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GEOCHEMISTRY

Peridotite Nodules from the Udachnaya Kimberlite Pipe: "Nonmantle" Oxygen Isotope Ratios in Garnets

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The peridotite nodules from kimberlites and basalts represent the lithospheric mantle and commonly show a very narrow range of $\delta^{18}O = +5.5 \pm 0.4‰$ [1]. This is typical of spinel and garnet (low- and high-temperature) peridotites, as well as diamond-bearing dunites and harzburgites. The $\delta^{18}O$ values of the metasomatized amphibole- and phlogopite-bearing peridotites also fall within the mantle interval [2]. The fractionation of oxygen isotopes at a high temperatures is insignificant. Nevertheless, the equilibrated minerals of mantle peridotites demonstrate progressive depletion in $\delta^{18}O$ in the orthopyroxene–clinopyroxene–garnet–olivine–spinel series in consistence with the crystal chemistry of these minerals [3]. The $\delta^{18}O$ of spinel varies from +3.8 to +4.8‰ [2], while the oxygen isotope ratios of other minerals fall within the mantle interval. In particular, the $\delta^{18}O$ of garnet is $+5.3 \pm 0.3‰$ [4].

Some recently obtained data testify to the isotopic disequilibrium of mantle minerals. For example, clinopyroxene in spinel peridotite nodules from the Rio Puerco alkali basalt (Mexico) has anomalously low $\delta^{18}O$ values probably due to the metasomatic alteration of the minerals by the silicate melt derived from the subducted oceanic crust [5]. About 30% of analyzed garnets from diamond-bearing peridotite nodules in Yakutian kimberlites have both higher and lower $\delta^{18}O$ ratios than the typical mantle values. These deviations are explained by hydrothermal alteration of their protoliths under the crustal conditions [6]. The present communication shows that the high-Cr garnets in mantle peridotites may inherit a low $\delta^{18}O$ ratio of the protolith mineral (Cr-spinel).

In the studied collection of garnet peridotites from the Udachnaya kimberlite pipe located in the central Siberian Craton, the common garnet-bearing samples are associated with samples containing garnets depleted in $\delta^{18}O$ (Table 1). The oxygen isotopic composition of garnets was determined at the Analytical Center of the Far East Geological Institute (Vladivostok) with fluorination using BrF_5 and application of a Nd-YAG infrared continuous laser ($\lambda = 1.064$ µm, CW, 100 W) for sample heating. The analytical accuracy (1σ) was 0.1‰ ($n = 5$) for international NBS-28 and NBS-30 standards [7]. The weight of the analyzed garnet separates was 1 or 2 mg. The $\delta^{18}O$ value was measured on a Finnigan MAT-252 mass spectrometer with the double inlet system. The reproducibility of $\delta^{18}O$ for samples was 0.2‰. The trace element contents in garnet were measured with SIMS at the Institute of Microelectronics and Informatics in Yaroslavl. The accuracy of measurements was not lower than 10% for concentrations of trace elements higher than 1 ppm and not lower than 20% for the concentration range of 1–0.01 ppm.

As mentioned above, the studied garnet peridotites represent the lithospheric mantle. According to calculated equilibrium pressures (Table 1), they formed at a depth of 120–200 km. The equilibrium temperature was estimated from the Mg–Fe exchange between garnet and olivine in harzburgite [8] and between pyroxenes in lherzolite [9]. The pressure was estimated from the distribution of Al between garnet and orthopyroxene [9]. The *PT* estimates obtained are consistent with a paleogeotherm of the Siberian Craton that fits a heat flow of 40 mW/m^2.

The major element contents in residual peridotites are interrelated and depend on constraints of rock formation: initial and final pressures and the degree of melting in the course of fractional polybaric melting of the mantle [10]. Table 2 presents the compositions of garnet peridotites and some minerals therein, as well as the calculated residue composition. Garnet peridotites (samples UV-9720 and UV-9729) are characterized by a high FeO content that testifies to a low initial pressure

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Table 1. Characteristics of peridotite nodules from the Udachnaya kimberlite pipe and oxygen isotopic composition of garnet

Sample	Texture	T, °C	P, kbar	Peridotite type	$\delta^{18}O$ in garnet, ‰
UV-9720	Protogranular	910	41	Medium-temperature harzburgite	4.6
UV-9730	Protogranular with cataclastic elements	1060	50	Medium-temperature harzburgite	4.6
UV-9723	The same	1100	58	Medium-temperature harzburgite	4.6
UV-9729	Porphyroclastic	1300	65	High-temperature lherzolite	4.9

Note: See text for methods of T and P calculation.

