

## Secondary Melt Inclusions in Olivine from Unaltered Kimberlites of the Udachnaya-East Pipe, Yakutia

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In the central part of the Udachnaya-East kimberlite pipe situated in the Daldyn–Alakit district of the Yakutian kimberlite province, unique (in the high degree of its preservation) kimberlitic rock with abundant olivine, which did not undergo serpentinization, was found at a depth of 350–650 m. This kimberlite can be regarded as a reference primary rock that retained all features of the deep-seated melt [1]. The chemical composition of this kimberlite is as follows (wt %): SiO<sub>2</sub> 29.8, TiO<sub>2</sub> 1.55, Al<sub>2</sub>O<sub>3</sub> 2.45, FeO<sub>tot</sub> 8.50, MnO 0.16, MgO 32.0, CaO 10.8, Na<sub>2</sub>O 0.30, K<sub>2</sub>O 0.80; P<sub>2</sub>O<sub>5</sub> 0.40, CO<sub>2</sub> 6.90, total 93.66. The comparison of this composition with compositions of various Yakutian kimberlites, including diamond-rich rocks from the Udachnaya and Mir pipes [2], confirms the unique character of the unaltered kimberlite. The rock is brecciated and contains olivine phenocrysts of two generations (olivine I, 1.0–2.5 mm in size, and olivine II, <0.5 mm) and rare phlogopite phenocrysts [1]. Marginal zones of olivine I and grains of olivine II contain crystallites of Cr-spinel, orthopyroxene, magnetite, rutile, phlogopite, and perovskite; ore minerals often decorate growth zones in olivine. Crystallites of Cr-spinel, magnetite, and perovskite are also typical as inclusions in phlogopite phenocrysts. The microgranular groundmass consists of calcite, phlogopite, perovskite, ore minerals (Cr-spinel, Ti-magnetite, and ilmenite), Na–Ca-carbonates, and sulfides.

Secondary melt inclusions are clustered as linear trails or patches confined to the microfractures in olivine I and olivine II. The inclusions have rounded, drop-like, irregular, or semifaceted shapes. Their size ranges from 2 to 80 μm. The phase composition is as follows: finely crystallized aggregate (carbonates + sulfates + chlorides) + gas ± transparent crystalline phases ± ore

phases (Fig. 1). Silicates (tetraferriphlogopite, phlogopite, olivine, humite-clinohumite, and diopside), carbonates (calcite, dolomite, siderite, and Na–Ca-carbonates), Na and K chlorides, and sulfates have been identified among transparent phases. Magnetite, djerfisherite, and Ni-pyrrhotite occur as ore phases (magnetite and sulfides are often intergrown). Inclusions with a variable phase composition are observed within one chain.

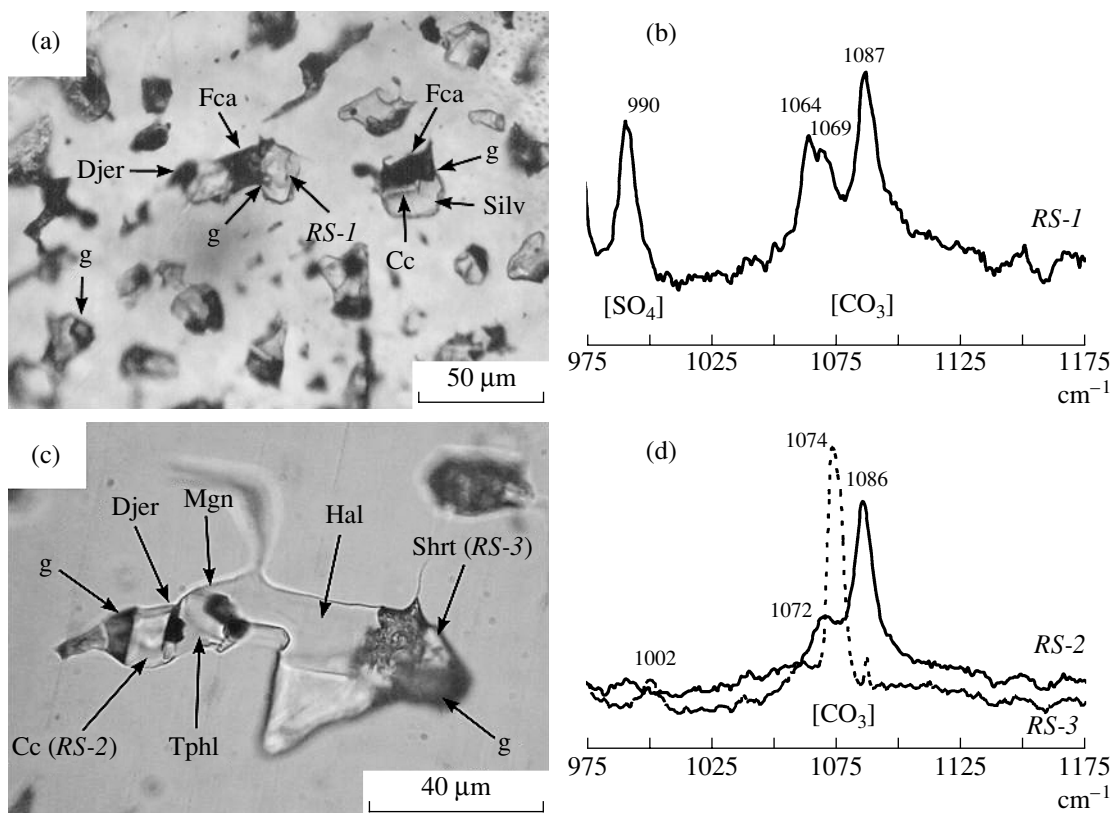
As was established from the cryometry, the fluid phase in inclusions is composed of a low-density carbon dioxide (triple point lies at –57.0 to –57.5°C). Thermometric experiments revealed that the inclusions completely homogenize in the range of 700–800°C. Our thermometric data are generally consistent with previous results on the secondary melt inclusions in olivine from kimberlites of the Udachnaya Pipe [3–6].

