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GEOCHEMISTRY

Chloride–Carbonate Fluid in Diamonds from the Eclogite Xenolith

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The important role of the fluid phase in mantle mineral formation is currently a subject of debate. Data on the composition of the fluid phase are mainly based on geochemical studies of metasomatized mantle rocks and inclusions in the xenolith minerals. Owing to its unique physical and chemical prosperities, a diamond could preserve primary inclusions of mineral-forming media during transportation to the surface with the kimberlite melt. Fluids or volatile-saturated melts were recently found in diamond-forming media [1–4]. This paper presents the first direct determinations of the composition of fluid inclusions in diamonds from eclogite xenoliths in the Udachnaya kimberlite pipe.

The studied xenolith (10 × 9 × 5 cm, about 800 g in weight) is the bimineral eclogite, which consists of green xenomorphic clinopyroxene (5–10 mm) and round garnet (3–10 mm) grains accounting for 55 and 45 vol %, respectively. The xenolith contains partially melted areas. The garnet and pyroxene are crosscut by veins consisting of glass and its replacement products. The glass veins in garnet contain spinel crystals. The partial melting areas in pyroxene are surrounded by a characteristic sponge rim.

The compositions of primary matrix minerals in xenolith were determined on a JEOL JXA-8100 microprobe at the Institute of Geology and Mineralogy, Novosibirsk (table). The compositions of garnets correspond to those in group B eclogites (Prp 46%, Alm 21%, Gross 25%) [5]. Clinopyroxene is represented by omphacite (Mg# 82%), which also corresponds to clinopyroxenes of Group B eclogites [6]. The temperature calculated from garnet–pyroxene equilibrium [7] is 1150°C at a pressure of 50 kbar.

We extracted 35 diamond crystals of different habits and their intergrowths (0.1–0.9 mm in size) from the central part of the xenolith by the thermochemical decomposition method. The intergrowths are mainly represented by aggregates of two to several tens of crystals. Both individual crystals and their intergrowths have distinct cubic habits. Numerous octahedral apices are observed on the cuboid surface. The diamonds show no traces of dissolution. Some crystals have an octahedral habit. In addition, intergrowths of cuboids and small octahedrals are also observed.

The cubic diamond crystals and their intergrowths from the xenolith have a black color owing to the presence of a thin outer rim (10–20 μm) with numerous dark microinclusions less than 1 μm in size (Fig. 1). Raman spectroscopy shows the presence of graphite in some microinclusions. The central part of the crystals is yellowish and transparent or semitransparent owing to the lower content of microinclusions. One can distinctly see that the microinclusions in the central part of the crystal mark out the fibrous internal structure.

The carbon isotopic composition in diamonds from the xenolith was determined using a Finnigan Mat Delta mass spectrometer at the Analytical Center of the Institute of Geology and Mineralogy according to the method described in [8]. The determined $\delta^{13}C$ (VPDB)

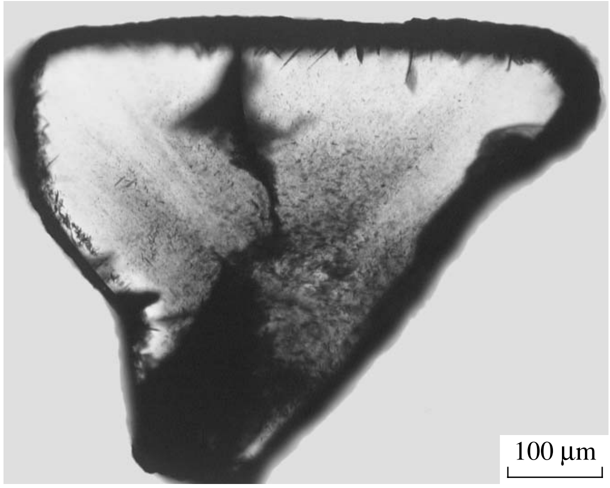

Fig. 1. Internal structure of the cubic diamond from the eclogite xenolith: plane-parallel plate of the diamond crystal oriented along 001 in transmitted light.