Table 2. Chemical composition (wt %) of garnet peridotites and some minerals therein

Mineral	SiO_2	TiO_2^*	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	Total
Sample UV-9720										
Bulk rock	42.72	0.05	0.7	0.34	7.97	0.12	47.56	0.57	0.1	100.33
Gt	40.63	0.17	16.49	9.63	8.01	0.53	18.07	6.84	n.d.	100.37
Cpx	54.75	0.10	2.08	3.18	1.99	n.d.	16.02	19.73	2.32	100.07
Cpx	54.93	n.a.	2.2	2.69	1.01	The same	15.54	20.21	2.35	98.93
Sample UV-9730										
Bulk rock	41.92	0.09	2.5	1.05	6.95	0.13	44.87	2.16	0.51	101.01
Gt	41.80	0.03	17.36	8.02	6.59	0.41	20.41	5.22	n.d.	99.84
Cpx (core)	54.69	0.23	2	2.2	2.59	n.d.	16.98	19.22	2.22	100.13
Cpx (rim)	55.78	0.21	0.68	1.54	2.38	The same	17.4	21.88	1.09	100.96
Sample UV-9723										
Bulk rock	45.29	0.03	1.11	0.48	7.57	0.12	44.77	1.25	0.1	100.48
Gt	41.22	0.06	17.12	8.04	7.54	n.d.	20.59	5.3	n.d.	99.87
Cpx	54.87	n.a.	1.79	2.36	2.66	0.15	15.91	18.43	2.33	98.50
Cpx	55.19	0.005	0.55	0.49	2.90	0.12	20.66	19.82	0.30	100.04
Sample UV-9729										
Bulk rock	43.91	0.11	1.68	0.39	7.95	0.12	44.74	1.43	0.21	100.42
Gt	42.11	0.60	19.49	5.05	6.78	0.30	20.72	5.14	n.d.	100.19
Cpx (core)	54.32	0.21	1.04	1.55	3.35	n.d.	19.01	18.79	1.11	99.38
Cpx (rim)	53.96	n.a.	0.54	0.96	2.86	The same	17.73	21.88	1.11	99.04
Residue	44.03		1.78		8.06		44.44	1.69		100

Note: (Gt) Garnet; (Cpx) clinopyroxene; (n.a.) not analyzed; (n.d.) not detected. The bulk rock compositions were determined with XRF at the Institute of Geochemistry, Siberian Division, RAS; compositions of minerals were determined on a LEO 1430VP SEM/Inca Energy 300 EDS, Oxford Instruments Ltd., at the Geological Institute, Siberian Division, RAS (accelerating voltage 20 kV, current 0.5 nA, beam diameter <1μm, and count time 50 s). Concentrations recalculated from ion microprobe results are indicated by an asterisk. The L.O.I. values for bulk rock compositions are 0.03, 0.54, –0.31, and –0.26, respectively. The residue composition was calculated for the polybaric fraction melting of the primitive mantle from 26 kbar and melting degree equal to 20%.

of the spinel-facies melting. The contents of SiO_2, MgO, and FeO in these peridotites are in agreement with the composition of residue calculated on the basis of experimental data for an initial pressure of 30–25 kbar and melting degree of 20–25%. Under such conditions, the residue should consist of olivine, orthopyroxene, and spinel. These samples resemble the high-temperature deformed peridotites from the lower section of the cratonic lithospheric mantle. The medium-temperature harzburgite (sample UV-9730) has unusual chemical composition with very low SiO_2 content, which is inconsistent with experimental data on Al_2O_3 and FeO contents. The Cr content is very high. The protolith of this sample could have been a cumulative harzburgite that was enriched in Cr-spinel and probably subjected to nonisochemical alteration. The composi-