The chemical composition of inclusions was determined on a Camebax microprobe at the United Institute of Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences, using the standard technique. Unfortunately, we failed to obtain reliable results on the composition of heated inclusions, because the homogeneous melt did not quench into glass and formed a fine crystalline aggregate that was partly disintegrated during opening. Nevertheless, higher Ca, Na, K, and volatile contents are recorded in the heated inclusions relative to the bulk kimberlite composition. Probably, high alkali and volatile contents in the melt render the formation of homogeneous glass impossible [7]. The composition of crystalline phase turned out to be most interesting.

*Silicates.* Tetraferriphlogopite with a variable Al<sub>2</sub>O<sub>3</sub> content (0.2–6.5 wt %) is the most abundant silicate. The almost Al-free tetraferriphlogopite is predominant (Table 1). The mineral of this composition forms individual grains, 2–10 μm in size, and occasionally occurs as rims around tetraferriphlogopite containing an Al<sub>2</sub>O<sub>3</sub> admixture. All micas from melt inclusions differ in phlogopite from the kimberlite groundmass and crystalline inclusions in olivine. The coherent enrichment of phlogopite of groundmass and especially olivine-hosted inclusions in TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> (Table 1) indicates that they were crystallized as minerals of the lherzolite assemblage. This is supported by analogy with primary

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**Fig. 1.** (a, b) Olivine-hosted secondary inclusions in unaltered kimberlite of the Udachnaya-East Pipe; (c, d) Raman spectra of some daughter phases in inclusions. (Hal) halite, (Sylv) sylvite, (Cc) calcite, (Shrt) Na–Ca-carbonate (shortite or zemkorite), Mgn (magnite), (Djer) djerfisherite, (Tphl) tetraferriphlogopite, (Fca) fine-crystalline aggregate; (g) gas; (RS-1–RS-3) Raman spectra.

phlogopite inclusions in diamond [8]. Rare olivine, diopside, and humite-clinohumite are also found in the inclusions (Table 1). Olivine from the inclusions corresponds to  $\text{Fo}_{97.0-94.7}\text{Fa}_{2.6-5.0}\text{La}_{0.4}$  in composition and substantially differs in this respect from the host olivine.

Some transparent crystalline phases from unheated inclusions were partly disintegrated during opening, and Raman spectroscopy was used to obtain more reliable results. The presence of carbonates and sulfates, identified in nonopened inclusions based on characteristic peaks in the region of anion group oscillations, was subsequently confirmed by microprobe results.

