GEOCHEMISTRY

Primary Melt and Fluid Inclusions in Regenerated Crystals and Phenocrysts of Olivine from Kimberlites of the Udachnaya-East Pipe, Yakutia: The Problem of the Kimberlite Melt

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Abstract—The primary melt and fluid inclusions in regenerated zonal crystals of olivine and homogeneous phenocrysts of olivine from kimberlites of the Udachnaya-East pipe, were first studied by means of microthermometry, optic and scanning electron microscopy, electron and ion microprobe analysis (SIMS), inductively coupled plasma mass-spectrometry (ICP MSC), and Raman spectroscopy. It was established that olivine crystals were regenerated from silicate–carbonate melts at a temperature of \sim 1100 $^{\circ}$ C.

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To identify the nature of kimberlite melts, the physicochemical conditions of their evolution at the stage of uplift to the surface and crystallization at the final stage of kimberlite formation have been determined; the role of water and fluids of complex structure in these processes is the subject of long-term studies, which have been presented in numerous published works and reviews $[1-3]$. In connection with this, we believe that studying melt and fluid inclusions in kimberlite minerals will make it possible to obtain new information on the composition of primary, intermediate, and residual kimberlite melts, as well as on the PT-conditions of kimberlite formation. One such mineral of hypabyssal kimberlites from the Udachnaya-East pipe that is confined to the Upper Devonian stage of productive kimberlite magmatism, including all acting diamond deposits $(367 \pm 3.0 \text{ Ma})$ according to isotope dates [4, 5]), is unchanged magnesian olivine ($F_0 = 85-94$ mol %) contained in the kimberlites as isolated round or idiomorphic xenocrystals and as phenocrysts (idiomorphic inclusions) that are usually less than 1.0 mm in size $[6-10]$. However, according to our estimates, typical phenocrysts are less than 5%, which is considerably different from the other estimates [3]. The chemical composition of the groundmass of kimberlite is the following, % wt: SiO_2 28.1–29.6, TiO₂ 2.1–1.54, Al₂O₃ 2.43–2.58, FeO_{tot.} 8.9–13.0, MnO 0.21, MgO 28.1– 32.2, CaO $10.7-17.3$, Na₂O 1.4-3.61, K₂O 0.8-1.3, P_2O_5 , 0.5–1.0, which is similar to the composition of the groundmass of the kimberlite in [11].

This work is focused on study of the primary melt and fluids inclusions in regenerated olivines and newly formed phenocrysts of olivine by means of microthermometry, optic and scanning electron microscopy (SEM), electron and ion microprobe analysis (SIMS), inductively coupled plasma mass-spectrometry (ICP MSC), and Raman spectroscopy. These inclusions were found in previous studies [7, 9]. The procedure for the analysis of melt and fluid inclusions in minerals by inductively coupled plasma mass-spectrometry (ICP MS) was published in [12].

Olivine xenocrystals are characterized by a heterogenous dominant central part of irregular shape and a narrow outer edge having a zonal structure (Fig. 1а) [6]. All newly formed phenocrysts of olivine are nonzonal (Fig. 1b). The compositions of the outer zones and the relicts of the central parts (cores) of the regenerated olivines with inclusions of clinopyroxene and pyrope $(Cr_2O_3$ from 1.4 to 9.14 wt %) that prove the high-pressure genesis of the central parts of olivines were presented in detail in [6].

The isotopic composition of oxygen $(\delta^{18}O)$ in the regenerated megacrystals of olivine varies from 5.02 to 5.28 ‰ V-SMOW, and in the olivine phenocrysts, it is 5.05‰ V-SMOW; i.e., they conform to the mantle values. A similar $\delta^{18}O$ was determined for the fresh (unchanged) olivines from the mantle xenoliths in the same kimberlite pipe.

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Fig 1. Microimages of primary melt inclusions (a) in the regenerated crystal of olivine and (b) in the olivine phenocryst from the kimberlite of the Udachnaya-East pipe, Yakutia: (c) primary silicate-carbonate–salt melt inclusion, (d) primary high-silica melt inclusion, (e) high-carbonate-salt inclusion; Spl, spinel; Phl, phlogopite; Mll, melilite; Mtc, monticellite; Ap, apatite; Cal, calcite; Gl(?), unidentified isotropic silicate phase (glass?), and Ore, ore phase. All images are presented in reflected electrons.

Primary melt inclusions were found in the outer zones of the regenerated crystal of olivine (Figs. 1а– 1e), and primary partially decrepitated fluid inclusions, which were similar to the inclusions in olivines from the kimberlites of the Malokuonapskaya pipe,

Fig. 2. Microimage of primary partially decrepitated fluid inclusions in the central zone of the regenerated crystal of olivine from kimberlites of the Udachnaya-East pipe.

were contained in the homogeneous central parts (cores) of olivine (Fig. 2) [13]. In nonzonal phenocrysts of olivine, the melt fluid inclusions are usually distributed throughout the entire crystal volume (Fig. 1b). It is also typical for the regenerated olivines under study to contain numerous secondary melt inclusions the preservation of which is related to the propagation and subsequent healing of microcracks in olivine megacrystals by the kimberlite melt. They have various compositions and nonconstant volume ratios of crystal phases and a fluid phase; therefore, they cannot be used to obtain accurate microthermometric data.