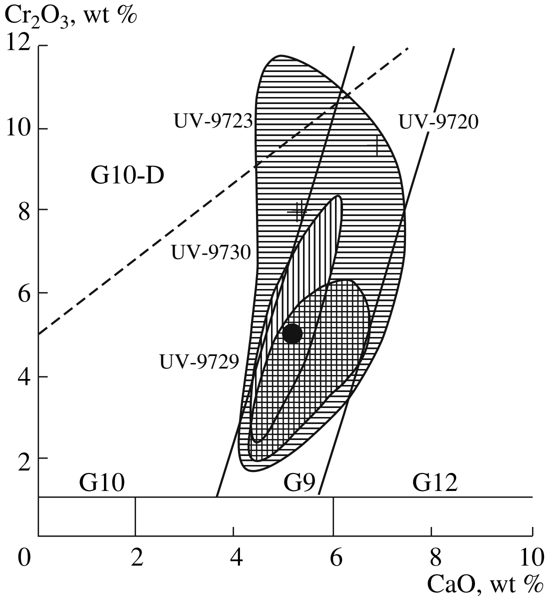

Fig. 1. Chemical compositions of garnets (crystal cores) in peridotites from the Udachnaya pipe plotted on the classification diagram of garnets from mantle-derived rocks [11]. (G10-D) Diamond-bearing peridotite; (G10) harzburgite; (G9) lherzolite; (G12) wehrlite.

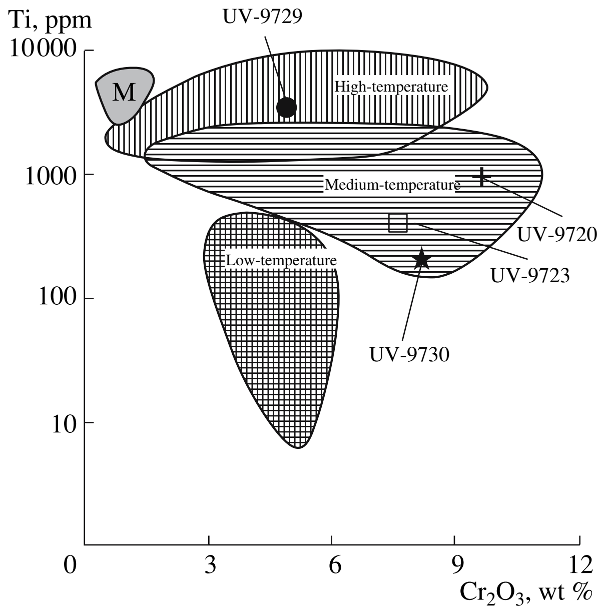

Fig. 2. Ti vs. Cr_2O_3 relationship in garnets (crystal cores) from high-, medium-, and low-temperature peridotites and megacrysts (M) in the Udachnaya pipe.

tion of sample UV-9723 is characterized by discordant contents of components, indicating either alteration of the rock or its nonresidual origin.

According to the proportions of Cr_2O_3 and CaO (Fig. 1), garnets from peridotites UV-9730 and UV-9723 represent subcalcic phases of the harzburgite assemblage. They are enriched in Cr (8.0–8.8 wt % Cr_2O_3). In terms of the Ti content, they occupy a transitional position between low- and high-temperature peridotites (Fig. 2). They are characterized by nonfractionated $LREE_N$ and $MREE_N$ patterns and high HREE contents ranging from 0.4–0.8 to 8 chondritic levels of Yb_N (Fig. 3a). Garnet with such a high Cr content and REE pattern cannot be in equilibrium with a melt. Similar REE patterns are typical of garnets from the least metasomatized low-temperature peridotites (Fig. 3a, field I). The low REE contents and negative correlation between Yb and Cr indicate that garnets from these rocks were formed by high-temperature subsolidus exsolution from orthopyroxene. If garnets from harzburgites UV-9730 and UV-9723 were formed like garnets from low-temperature peridotites, the high Cr content in these minerals would be accompanied by very low Yb contents. This is not observed in our case. The compared rock series are obviously different. Garnet in samples UV-9730 and UV-9723 could be formed according to the reaction orthopyroxene + spinel $\rightarrow$ garnet + olivine. In this case, the garnet inherits low REE concentrations from initial minerals and high Cr contents and low $\delta^{18}O$ values from Cr-spinel. The high LREE and MREE contents are probably caused by the subsequent metasomatic alteration of garnet during the interaction of rock with a percolating fluid or a high-silicic melt. The presence of a very small amount of clinopyroxene of obviously metasomatic origin in this rock suggests its epigenetic alteration. Clinopyroxene grains are small (200–500 μm) and irregular. They are characterized by the absence of exsolution structures and variable contents of Cr, Fe, Mg, and Na (Table 2). In addition, the appearance of small (up to 50 μm) monticellite grains at olivine–clinopyroxenite boundaries in sample UV-9730 testifies to the gain of Ca. This is recorded in the bulk chemical composition of the rock.

