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### ISOTOPE HETEROGENEITY FROM OXYGEN IN ROCKS OF LITHOSPHERE MANTLE

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Early studies (Mattey et al, 1994a,b) clearly recognized that  $\delta^{18}$ O values are invariant for each of the minerals composing the rocks of the lithosphere mantle. The conclusion about invariant oxygen (O<sub>2</sub>) isotopic composition for minerals of the lithosphere mantle irrespective of paragenesis and facies (spinel -, garnet-, diamond-bearing) is related to the concept of the "mantle range", "mantle value", as an O2 isotopic characteristic for mantle rocks (Mattey et al, 1994; Taylor et al, 2005). Average values  $\pm$  a standard deviation for  $\delta^{18}$ O were determined for major minerals of the lithosphere mantle olivine (Ol), garnet (Grt), clinopyroxene (Cpx), orthopyroxene (Opx). If  $\delta^{18}$ O values fall outside the limits of the mantle range, they are considered as anomalous. Different hypotheses are proposed to explain values lying outside the mantle range, e.g. the contribution of the oceanic crust to the formation of the lithosphere mantle (Taylor et al, 2005). The main goal of the present study is to obtain an O<sub>2</sub> isotope systematics for high-pressure minerals of different parageneses from mantle xenoliths and kimberlites of the Yakutian province and to consider the possible reasons of variations of  $\delta^{18}$ O values in minerals.

Minerals for studies were sampled from kimberlite pipe Udachnaya -Eastern (Daldyn field), which is unique by fresh kimberlites, and from mantle xenoliths. Kimberlites from Komsomolskaya-Magnitnaya pipe (Upper Muna field) were analyzed as well. Oxygen isotopic composition was studied for Ol being the rock-forming mineral of kimberlites that started to crystallize at the mantle depth and terminated crystallizing in pipe conditions when rock matrix was formed, as well as for minerals from low-T<sup>0</sup> granular and high-T<sup>0</sup> deformed peridotites - Ol, Grt, Opx, Cpx, chromespinelid (CrSp) and picroilmenite (IIm), and for minerals of low-Cr megacryst association. The total number of analyses is 146, including those for minerals: Ol - 61, Grt - 33, Cpx - 17, Opx - 18, IIm - 9, CrSp-3.

Oxygen isotopic composition was determined at the Analytical Center of Far East Geological Institute, Far East Branch of Russian Academy of Sciences by a laser fluorination (LF) using BrF5 and infra-red continuous Nd-YAG laser (l=1.064 mm, CW, 100W) for heating the sample (Ignatyev, Velivetskaya, 2004). The accuracy of the method (1  $\sigma$ ) is 0.1 ‰ (n =5) for international standards NBS-28, NBS-30. The weight of analyzed garnet monofractions made up 1-2 mg.  $\delta^{18}$ O were measured via mass-spectrometer Finnigan MAT 252 with a double system of lap joint. The reproducibility of  $\delta^{18}$ O determinations for samples constituted 0.1 ‰. The oxygen isotope data, given by other researchers for peridotites from Udachnaya pipe (Taylor et al, 2005) as a whole well agree with the data obtained by us (Table 3).

#### **Results of studies**

Table 1 gives the average  $\delta^{18}O \pm a$  standard deviation values for mantle minerals of different parageneses. We calculated both Ol from megacrysts and from mantle xenoliths. Tables 2-4 present the oxygen isotopic ( $\delta^{18}O$ ) composition and the main chemical characteristics for Ol, Grt, Opx and Cpx.

**Table 1.** Average  $\delta^{18}$ O values for different mantle minerals.

Mine	Opx	Срх	Grt	Ol	Ilm	CrSp
-ral	(18)	(17)	(45)	(53)	(9)	(3)
$\delta O^{18}$ ,	5,51±	5,39±	5,1±	5,02±	$3,60\pm$	1,25±
‰	0.27	0,21	0,24	0,16	0,35	0,95

 Table.
 2. Average composition of different parageneses olivine.

	Peridot	ites	Megacrysts		Ol
	Granular	Defor med (15)	Green	Yellow -brown	from matrix (8)
FeO	7,66 ±1,10	9,47± 1,69	$7,18\pm$ 1,07	13,07± 0,96	
MgO	50,3±0,84	49,40± 1,46	51,2± 0,81	46,41± 1,28	
Mg#	92,2±1,05	90,24± 1,70	92,8± 0,81	86,9± 1,74	88,9- 92,5*
δ <sup>18</sup> O, ‰	5,10±0,14	4,96± 0,1	5,14± 0,14	4,8± 1,21	4,76± 0,07

Ol of the matrix, forming idiomorphic and subidiomorphic phenocrysts with the size ranging from 0,25 up to 2 mm, was studied from kimberlites of Udachnaya-Eastern and

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Komsomolskaya-Magnitnaya pipes (Upper Muna field). The forsterite minal concentration in Ol from Udachnaya-Eastern kimberlites varies in the range from 88,9 to 92,5 % (Kostrovitsky, 1986). Variability in the  $\delta^{18}$ O of Ol from the matrix ranges in the interval as 4,7-4,9 ‰, averaging 4,76+0,07 ‰.