Silicate-carbonate-salt, high-silica, and syngenetic high-carbonate-salt inclusions were identified among the primary melt inclusions (Figs. 1c–1e). The silicate-carbonate-salt melt inclusions are usually typical of the earliest zones of olivine regeneration (Fig. 1c). All melt inclusions from the outer zones of the regenerated olivine crystals and olivine phenocrysts are usually decrystalline. The composition of high-silica (Fig. 1d) and silicate-carbonate-salt melt inclusions is represented by several crystal phases and a gas phase: orthopyroxene, with an increased content of Ca, Fe, and Al, as compared to the crystal inclusions of orthopyroxene from the central zones of olivine [6]; melilite, monti-

Component	Opx	Mll	Mtc	Phl	Dol	Cal	Na, K, Ca- carbonate	Spl
SiO ₂	56.2	42.8	36.6	40.1			0.0	
TiO ₂	0.2	0.1	0.1	2.8			$0.0\,$	4.4
Al_2O_3	1.2	6.7	0.2	13.7			0.0	11.6
FeO	6.4	4.7	6.7	4.6	1.4	0.4	0.7	25.3
MnO	0.1	0.1	0.1		0.3	0.1	0.0	0.3
MgO	34.2	7.6	21.1	23.2	23.6	0.7	0.5	12.7
Cr_2O_3	0.3	$\qquad \qquad \longleftarrow$		1.0				44.5
CaO	1.0	32.9	33.9	0.0	29.7	55.6	43.8	0.0
Na ₂ O	0.2	3.5		0.0	0.0	0.0	8.3	
K_2O		0.3		9.8	0.0	0.0	5.2	
Total	98.9	98.7	98.5	95.2	55.0	56.8	58.5	98.8

Table 1. Representative composition of crystal phases in melt inclusions from the outer zones of regenerated olivines and olivine phenocrysts, wt %

Here, Opx, orthopyroxene; Mll, melilite; Mtc, monticellite; Phl, phlogopite; Dol, dolomite; Cal, calcite; Na,K,Ca-сarbonate, alkali carbonate; Spl, Cr-bearing spinel.

cellite, titanophlogopite (Table 1), and apatite (Raman lines are 430, 581, 963, 1081 cm⁻¹) and by an unidentified isotropic silicate phase (glass?), wt %: SiO₂ 60.8–62.6, TiO₂ 0.1–0.2, Al₂O₃ 1.4–4.7, FeO 1.3–4.8, MgO 10.5–15.2, CaO 8.8–10.6, Na₂O 3.6– 1.7, K₂O $0.9-1.7$, and Cl 0.9.

Along with these phases, the silicate-carbonatesalt inclusions usually contain Na and K chlorides and carbonates, such as magnesite (Raman lines are 212, $329, 738,$ and 1094 cm^{-1} , dolomite, and calcite (Table 1). In addition high-silica and silicate-carbonate-salt melt inclusions can also have chrome-bearing spinel (Table 1) with an increased content of Al and a decreased content of Fe and Cr, as compared to crystal inclusions of spinel from regenerated zones of olivine (Table 2), and perovskite.

Along with Na and K chlorides, the high-carbonate-salt melt inclusions (Fig. 1e) contained magnesite, dolomite, calcite, alkali carbonates (Table 1), strontianite (Raman lines are 1057, 1073 cm⁻¹), apatite, perovskite, chromite, titanomagnetite, and, in a few cases, Cr-bearing phlogopite, $\%$ wt: SiO₂ 40.6, TiO₂ 1.7, Al_2O_3 13.1, FeO 4.3, Cr₂O₃ 2.4, MgO 23.9, and $K₂O$ 9.4. Chromite, titanomagnetite, and Cr-bearing phlogopite are likely to be xenogenic phases for all these inclusions.

In accordance with the results of the ion microprobe analysis (SIMS), the water content in the isotropic silicate phase (glass?) and daughter phlogopites in silicate-carbonate-salt inclusions is 2.9 and 2.1% wt, and the content of rare and rare-earth elements is the following, g/t: Ba 21.1, Rb 1.6, Sr 38.8, Nb 4.6, Ta 0.03, La 0.8, Eu 0.05, Sm 0.13, Ce 2.13, and Gd 0.29 and Ba 83.8, Rb 99.7, Sr 28.2, Nb 1.47, Ta 0.41,

