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GEOCHEMISTRY

Sr–Nd Isotopic and Geochemical Compositions of Kimberlites from the Eastern Azov Region, Their Age, and Nature of the Lithospheric Source

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This paper reports first data on Rb–Sr and Sm–Nd isotope systems, as well as REE distribution (based on ICP-MS), in kimberlites of the eastern Azov region. The results obtained made it possible to characterize and compare their geochemistry with that of kimberlites from Arkhangel'sk and other regions. Like previous studies of kimberlites from the northern margin of the East European Platform [1], new data can be used for solving fundamental petrological problems: deciphering the kimberlite sources and deep-seated structure of one of the Earth's largest structures, namely, the East European Platform, in particular, its southern margin.

The studied kimberlites (four pipes and two dikes) are restricted to the easternmost block of the Ukrainian Shield (Azov crystalline massif) or, more precisely, to its northern conjunction with Donbass. This block of Lower Proterozoic granitoids was consolidated in Archean and reworked in Proterozoic. Kimberlites were found among the diverse Devonian volcanic and explosive rocks (limburgites, wehrlites, basalts, and others). No diamonds were found in the pipes. However, both kimberlitic and metamorphic diamonds were found in postkimberlite reservoirs [2].

In the framework of this investigation, we obtained new Rb–Sr biotite and whole-rock ages of 383 ± 3.8 Ma (Sample 293/11) for the Novolaspinsk pipe and 384.7 ± 3.9 Ma (Sample 1459a) for the Yuzhnaya pipe.

The four least altered samples (table) were taken for investigations from the available collection (12 core samples taken from depths ranging from 19 to 115 m in boreholes of the Petrovskii area and the Novolaspinsk, Nadezhda, and Yuzhnaya pipes). Samples 293/11 (Novolaspinsk pipe), 396/4b (Novolaspinsk dike) and 1459a (Yuzhnaya pipe) are brecciated porphyric rocks with predominant fragments of the host rocks. Phenocrysts are serpentinized olivine and partly chloritized phlogopite. Serpentine pseudomorphs after olivine reveal zoning inherited from the parental olivine crystals. Serpentine has a strongly variable composition, suggesting different Mg numbers in the parental minerals. In Sample 293/11, *mg*# reaches 0.9 in serpentine developed after large olivine megacrysts and decreases to 0.82 in the groundmass. In sample 396/4b, primary olivine was presumably even more enriched in Fe (*mg*# of serpentine in the groundmass is 0.72).

One can distinguish two phlogopite generations. Phlogopite I (*mg*# 0.86–0.88) is observed as large megacrysts up to 1 cm, while phlogopite II (*mg*# 0.86–0.92) occurs as fine flakes (3–5 vol %) in the groundmass. They have similar chemical compositions. However, phlogopite II is depleted in TiO_2 relative to phlogopite I (1.1–2.4 and 1.4–2.7 wt %, respectively) and shows wider Al_2O_3 and K_2O variations. The groundmass also contains picroilmenite, perovskite, titanomagnetite, and sphene. Kimberlites from the Novolaspinsk dike (Sample 396/4b) are enriched in calcitic microlites (~25%), which affect the chemical composition of the rock.

Sample 401/8 from the Yuzhnaya pipe sharply differs from the above samples. This is a massive dark, partly crystallized rock with equigranular texture. The major minerals are clinopyroxene (*mg*# 0.75–0.78) of the augite composition and high-K micalike mineral (K_2O 6.6–8.2 wt %, *mg*# 0.47–0.56), which compositionally resembles muscovite. The accessory minerals are ilmenite (MnO up to 4.4 wt %) and fine sulfides regularly distributed over the rock. The groundmass is completely chloritized. The normative composition of this sample is dominated by plagioclase (34%) and quartz (2%). Nepheline is absent. Based on the petrographic, mineral, and petrochemical characteristics (FeO_{tot} 16.2, TiO_2 7 wt %), the rock is identified as ferrobasalt.

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Table 1. Characteristics of the potassic ultramafic rocks of the eastern Azov region

Sample no.	Object	Depth, m	Area, m^2	Mineral composition	Rock
293/11	Novolaspinsk pipe	95.5	50–70	(Ol), Phl, Ilm, Prv, Ti-Mag, Spn, Cal	Kimberlite
396/4b	Novolaspinsk dike	50.0	no data	(Ol), Phl, Ilm, Ti-Mag, Cal, Spn	The same
1459-a	Yuzhnaya pipe	85.0	250	(Ol), Phl, Ilm, Ti-Mag, Chl	"
401/8	Yuzhnaya pipe	66.4	250	Cpx, Ms?, Chl, Ilm, Mag, Opaq	Ferrobasalt

Note: (Ol) Serpentine pseudomorphs after olivine, (Phl) phlogopite, (Cal) calcite, (Cpx) clinopyroxene, (Prv) perovskite, (Ilm) ilmenite, (Ti-Mag) titanomagnetite, (Spn) sphene, (Mag) magnetite, (Chl) chlorite, (Opaq) ore mineral, (Ms) muscovite.