Garnets in peridotites of samples UV-9729 and UV-9720 correspond to the lherzolite assemblage. Garnet from high-temperature lherzolite UV-9729 is distinguished by the lowest Cr content (Fig. 1) and the highest Ti content (Fig. 2) in comparison with other samples. The chondrite-normalized REE contents increase from LREE to HREE in line with decreasing ionic radii (Fig. 3b). This REE pattern is typical of garnets in equilibrium with the melt. Such REE patterns are common for garnets from high-temperature peridotites that occur at the bottom of the lithospheric mantle. According to [12], harzburgitic protoliths of these rocks interact with percolating ultramafic melts generated at a lower degree of partial melting in the asthenospheric mantle. This process gives rise to further growth of garnet. Consequently, its composition changes from the harzburgite type to the lherzolite type due to depletion in Cr and enrichment in Ca and Ti. The interaction with the ultramafic melt also results in the formation of large clinopyroxene grains (~10%) without exsolution structures; elevated Ti contents; and variations in Cr, Al, Fe,

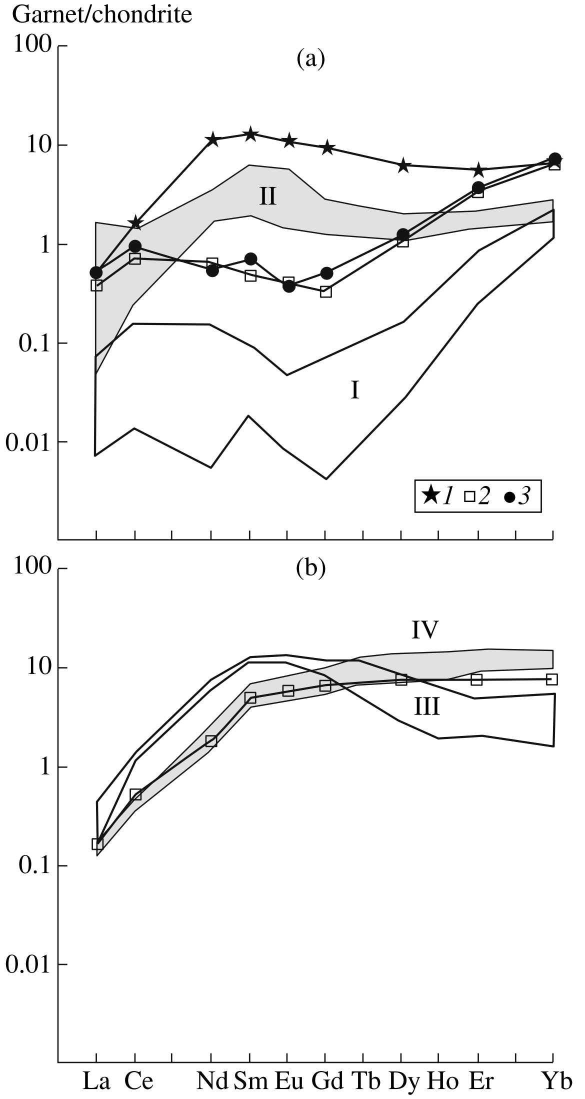

Fig. 3. REE patterns in garnets. (a) Medium-temperature peridotites: (*1*) UV-9720, (*2*) UV-9730, (*3*) UV-9723; fields of low-temperature peridotites: (I) least metasomatized, (II) most metasomatized. (b) High-temperature peridotites: (*2*) UV-9729; peridotite fields [12]: (III) medium-temperature, (IV) high-temperature.