Ol megacrysts from Udachnaya-Eastern kimberlites form two genetic groups. The first group includes high Mg# Ol of green color (92,5-93,9 Fo minal), belonging to diamond-bearing dunite-harzburgite paragenesis (Sobolev et al, 1984; Pokhilenko et al,1993). The second group of Ol megacrysts of yellow-brown color demonstrates low Mg# (table 2) and belongs to low-Cr megacryst association.  $\delta^{18}$ O values in Ol megacrysts of the 1<sup>st</sup> and 2<sup>nd</sup> groups vary within the range as 4,9-5,4 and 4,6-5,0 ‰, correspondingly.

 $\delta^{18}$ O values in olivines from low-T<sup>0</sup> granular and high-T<sup>0</sup> deformed peridotites vary within 4,8-5,4 and 4,7-5,1 ‰, correspondingly. The latter are characterized by low Mg# (Table 2).

 Table 3.
 Average composition of garnet of different parageneses.

	Gra	nular	Deformed	Mega-
	lher	zolites	lherzolites	crysts
	(11)			
		(Taylor et		
	(17)	al, 2005)	(12)	(5)
$Al_2O_3$	20,2±1,94	20,3±1,8	17,4±2,7	19,4±1,0
Cr <sub>2</sub> O <sub>3</sub>	4,73±2,45	3,7±2,8	5,8±3,3	2,1±1,1
Mg#	81,1±1,69	83,6±4,0	82,0±2,1	79,0±2,4
δ <sup>18</sup> O, ‰	5,15±0,27	5,2±0,17	5,0±0,27	4,98±0,13

 Table 4. Average composition of pyroxene of different parageneses.

	Granular				Mega-
	lherzolites		Deformed lherzolites		cryst
	Срх	Opx (9)	Cpx (9)		Срх
	(7)			Opx (9)	(1)
	54,81	58,16±	55,21±	57,88±	
SiO <sub>2</sub>	±0,63	0,34	0,79	0,55	54,65
	2,19±	0,61±	1,52±	0,56±	
$Al_2O_3$	0,56	0,23	0,52	0,1	1,72
	1,73±	0,32±	1,03±	0,27±	
$Cr_2O_3$	0,92	0,22	0,47	0,12	0,32
	1,98±	4,81±	3,61±	5,49±	
FeO	0,55	0,53	0,73	0,77	3,84
	16,43	35,45±	18,72±	34,5±	
MgO	±0,71	0,94	0,96	0,82	16,23
	20,62	0,51±	17,74±	$0,88\pm$	
CaO	±1,2	0,42	1,31	0,21	20,62
	1,71±	0,04±	1,5±	0,22±	
Na <sub>2</sub> O	0,39	0,05	0,57	0,11	1,58
	93,66	92,91±	90,17±	91,83±	
Mg#	±1,57	0,84	1,97	1,3	88,28
δ <sup>18</sup> O,	5,57±	5,66±	5,24±	5,37±	5,2
‰	0,18	0,21	0,09	0,26	

A significant difference  $\delta^{18}$ O is found when Grt and Prx from different groups of megacrysts and xenoliths are compared. As Tables 3 and 4 demonstrate the low Mg# minerals from megacrysts and deformed peridotites are <sup>18</sup>O depleted in comparison with low-T<sup>0</sup> granular peridotites.

#### Discussion

The decrease in  $\delta^{18}$ O values in mineral succession Opx>Cpx>Grt>Ol>Ilm>CrSp (Table 1) completely corresponds to that for mantle minerals, recognized in early studies (Mattey et al, 1994; Zheng, 1997). The oxides demonstrate <sup>18</sup>O depletion while silicates are characterized by <sup>18</sup>O enrichment. Precise distinctions in  $\delta^{18}$ O values for different minerals are due to the isotope fractionation resulting from crystal-chemical features (composition and structure).

Fig. 1-3 show an evident direct correlation between  $\delta^{18}O$  values and Mg# of olivine and pyroxenes, a reverse correlation between  $\delta^{18}O$  and  $Cr_2O_3$  content and a direct correlation of  $\delta^{18}O$  with Al<sub>2</sub>O<sub>3</sub> content in garnets.



**Fig. 1.** Diagram Mg/(Mg+Fe)\*100 -  $\delta^{18}$ O for olivines of different parageneses: 1 – granular lherzolites; 2 –deformed lherzolites; 3 – low-Cr megacrysts; 4 – megacryst dunite-harzburgites. The line 5.19±0.26 correspond to the average value  $\delta^{18}$ O of "mantle range" for Ol (Mattey et al, 1994).