**Carbonates.** The melt inclusions contain the following carbonate phases: calcite, dolomite, carbonate of the magnesite–siderite isomorphic series, and Na–Ca-carbonates (Table 2). Calcite is practically homogeneous with insignificant variations in CaO (54–57 wt %) and SrO (0.2–1.5 wt %) contents; MgO (up to 3.7 wt %) and FeO (up to 5.9 wt %) admixtures were recorded in particular grains. The high Na<sub>2</sub>O content (up to 13 wt %) in some crystalline phases from the inclusions indicates that they are probably composed of shortite or zemkorite [9, 10]. Raman peaks in the 1060–1075 cm<sup>-1</sup> region allow us to suggest that several Na–Ca-carbonate phases exist in the inclusions (Fig. 1).

**Chlorides, sulfates, and phosphate.** The determination of sulfates and chlorides from the melt inclusions turned out to be a complex task, because they are small and hygroscopic. Nevertheless, we succeeded in analyzing some inclusions containing abundant salt plates. Halite and sylvite, often closely intergrown with each other, were reliably identified. In addition the inclusions probably contain chloromagnesite  $\text{MgCl}_2$  and an unidentified Na–Mg chloride (Mg 15.6 wt %, Na 26.3 wt %, and Cl 14.1 wt %). Identification of sulfates was most difficult. According to the Raman spectra of [SO<sub>4</sub>] groups in the 980–1010 cm<sup>-1</sup> region (Fig. 1), the occurrence of thenardite, glauberite, and aphanthalite, as well as barite and celestite, is most probable. However, microprobe results yielded no more than 3 wt % SO<sub>3</sub> in most inclusions, and Ba and Sr were not detected. Aphanthalite  $\text{K}_2\text{Na}_2(\text{SO}_4)_2$  was detected in only one inclusion. The Mg phosphate was identified in some inclusions in association with Ca-carbonates (Table 2).

**Oxides.** Magnetite reveals insignificant variations in MgO (2.6–5.6 wt %) and FeO (85–89 wt %). The mineral belongs to the  $\text{MgFe}_2\text{O}_4$ – $\text{FeFe}_2\text{O}_4$  series with <1 mole % of other end members.

**Sulfides.** Djerfisherite from the inclusions is characterized by a wide compositional range (wt %): Fe 32.6–38.5, Ni 4.2–23.1, Co 0.1–0.5, Cu 0–17.6, K 8.9–9.1,

**Table 1.** Chemical composition (wt %) of daughter silicate phases in olivine-hosted secondary melt inclusions from the Udachnaya-East Pipe kimberlite

Component	1 (4)	2 (2)	3 (2)	4 (2)	5 (4)	6 (3)	7 (3)	8 (2)	9 (1)	10 (3)
SiO <sub>2</sub>	41.31	40.57	40.47	40.43	40.24	40.39	41.13	37.43	37.99	55.48
TiO <sub>2</sub>	0.59	2.42	0.20	0.07	0.06	0.04	n.d.	0.10	0.93	n.d.
Cr <sub>2</sub> O <sub>3</sub>	0.19	1.43	n.d.	n.d.	n.d.	n.d.	"	n.d.	n.d.	"
Al <sub>2</sub> O <sub>3</sub>	12.14	13.04	6.52	0.23	0.09	0.15	"	"	"	"
FeO	5.17	4.96	12.05	12.41	16.71	17.20	7.05	1.88	2.33	1.94
MnO	0.05	0.07	n.a.	n.a.	n.a.	n.a.	0.09	n.d.	n.a.	0.03
MgO	25.38	23.64	25.08	27.45	26.60	26.44	51.14	57.40	56.05	17.40
NiO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.35	n.a.	n.a.	n.a.
CaO	0.04	n.d.	0.03	0.04	n.d.	n.d.	0.05	0.12	n.d.	25.03
BaO	0.06	0.11	n.d.	n.d.	"	"	n.d.	n.d.	"	n.d.
Na <sub>2</sub> O	0.10	0.06	0.12	0.23	0.13	0.16	"	"	"	0.33
K <sub>2</sub> O	10.26	10.26	10.12	10.36	10.24	10.15	"	"	"	n.d.
F	0.42	0.50	0.15	0.44	0.44	0.16	n.a.	3.39	2.50	n.a.
Cl	0.06	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.d.
Total	95.75	97.12	94.73	91.65	94.50	94.69	99.81	100.32	99.80	100.22
O=F <sub>2</sub>	0.18	0.21	0.06	0.19	0.19	0.07	0.00	1.43	1.05	0.00
Total	95.58	96.91	94.67	91.47	94.31	94.62	99.81	98.89	98.74	100.22

Note: (1) Phlogopite in groundmass; (2) phlogopite inclusion in olivine; tetraferriphlogopite in olivine-hosted melt inclusions: (3, 4) core and margin of one crystal, (5, 6) separate grains; (7) host olivine; (8, 9) humite-clinohumite in inclusions; (10) diopside in inclusions. Numerals in parentheses are numbers of analyses. Detection limit is 0.11 wt % for F and 0.02 wt % for Cl. (n.d.) Not detected; (n.a.) not analyze.