La 7.38, Eu 1.02, Sm 2.23, Ce 14.4, and Gd 5.53, respectively. According to the ICP MS data, the melt inclusions contained the following, g/t: Rb 0.38–2.4, Sr 3.0–11.7, Y 0.04–0.20, Zr 0.03–0.08, Nb 0.08– 0.18, Ta 0.001–0.005, Cs 0.02–0.05, Ba 5.7–15.0, La 0.12–0.57, Ce 0.19–0.88, Pr 0.02–0.09, Nd 0.05– 0.19, Sm 0.01–0.05, Eu 0.01–0.02, Gd 0.01–0.05, Dy 0.01–0.03, Ho 0.002–0.01, Er 0.004–0.01, and Yb 0.002–0.005. Here, the melt inclusions in the regenerated megacrystals of olivine were more enriched in heavy rare-earth elements $((La/Yb)_n = 48-110$ and 100–148, respectively), as compared to kimberlites. The isotopic composition of carbon in carbonates of the melt inclusions from the phenocrysts and the regenerated crystals of olivine is found within the mantle values ($\delta^{13}C = -5.05\%$ V-PDB) [9]. Homogenization of primary melt inclusions from the regenerated zones of olivine crystals and olivine phenocrysts takes place at 1100°C.

In addition to the melt and fluid inclusions, the outer zones of the regenerated megacrystals of olivine usually contain multiple crystal inclusions, among which we detected Cr-bearing spinel, chromite, titanomagnetite, perovskite, Cr-bearing phlogopite, and rutile that ornament the zones of olivine growth. The data of the ion microprobe analysis showed that the water content in the phlogopite crystallites from the outer zones of the regenerated megacrystals of olivine is \sim 1.7% wt.

The primary partially decrepitated fluid inclusions, which were found in the homogeneous central parts of the regenerated olivines from the kimberlites of the Udachnaya-East pipe, had similar composition to the fluid inclusions in the identical olivines from the Malokuonapskaya pipe [13]. According to the Raman

Table 2. Representative composition of minerals from the groundmass of kimberlites and crystal inclusions from the outer zones of regenerated olivines, wt %

Compo- nents	$Per-1$			Per Phl-1 Phl-2 Spl-1 Spl-2 Chr				Rut
SiO ₂			41.0	39.9				
TiO ₂	55.4	54.8	1.6	3.7	5.2	4.3	1.3	88.8
Al_2O_3	0.0	0.2	13.8	15.6	5.6	8.5	2.3	0.0
FeO	1.3	1.2	4.5	5.4	28.0	27.8	21.9	1.7
MnO			0.0	0.0	0.3	0.2	0.4	0.02
MgO	0.0	0.1	22.7	21.6	11.7	12.4	11.2	1.4
NiO					0.2	0.2		0.05
Cr_2O_3			2.5	0.1	47.9	45.7	62.2	3.4
CaO	37.6	34.5	0.0	0.0	0.1	0.0		0.03
Na ₂ O	0.5	0.8	0.0	0.0				
K_2O			10.0	9.8				
CeO ₂	1.1	3.4						
SrO	0.4	0.4						
Nb ₂ O ₃	2.0	1.2						
La ₂ O ₃	0.6	1.2						
ZrO ₂	0.2	0.1						
NdO ₃	0.4	1.4						
Total	99.5	99.3 96.1		96.1	99.0	99.2	99.3	95.4

Here, Per-1, perovskite crystal from the outer zone of the regenerated olivine; Per-2, perovskite crystal from the groundmass of the kimberlite; Spl-1, Cr-bearing spinel crystal from the groundmass of the kimberlite; Spl-2, Cr-bearing spinel crystal from the outer zone of the regenerated olivine; Chr, chromite from the outer zone of the regenerated olivine; Rut, rutile from the outer zone of the regenerated olivine; Phl-1, Cr-bearing phlogopite from the outer zone of the regenerated olivine; Phl-2, phlogopite from the groundmass of the kimberlite.

spectroscopy data, they also contained carbon dioxide, nitrogen, water, hydrogen, as well as methane, and other hydrocarbons that are heavier than $CH₄$, and some of them had magnesite and talc. The occurrence of high-density fluid inclusions that later underwent partial decrepitation confirms the high-pressure genesis of the central part of the olivines from the kimberlites of the Udachanya-East pipe [6].

Thus, at the early stages, the regeneration of olivine megacrystals and the growth of olivine phenocrysts occurred from silicate-carbonate-salt melts at \sim 1100 $\rm ^{\circ}C$ and, at the subsequent stages, from heterogeneous melts, representing immiscible silicate and carbonate-salt liquids. This is proved by the combined presence of silicate and their syngenetic carbonate-salt melt inclusions in the zone of growth. At the final (late magmatic) stage, the Udachanya-East pipe was formed from mostly carbonate-chloride melts at \sim 900 $^{\circ}$ C [14].

The results indicate that the kimberlite melt was enriched in volatile components, where hydrocarbons and their derivatives, as well as N, Cl, and sulfur-containing compounds played an important role along with carbon acid and water [15].

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