

# Interface partition coefficients of trace elements in carbonate–silicate parental media for diamonds and paragenetic inclusions (experiments at 7.0–8.5 GPa)

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## Abstract

Interface partition coefficients  $K_D^{\text{TE}}$  of a representative set of trace elements (TE) in the partly molten diamond-forming peridotite–eclogite–carbonatite system are experimentally determined at 7.0–8.5 GPa. The experimental data evidence that trace-element partition does not depend on the melt composition, with heavy rare-earth elements (HREE) concentrating mainly in garnet. Model TE partition coefficients for the natural diamond-producing carbonatite melts of mantle chambers are calculated based on TE concentrations in minerals of peridotite and eclogite parageneses of diamond inclusions, on the one hand, and on the experimental  $K_D^{\text{TE}}$  coefficients, on the other. The results show that the TE of the parental media are mostly the mantle peridotite components, with the parental media being depleted in medium (Ba, La, Ce, Pr, Nd, Sm, Eu, Gd) and heavy (Tb, Dy, Ho, Er, Yb, Lu, Hf) rare-earth elements relative to the primitive peridotite. The elevated contents of Sr, Nb, and Ce in the completely miscible carbonate–silicate melts might be due to the participation of “metasomatic agents” in the formation of chambers of diamond-forming carbonatite magmas.

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**Keywords:** trace elements; carbonate–silicate system; diamond genesis; diamond formation chamber; experiment

## Introduction

Trace elements in paragenetic phases included in natural diamonds make up the general geochemical background of diamond-forming processes in the Earth's mantle. Diamond-hosted paragenetic inclusions are fragments of multiphase diamond-forming media, which testify to their variable multi-component chemical composition. The mantle-carbonatite theory of diamond genesis (Litvin, 2013a) describes the patterns of variation in the chemical composition and phase state of parental media and resulting formation of diamonds and paragenetic inclusions. The summarized results of physicochemical studies of diamond-forming systems (Litvin, 2007; Litvin et al., 2012; Shushkanova and Litvin, 2008) and data of mineralogical analysis of inclusions (Logvinova et al., 2008; Schrauder and Navon, 1994; Sobolev, 1977; Zedgenizov et al., 2009) suggest that completely miscible carbonate–silicate (carbonatitic) melts with dissolved carbon serve as a basis for

parental media. The main argument is that only these media can meet the criterion of syngensis of diamonds and primary inclusions (Litvin, 2004, 2007) to ensure joint formation of diamonds and all the paragenetic phases (and their fragmentary inclusions).

Trace elements were determined both in the peridotitic (Stachel and Harris, 1997) and eclogitic (Stachel et al., 2004) minerals of inclusions and in isolated carbonatite phases (Schrauder et al., 1996; Weiss et al., 2013). It seems the most likely that multicomponent carbonatite phases in diamond-hosted leak-tight inclusions are solidified fragments of completely miscible carbonate–silicate (carbonatitic) parental melts. The diamond-producing capability of such melts cannot be determined from mineralogical data alone. However, test experiments with melts whose compositions reproduced the compositions of carbonatite inclusions in diamonds of Botswana (Schrauder and Navon, 1994) clearly showed their high diamond-producing capability (Litvin and Zharikov, 2000). Note that the SiO<sub>2</sub> content of the carbonatitic melts varied from 13.6 to 45.1 wt.%. The fact that such parental melts meet the criterion of syngensis of diamonds and primary inclusions was confirmed by physicochemical experiment (Litvin et al.,

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2012). The trace-element contents of phases included in diamonds are sometimes used to find out the possible chemical nature of diamond-forming media. For example, the trace-element contents of isolated primary garnet and clinopyroxene inclusions in polycrystalline diamondites suggest the participation of carbonatitic melts in diamond genesis (Kurat and Dobosi, 2000). This agreed with the results of test experiments on diamond crystallization in the carbonate–carbon systems (Litvin, 1998; Pal'yanov et al., 1999; Sokol et al., 1998). Microinclusions of solidified high-density parental melts with a carbonatitic component were repeatedly detected in diamonds (Navon et al., 1988; Schrauder and Navon, 1994). Physicochemical experimental studies showed that such inclusions give an important insight into the fundamental physicochemical features of the parental media of diamonds and their syngenetic inclusions (Litvin et al., 2012).