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Composition of rock-forming minerals and microinclusions in the diamonds from eclogite xenolith

Component	Cpx	Grt	Fluid 1	Fluid 2	Fluid 3	Fluid 4	Udr-9	
							core	rim
SiO_2	56.3	41.2	2.5	2.66	1.49	2.2	4.51	4.60
TiO_2	0.15	0.27	4.64	2.16	4.3	3.02	5.36	6.35
Al_2O_3	7.64	22.8	1.18	1.51	1.08	1.33	1.54	1.24
Cr_2O_3	0.02	0.06	–	0.97	–	–	0.32	0.69
MnO	0.05	0.29	–	0.87	0.04	–	0.65	0.33
FeO	3.53	13.0	14.9	9.1	8.3	12.9	14.0	16.7
MgO	11.0	12.5	0.57	2.54	0.72	3.34	2.96	2.00
CaO	16.4	9.51	7.85	2.6	7.9	9.64	9.06	10.1
BaO	n.a.	n.a.	11.9	5.74	24.8	14.1	n.a.	n.a.
Na_2O	4.09	0.10	8.4	12.6	10.1	13.8	5.01	4.88
K_2O	0.14	0.01	12.9	22.9	11.1	9.6	20.8	19.0
Cl	n.a.	n.a.	16.3	21.4	18.1	17	24.3	24.5
Total	99.33	99.65	–	–	–	–	–	–

Note: (Cpx) Rock-forming clinopyroxene; (Grt) rock-forming garnet; (Fluid 1–4) individual microinclusions in the diamonds; (Udr-9) average composition of the fluid microinclusions in the central and marginal parts of a single diamond crystal. (n.a.) Not analyzed.

values vary from –3.5 to –6.8‰ for cubic diamonds. The average $\delta^{13}C$ of –4.8‰ ($\sigma = 1.07$, $n = 11$) practically coincides with that of cubic diamonds from the Udachnaya Pipe (–4.5‰) [9] and is close to the average mantle value [10].

Based on IR Fourier spectroscopy, the diamonds from the xenolith correspond to type IaA (Fig. 2); i.e., they contain A centers (paired nitrogen atoms replacing carbon), which are typical of cubic diamonds from this deposit [9]. The total content of the nitrogen admixture varies from 400 to 900 ppm. The presence of an additional line 3107 cm^{-1} in the studied diamonds is related to the structural hydrogen admixture. In addition to the absorption bands related to the admixture of nitrogen and hydrogen centers, lines related to the microinclusions of water (3420 and 1650 cm^{-1}), carbonates (1430 and 880 cm^{-1}), and silicates (1050, 1015, and 970 cm^{-1}) are also present in the absorption spectra of diamonds.

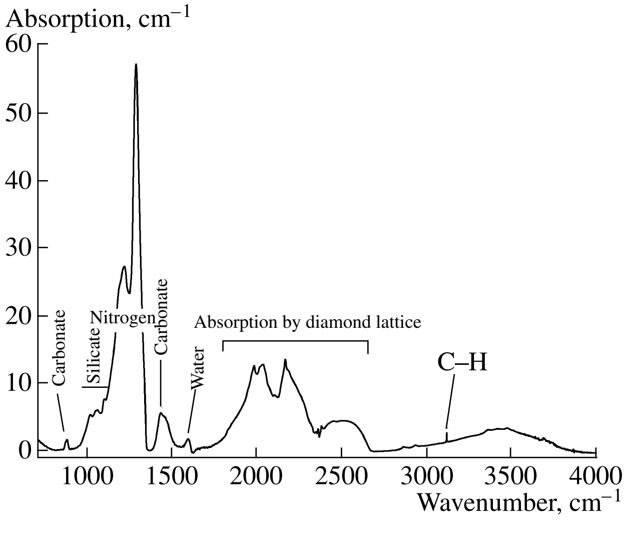

Fig. 2. IR absorption spectrum of diamonds with microinclusions from the eclogite xenolith.

Plane parallel plates 50 μm thick were cut from some diamonds to study microinclusions. The composition of near-surface microinclusions was determined using a JEOL JSM 6380-LA scanning electron microscope equipped with an energy-dispersive spectrometer (ion current 15 keV, acceleration voltage 10 nA). The contents of major elements were normalized to 100%. They show wide variations for individual microinclusions (table, fluids 1–4). The table demonstrates the average compositions of microinclusions in the central ($n = 15$) and peripheral ($n = 15$) parts of crystal Udr-9 (Fig. 1).

The studied microinclusions are characterized by extremely high contents of Cl and alkalis (especially K_2O), high content of BaO, and a relatively high content of FeO ($Mg^{\#}$ 9–14%). At the same time, the contents of SiO_2, Al_2O_3, and MgO are extremely low. The microinclusions in the studied diamonds from the eclogite xenolith have a higher K content and an unusually high Cl content as compared to those in the diamonds from the Udachnaya Pipe (Fig. 3). The K/Cl ratio (0.6–0.7) is significantly lower than those in microinclusions from other diamonds of this deposit (~2.5). At the same time, this ratio is significantly higher in the mantle (7 (±2)) [11]. This fact indicates the important role of brines in the crystallization of diamonds from the xenolith. In addition to chlorides, carbonates also occur in the studied microinclusions (IR data indicate that the carbonate/(carbonate + water) ratio is ~90%). Thus, the obtained data indicate that the diamonds were derived from the ultrapotassic chloride–carbonate fluid/melt, which could be generated either by mantle differentiation or subduction of oceanic sediments and seawater.