The presence of different families of the magmatic rocks within a single sequence (Yuzhnaya pipe) is confirmed, in particular, by their chemical composition. In the MgO–NiO discriminant diagram after [3] (Fig. 1), they are plotted in the fields of kimberlite (field *4*) and basalts (overlapping of fields *1* and *2*).

The obtained data on kimberlites from the eastern Azov region were compared with those on the northern East European Platform, first of all, with kimberlites from the Arkhangel'sk province (using mainly original data obtained from the same laboratories [1]), South Africa (groups I and II), West Africa (Sierra Leone and Koidu), and North Australia (Aries) [4, 5]. The results obtained were plotted in several diagrams (Figs. 2–4) with fields of generally accepted kimberlite and lamproite groups adopted from the reference works. The analyzed kimberlites have increased contamination index C.I. of 1.82 and 1.72 in Sample 396/4b (Novolaspinsk dike) and Sample 1459a (Yuzhnaya pipe), respectively.* Only sample 293/11 (C.I. = 1.27, Novolaspinsk pipe) meets the necessary requirements [4].

Like all kimberlites, the studied samples are enriched in trace and rare earth elements. The REE contents are rather stable in three kimberlite samples. The characteristic ratio $(La/Yb)_n$ ranges within 98.6–163.8 in kimberlites of the eastern Azov region and is only 28.3 in ferrobasalts (Yuzhnaya pipe, Sample 401/8). The REE distribution (Fig. 2) in kimberlites from the eastern Azov region nearly mimics the pattern in samples of the Kepino field of the Arkhangel'sk province.

Judging from the trace element distribution (Fig. 3), the mantle sources of the studied potassic magmatic rocks were enriched in incompatible elements. Their trace element composition is similar to that of the Kepino kimberlites, except for some variations in incompatible elements, especially HFSE. In particular, samples 1459a and 396/4b exhibit high Pb contents (31.11 and 19.06 ppm, respectively). The Pb content in Sample 1459a (Yuzhnaya pipe) is almost five times higher than that in Sample 293/11 (Novolaspinsk pipe).

The anomalously high Zr and Hf contents (521–604 and 12.8–14.8 ppm, respectively) are typical of all the analyzed kimberlites. The high Zr content is presumably the characteristic feature of this region. For example, high Zr contents were found in pyrope from the pipes of the eastern Azov region [7]. Zirconium mineralization is typical of rocks of the adjacent Mariupol Complex. Such high Zr contents are observed in some kimberlites, in particular, in Benfontein Sills [8], but were not found in the kimberlites from the northern margin of the East European Platform, including the Arkhangel'sk province.

The Sr and Nd isotopic ratios in the studied rocks are presented in Fig. 4. The ε_{Sr} value slightly varies (from 0.7 to 29) in the studied samples and significantly decreases to –20.46 in ferrobasalts. It should be noted that the ε_{Sr} value in lamproites of West Australia ranges from +94 to +228 [9]. Somewhat increased ε_{Sr} values in samples 1459a and 396/4b correlate with the higher contamination index as compared to those in Sample 293/11, thus possibly reflecting the enrichment in crustal material. The studied rocks show mainly positive ε_{Nd} values ranging from +1.9 to –0.1 in kimberlites and increasing to +3.3 in basalts. In the ε_{Sr}–ε_{Nd} diagram (Fig. 4), the data points of kimberlites from the eastern Azov region are plotted within or near the kimberlites of the Kepino field of the Arkhangel'sk province, while those in Sample 396/4b (Novolaspinsk dike) are restricted to the field of highly diamondiferous Grib pipe.

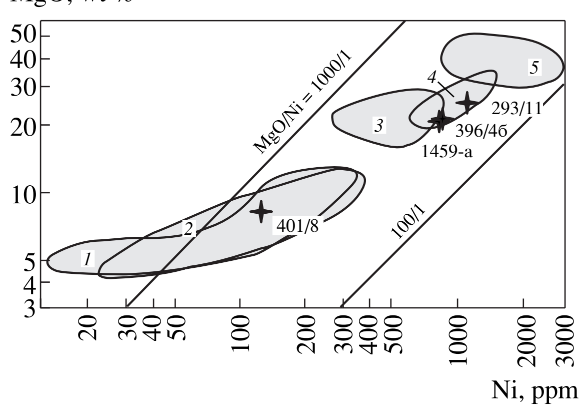

Fig. 1. MgO vs. Ni in samples from the eastern Azov region. Compositional fields: (*1*) alkaline basalts, (*2*) subalkaline basalts, (*3*) pyroxenites, (*4*) kimberlites, (*5*) ultramafic rocks.