**Table 2.** Chemical composition (wt %) of carbonates, sulfate, and phosphate in olivine-hosted secondary melt inclusions from the Udachnaya-East Pipe kimberlite

Component	1 (1)	2 (1)	3 (1)	4 (2)	5 (2)	6 (1)	7 (2)	8(2)
SiO <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.43
FeO	0.53	0.30	0.18	25.66	1.68	0.63	0.63	4.27
MgO	0.21	0.19	0.21	40.79	23.34	0.54	0.06	45.94
CaO	57.19	54.26	54.03	0.00	29.20	43.41	0.13	1.05
BaO	n.d.	n.d.	n.d.	0.10	n.d.	n.d.	0.09	n.d.
SrO	0.58	1.22	1.54	n.d.	0.42	1.01	n.a.	0.22
Na <sub>2</sub> O	n.d.	0.24	0.31	"	0.06	11.08	19.03	2.48
K <sub>2</sub> O	"	n.d.	n.d.	"	n.d.	4.87	29.08	0.16
P <sub>2</sub> O <sub>5</sub>	"	"	"	"	"	n.d.	n.a.	45.30
SO <sub>3</sub>	"	"	"	"	"	1.61	50.50	n.d.
Total	58.52	56.22	56.27	66.55	54.70	63.15	99.52	99.85

Note: (1–3) Calcite; (4) carbonate of the magnesite–siderite series; (5) dolomite; (6) Na–Ca-carbonate (shortite?, the trapping of calcite during microprobe analysis is possible); (7) apthitalite; (8) Mg-phosphate.

Na up to 0.7, S 32.7–33.4, and Cl 1.2–1.4. Variations of Fe, Ni, and Cu within a particular grain from the center to margin are insignificant. In addition to djerfisherite, Ni-pyrrhotite (Fe 55.1 wt %, Ni 4.4 wt %, Co 0.4 wt %, Cu 0.8 wt %, and S 38.9 wt %) was identified in one case. Djerfisherite was previously found in kimberlites as rims around sulfide segregations in diamond and xenoliths and as a late magmatic phase in the groundmass [11–13].

The highest possible pressure of inclusion entrapment calculated with a FLINCOR program is <1 kbar at 800°C. Hence, the inclusions were trapped at a shallow depth and likely are relicts of the highly evolved kimberlitic melt. Judging from the assemblage of crystalline phases in the melt inclusions, the kimberlitic melt presumably had a silicate–carbonate composition with high volatile (Cl, S) contents at the late stage of

crystallization. Thus, the evolution of kimberlitic melt during crystallization was directed toward enrichment in CaO, Na<sub>2</sub>O, K<sub>2</sub>O, FeO, and volatile components and the depletion in SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub>. After the crystallization of olivine II, the melt acquired silicate-carbonate composition with a marked carbonatitic trend. The further crystallization of minerals in the groundmass (phlogopite, Ti-magnetite, and perovskite) gave rise to the formation of alkaline-carbonatitic residual melt. At the same time, Ca, K, CO<sub>2</sub>, and incompatible elements (Na, Cu, Ni, Cl, and S) were accumulated in this melt. The last drops of melt, left after the crystallization of ore minerals and carbonates, were enriched in Cl and S, promoting the formation of chlorides and sulfates. It cannot be ruled out that the kimberlitic melt was able to assimilate some evaporites from the country rocks that served as an additional source of Na, K, S, and Cl.

The study of olivine-hosted inclusions has shown that Ca-Mg-Fe-carbonates, Na-Ca-carbonates, and djerfisherite were formed in kimberlites of the Udachnaya-East Pipe at the late magmatic stage. In the process of crystallization, the kimberlitic melt evolved toward carbonatites. Thermobarogeochemical investigations of the Palaborwa alkaline-carbonatite complex (South Africa) have shown that the melt inclusions in minerals from this complex are characterized by approximately the same assemblage of crystalline phases as the secondary inclusions in olivine from kimberlites of the Udachnaya-East Pipe [14, 15].

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