_2$stp) Staropetrovo, ($V_2$sal) Salikhovo, ($V_2$kar) Karlin. The concentrations and isotopic compositions of Sm and Nd were determined with the mass-spectrometric method of isotopic dilution using a mixed $^{149}Sm + ^{150}Nd$ spike and acid decomposition of the initial material [9]. Reproducibility of the measured $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios was controlled with La Jolla and BCR-2 standards. The procedure blank for Sm and Nd was not higher than 70 and 90 pg, respectively.
* Conditional values of age accepted for calculation of $\varepsilon_{Nd}(t)$.
** Uncertainties are not higher than ±0.5% (2σ).

and Karlin levels. In contrast, the argillites of the Salikhovo Formation taken from Borehole Akhmerovo-6 drilled near the Bashkir Anticlinorium have a Ce/Cr ratio an order of magnitude higher and an Nd model age of ~1.6 Ga, i.e., 0.4–0.7 Ga less relative to the under- and overlying argillites (Fig. 4). The abrupt decrease in the Nd model age of the fine-grained terrigenous rocks at only one level of the Upper Vendian in the Shkapovo–Shikhan Depression can be explained only by the supply of clastic material from the rising Beloretsk Uplift or Terrane (a fragment of the Cadomian Orogen) located on the eastern slope of the Bashkir Anticlinorium (in present-day coordinates). On the western slope of the Bashkir Anticlinorium, processes of accumulation and disintegration of rocks of the Salikhovo Formation were accompanied by the deposition of conglomerates and sandstones of the Kukkarauk Formation that contained zircons with a U–Pb age of ~512–643 Ma. The metamorphic rocks of the Beloretsk Terrane served as a source of the conglomerates and sandstones and zircons contained therein [15].

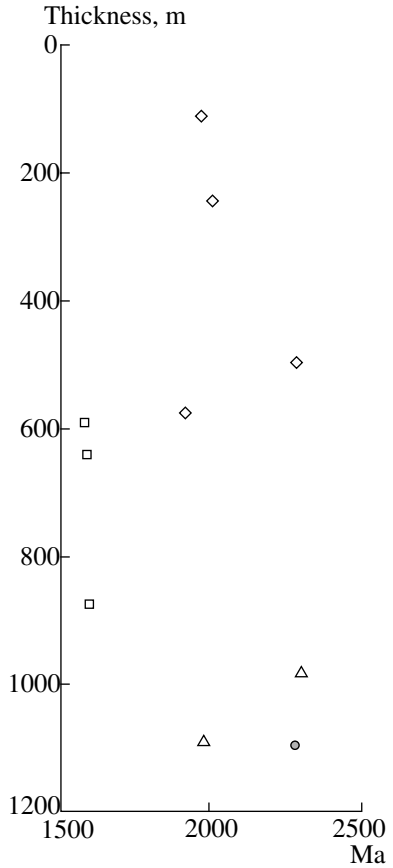


**Fig. 4.** Variations of Nd model age of argillites in the integral section of the Bizhbulyak Complex. See Fig. 2 for legend.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 03-05-64121); Program no. 25 “Origin and Evolution of Biosphere” of the Presidium of the Russian Academy of Sciences (State Contract no. 10104-71/P-25/155-353/090605-013); and Program no. 7 of the Division of Earth Sciences, Russian Academy of Sciences.

## REFERENCES

1. *Stratigraphic Chart of Riphean and Vendian Rocks in the Volga–Ural Province. Explanatory Notes* (Inst. Geol., Ufa Nauch. Tsentr Ross. Akad. Nauk, 2000) [in Russian].
2. *Geological Map of the East European Platform and Its Fold Framing (within Borders of the Former Soviet*

*Union): Pre-Vendian Rocks*, Ed. by Yu. R. Bekker (VSEGEI, St. Petersburg, 1996), 4 Sheets [in Russian].

3. *Deep Structure and Geodynamics of the Southern Urals (Uralseis Project)*, Ed. by A.F. Morozov (GERS, Tver, 2001) [in Russian].
4. Z. P. Ivanova, M. M. Veselovskaya, A. A. Klevstova, et al., *Petroliferous and Prospective Complexes of the Central and Eastern Russian Platform: Vol. 1. Pre-Ordovician Rocks of the Central and Eastern Russian Platform* (Leningrad, Nedra, 1969) [in Russian].
5. M. M. Aliev, S. G. Morozov, I. E. Postnikov, et al., *Geology and Petroleum Potential of Riphean and Vendian Rocks of the Volga–Ural Province* (Nedra, Moscow, 1977) [in Russian].
6. Yu. R. Bekker, *Upper Precambrian Molasse in the Southern Urals* (Leningrad, Nedra, 1968) [in Russian].
7. *Stratotype of the Riphean. Stratigraphy. Geochronology*, Ed. by B. M. Keller and N. M. Chumakov (Nauka, Moscow, 1983) [in Russian].
8. M. M. Herron, J. Sed. Petrol. **58**, 820 (1988).
9. Yu. L. Ronkin, O. P. Lepikhina, S. V. Golik, et al., in *Yearbook-2004* (Inst. Geol. Geokhim., Yekaterinburg 2005), pp. 423–433 [in Russian].
10. Ya. E. Yudovich and M. P. Ketris, *Principles of Lithochemistry* (Nauka, St. Petersburg, 2000) [in Russian].
11. S. R. Taylor and S. M. McLennan, *The Continental Crust: Its Composition and Evolution* (Blackwell, Oxford, 1985; Mir, Moscow, 1988).
12. S. R. Taylor and S. M. McLennan, Rev. Geophys. **33**, 241 (1995).
13. D. J. DePaolo, Nature **291**, 705 (1981).
14. K. C. Condie, Geochim. Cosmochim. Acta **55**, 2527 (1991).
15. V. N. Puchkov, *Paleogeodynamics of the Southern and Central Urals* (Dauriya, Ufa, 2000) [in Russian].