* C.I. = $(SiO_2 + Al_2O_3 + Na_2O)/(2K_2O + MgO)$ [6].

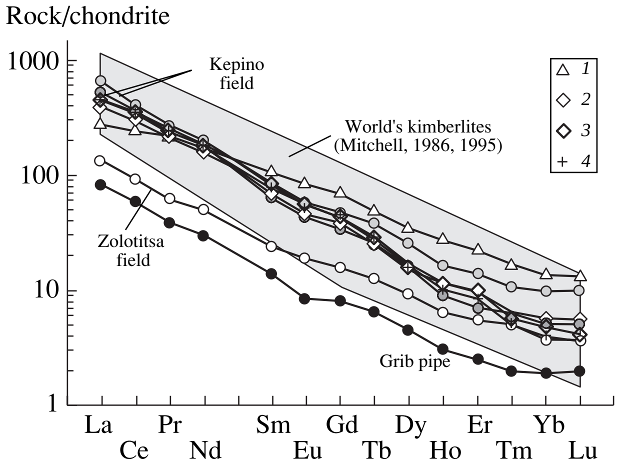

Fig. 2. Chondrite-normalized [10] REE distribution patterns in kimberlites. (*1*) Fe–Ti basalt, Sample 401/8; kimberlites: (*2*) Sample 396/4b, (*3*) Sample 1459a, (*4*) Sample 293/11.

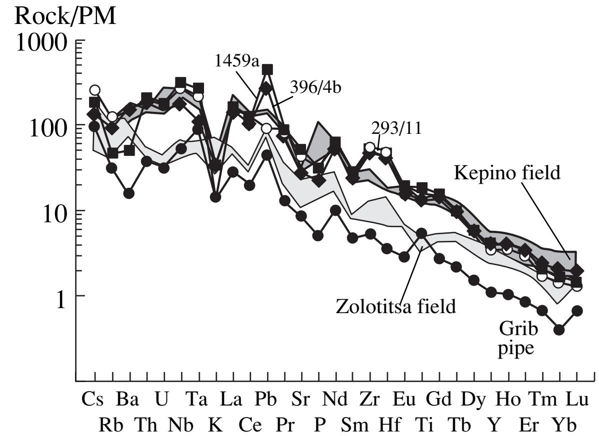

Fig. 3. Primitive mantle (PM)-normalized [10] trace element distribution in kimberlites from the eastern Azov region.

Sample 293/11 with the lowest C.I. value (1.27) is plotted in the central part of the Kepino field (Fig. 4).

The following conclusions can be drawn from our study.

(1) Kimberlites and basaltoids occur within single geological sequences. However, they formed from different mantle sources approximating BSE and PREMA, respectively.

(2) In terms of composition (trace element enrichment, Sr and Nd isotopic compositions, and other features), kimberlites of the eastern Azov region are close to those of the Kepino field of the Arkhangel'sk region and Middle Timan, as well as to Group I kimberlites of South Africa.

(3) High Zr and Hf contents in all of the studied rock types and mantle minerals (pyrope) suggest that the mantle of this region was presumably enriched in these elements.

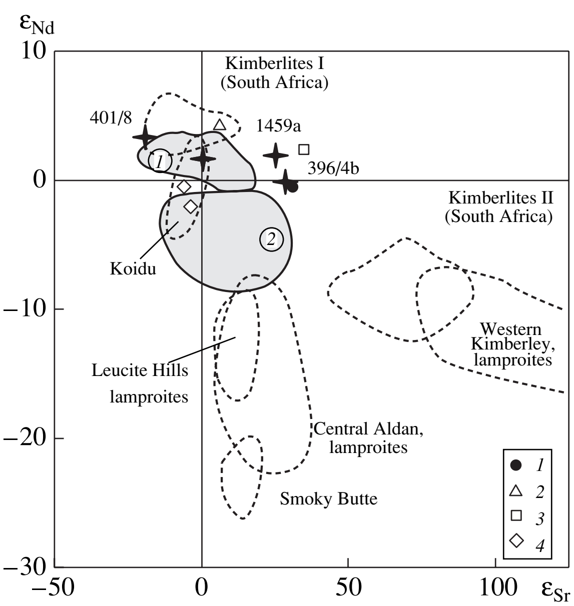

Fig. 4. Sr vs. Nd isotopic compositions in the rocks of the eastern Azov region as compared to the world's kimberlites and lamproites. Kimberlites from the northern margin of the East European Platform: (*1*) Verkhotina field (Grib pipe), (*2*) Kandalaksha, (*3*) Middle Timan, (*4*) Terskii Coast. Numbers in circles are compositional fields of kimberlites of the Arkhangel'sk province: (*1*) Kepino field, (*2*) Zolotitsa field. Fields of the world's kimberlites and lamproites are given after [4, 5].

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