The high K_2O content regardless of contents of other components is a characteristic feature of many diamonds from kimberlites and lamproites in different regions of the world. The cloudy microinclusions in diamonds from the Koffiefontein kimberlite pipe (South Africa) contain high-Cl brines (water–salt inclusions) [12]. These microinclusions, as in our case, have an extremely low K/Cl ratio (0.5–0.6). The same K/Cl ratio was found in the brine inclusions in diamonds from the Diavik Mine, Canada [13]. The authors of the cited work noted that the main component of brines in diamonds from different cratons has a similar composition. Our data confirm this conclusion. At the same time, the studied inclusions from the xenolith diamond slightly differ from those in diamonds from Canada and South Africa. Primarily, they have significantly lower water content. It is worth mentioning that kimberlites from the Udachnaya–Vostochnaya Pipe are distinguished from kimberlites of type I by the extremely low water content (<1 wt %) [14]. The studied inclusions are also characterized by high Ti content and low Mg#, which can be explained by interaction of the carbonate-salt melt with the protolith.

Continuous compositional transitions between water–silicate and carbonate inclusions and between carbonatite and water–salt inclusions coupled with the absence of intermediate compositions between water–silicate and salt end members suggest a possible immiscibility between carbonate–salt and water–silicate carbonate liquids in mantle conditions (Fig. 4). The immiscibility is also indicated by the presence of chloride–carbonate segregations in the kimberlites from the Udachnaya Pipe [14]. The immiscibility model in the mantle ultrapotassic liquids could explain the specific evolution of these media. A continuous compositional series of chloride–carbonate microinclusions in the cubic diamonds from the Udachnaya Pipe is consistent with experimentally determined temperature trends for chloride–carbonate liquid: increase in contents of carbonates and Si with decreasing temperature [15]. The influx of this fluid in the eclogite protolith presumably was responsible for diamond formation. The low aggregation state of nitrogen centers in the studied diamonds indicates their relatively short residence time in the mantle. This fact together with similar K/Cl ratios in kimberlites from the Udachnaya Pipe and the studied inclusions, as well as the low water content, indicates a close relation between diamond formation and kimberlite magmatism.

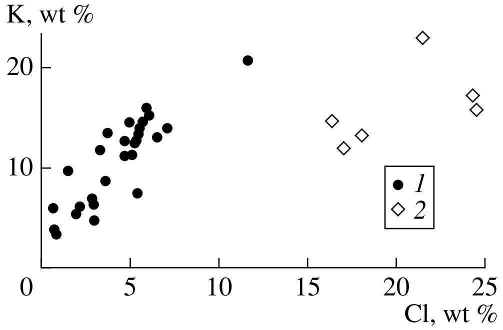

Fig. 3. K vs. Cl (wt %) relationship in the microinclusions from cubic diamonds from the Udachnaya kimberlite pipe (*1*) and eclogite xenolith (*2*).

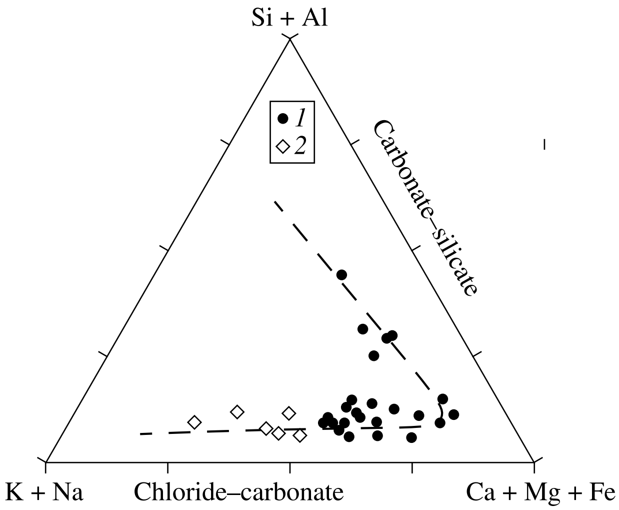

Fig. 4. Compositional features of microinclusions in the cubic diamonds from the Udachnaya kimberlite pipe (*1*) and eclogite xenolith (*2*).

Thus, the results obtained in this study confirm the role of chloride–carbonate liquids in the formation of diamonds and generation and evolution of compositionally extremal kimberlite magmas.

ACKNOWLEDGMENTS

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