The lowest  $\delta^{18}$ O values are typical of Ol from the kimberlite groundmass, for Ol megacrysts of low-Cr association and for Ol from deformed peridotites. Though the above olivines belong to different parageneses, the general features of them are high FeO content and accordingly low Mg#. High-Mg# Ol from grained peridotites and megacrysts of dunite-harzburgite paragenesis demonstrate relatively high  $\delta^{18}$ O values. Similar ratios are found for pyroxenes (Table 4, Fig. 3). Pyroxenes from deformed lherzolite and low-Cr megacryst association, characterized

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by relatively high FeO content (low Mg#), show lower  $\delta^{18}O$  values.

The another correlation of  $\delta^{18}$ O on the mineral composition is found for Grt. The major factor of its variability is not Mg#, but Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> concentrations in the mineral. The corresponding plots (we used and literature data of Taylor et al, 2005) show a direct correlation between  $\delta^{18}$ O values and Al<sub>2</sub>O<sub>3</sub> content and a reverse correlation of  $\delta^{18}$ O with Cr<sub>2</sub>O<sub>3</sub> (Fig. 2).



**Fig. 2.** Diagrams Al<sub>2</sub>O<sub>3</sub> -  $\delta$ O<sup>18</sup>, Cr<sub>2</sub>O<sub>3</sub> -  $\delta$ <sup>18</sup>O and Mg/(Mg+Fe)\*100 -  $\delta$ <sup>18</sup>O for garnets of different parageneses: 1 – granular lherzolites; 2 - granular lherzolites (by Taylor et al., 2005); 3 – deformed lherzolites; 4 – low-Cr megacrysts; 5 – lherzolites from Obnajennaya pipe (by Taylor et al., 2005). The line 5.3±0.3 correspond to the average value  $\delta$ <sup>18</sup>O of "mantle range" for Grt (Taylor et al, 2005).

These correlations are characteristic both of high-T<sup>0</sup> deformed peridotites, low-Cr megacrysts and low-T<sup>0</sup> grained peridotites. The conclusions about these correlations are confirmed by the data published in the paper by L.Taylor et al. (See Fig. 2). The lowest  $\delta^{18}O$  (<5,0 ‰) values are observed for garnets from Udachnaya peridotites with high-Cr content (5-8 % Cr<sub>2</sub>O<sub>3</sub>), while the highest  $\delta^{18}O$  values (≥5,4 ‰) are characteristic of low-Cr garnets (<2,5 % Cr<sub>2</sub>O<sub>3</sub>), of high-Al garnets (23,6 % Al<sub>2</sub>O<sub>3</sub>). A reverse correlation between  $\delta^{18}O$  and Cr<sub>2</sub>O<sub>3</sub> is found in garnet inclusions of Finsch diamonds (Lowry et al, 1999), in garnets from polymict peridotites of the Kaapvaal craton, Republic of South Africa (Zhang et al, 2003).

Thus, we can conclude, that the oxygen isotopic composition is a function of integrated effect on the concentrations of the basic oxides, composing a mineral. Isotope  $O_2$  fractionation is defined by a different isomorphous capacity of heavy  $O_2$  isotope for various oxides. If the contents of light oxides (SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>) in the mineral are high, the oxygen isotopic composition is heavy. If the contents of Fe and Cr oxides are high in the garnet, the content of <sup>18</sup>O is relatively low.

Oxygen isotope systematics of mantle minerals and the observed correlations cannot be explained only by change in the mineral chemistry. <sup>18</sup>O depletion of minerals from the deformed peridotites and low-Cr megacrysts in comparison with minerals of low-T<sup>0</sup> grained peridotites and high-Mg# megacrysts can be considered as result of the influence of <sup>18</sup>O depleted astenosphere substance on lithosphere-astenosphere boundary during kimberlite formation. <sup>18</sup>O depletion with the depth (from the crust to the lower mantle) is owing to the increase of P-T parameters, to spinel and perovskite textures of minerals at the greater depth and the decrease in the silicate tetrahedron content (Zheng, 1997). This approach logically agrees with the idea about the significant contribution of the deepseated substance from transition zone and the lower mantle in the astenosphere, brought by the plume uplifted to the lithosphere bottom (Solov'eva et al., 2008).

This bring up the question: What factor was the predominant in <sup>18</sup>O depletion of minerals from deformed lherzolites and megacrysts: 1) higher content Fe in Ol and Cpx, and higher content Cr and lower content Al in Grt (the dependence of  $\delta^{18}$ O values from mineral composition); or 2) the influence of the astenosphere? We leave this question still open for debate - as additional studies are required. But it is obvious that the lithosphere mantle is not homogeneous by oxygen isotopic composition. The granular (coarce) and deformed lherzolites are characterized by different  $\delta^{18}$ O values.



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**Fig. 3.** Diagrams Mg/(Mg+Fe)\*100 -  $\delta^{18}$ O for clino- and orthopyroxenes of different parageneses: *I* – granular lherzolites; *2* – deformed lherzolites; *3* – low-Cr megacryst. The lines 5.61 and 5.73 correspond to the average values  $\delta^{18}$ O of "mantle range" for Cpx and Opx (Mattey et al, 1994).

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