Mg, and Ca concentrations (Table 2). This garnet sample is distinguished from other samples by obvious alteration under the influence of ultramafic melt with a mantle isotopic signature. Therefore, the $\delta^{18}O$ value of this garnet is close to the mantle interval (Table 1).

The garnet from medium-temperature harzburgite (sample UV-9720) is close in Cr and Ti contents to samples UV-9730 and UV-9723 (Figs. 1, 2). The REE pattern in the core of the garnet grain is sinusoidal with $(La/Yb)_N < 1$ and a Sm_N maximum (Fig. 3b). The sinusoidal REE pattern may be a result of metasomatic alteration under the influence of a subduction-related fluid or a high-Si melt component, as in the case of intensely metasomatized low-temperature peridotites. In addition, a similar pattern appears at margins of zonal garnets that continue to grow from the fractionated ultramafic melt, as has been established in the Jagersfontein kimberlite pipe, South Africa [12]. Most likely, this garnet was enriched in Ca, LREE, and MREE owing to the interaction of rocks with a subduction-related fluid or melt depleted in Ti. This is reflected in the low Ti concentration in garnet. Further growth of garnet from the ultramafic melt should be accompanied by depletion in Cr along with enrichment in Ca, but such a variation is not established. The appearance of small clinopyroxene grains of variable composition, the absence of exsolution structures (Table 2), and the presence of large phlogopite and Cr-spinel grains indicate intense metasomatism as well.

The high-Cr garnets mentioned above are distinguished by low $\delta^{18}O$ values. The protoliths of peridotites with such garnets could have been formed either as cumulative spinel-bearing harzburgite or as residues owing to the partial melting of mantle at the spinel-facies depth. Garnet was formed from orthopyroxene and spinel in the course of subsidence of rocks. The garnet and clinopyroxene compositions suggest further metasomatic alteration of a part of peridotites (samples UV-9730, UV-9723, UV-9720) by subduction-related fluids or melts. Sample UV-9729 represents peridotites altered by the asthenosphere-derived ultramafic melt. The interaction of peridotite xenoliths with the kimberlitic melt and the subsequent hydrothermal alteration could not have led to the depletion of garnet in $\delta^{18}O$, because $\delta^{18}O$ of kimberlite from the Udachnaya pipe varies from +6.6 to +23.9‰ [13].

Thus, the depletion of garnet in $\delta^{18}O$ is a mantle signature. The data presented above suggest that the formation of the mantle-derived garnet peridotites from xenoliths in kimberlitic pipes may be explained in terms of different genetic models.

Let us consider various versions of processes responsible for low oxygen isotopic compositions in the garnets.

(1) Inheritance of the low $\delta^{18}O$ signature of spinel by garnet.

This interpretation looks the most plausible, because the depletion in $\delta^{18}O$ has been established only in high-Cr garnets. Such garnets could only be formed from Cr-spinel.

(2) Disturbance of isotopic equilibrium in minerals of garnet peridotites under the influence of subduction-related fluids or melts with a low $\delta^{18}O$. In this case, the deviation from the mantle $\delta^{18}O$ values should increase in the olivine–garnet–pyroxene series in line with diffusion rate in mantle minerals [15]. As in the first version, the bulk $\delta^{18}O$ of rock may remain within the mantle interval.

(3) High-temperature hydrothermal alteration of protoliths of garnet peridotites.

The high-temperature oceanic metamorphism is caused by percolation of seawater into the lithosphere along transform faults down to a depth of ~26 km [14]. Hence, both cumulative and residual peridotites formed in mid-ocean ridges may undergo hydrothermal alteration. This process should decrease the $\delta^{18}O$ of the bulk rock and, in particular, of garnet.

Thus, the low $\delta^{18}O$ values of garnet can reflect a disturbance of isotopic equilibrium in minerals of mantle peridotites. Depletion of garnet in $\delta^{18}O$ cannot be a decisive argument for the crustal origin of the peridotite protolith.

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