Recently, abundant analytical data have been obtained on the trace-element contents of isolated inclusions with solidified melt and volatile components in fibrous and coated diamonds (Klein-BenDavid et al., 2010, 2014; Weiss et al., 2013; Zedgenizov et al., 2007). Particularly interesting are some analyses of the trace-element contents of silicate minerals and fragments of carbonatitic parental melts coexisting in one inclusion (Tomlinson et al., 2009). Note the low accuracy of the analysis of the included phases for major and trace elements because of their small size and, maybe, the inevitable contribution of the neighboring phases. Nevertheless, an attempt was made at estimating the partition coefficients of trace elements (Sr, Y, Lu, Tm, Er, Ho, Tb, Dy, Eu, Sm, Nd, Pr, Ce, La, Ti, and Nb) in inclusions in diamonds of the Panda kimberlite pipe, Canada, which contain peridotitic (Cr-clinopyroxene) and eclogitic (omphacite and garnet) mineral phases coexisting with a multiphase fluid. In reality, the fluid is mainly a mixture of solidified multicomponent carbonate melt and potassium chloride with some amount of volatile compound H<sub>2</sub>O. Strictly speaking, the obtained trace-element partition coefficients cannot be extended to the pairs mineral–carbonatitic melt of parental media free of chloride inclusions, which is more typical of the association of primary inclusions in natural diamonds. The more so, as carbonate and chloride melts can show liquid immiscibility under diamond-forming conditions, according to experimental data in (Safonov et al., 2007). It is possible that the trace-element partition between these melts influences their relative contents in the pair mineral–carbonatitic melt. Therefore, note that for the eclogitic pairs clinopyroxene–fluid and garnet–fluid, the partition coefficients for almost all the trace elements considered in (Tomlinson et al., 2009) are more than an order of magnitude higher than the coefficients for the same trace elements experimentally determined for the pairs of eclogitic clinopyroxene and garnet with completely miscible carbonate–silicate melt (Kuzyura et al., 2010).

A direct approach to the study of the interface partition of trace elements between peridotitic and eclogitic paragenetic minerals and carbonatitic melts, which are parental for both diamonds and paragenetic minerals, is based on the mantle–carbonatite theory of diamond genesis. It has become possible

to determine the geochemical background of diamond-forming processes by experiment, with a reliable modeling of the compositions of the mantle parental media of diamonds and paragenetic inclusions (Kuzyura et al., 2010, 2014).

The present study is aimed at direct experimental determination of the interface partition coefficients of Rb, Cs, Pb, Ba, Th, U, Nb, Ta, La, Ce, Sr, Pr, Nd, Zr, Hf, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, and Sc in the multicomponent diamond-forming peridotite–carbonatite and eclogite–carbonatite systems under *PT*-conditions of the thermodynamic stability of diamond. The results obtained are applied to the assessment of the metasomatic–magmatic model for the origin of the parental media of diamonds and syngenetic inclusions and the relative contribution of the mantle source, on the one hand, and its metasomatizing agent, on the other.

## Methods

Previously, phase transformations and the interface partition of trace elements in the case of partial melting of natural carbonatite were studied by the authors at high pressure (Kuzyura et al., 2010). Preliminary data on the peridotite–carbonatite system are presented in (Kuzyura et al., 2014). The compositions of the chemically variable carbonate–silicate growth medium for diamond were modeled by the melanocratic carbonatites of the Chagatai complex (Uzbekistan), whose melts are highly efficient for the nucleation of the diamond phase (Litvin et al., 2001, 2005). The diamond formation is accompanied by the formation of syngenetic garnet and clinopyroxene, similar to those in assemblages in high-Ca diamond-bearing eclogites and grosspidites (Bobrov et al., 2004).

The subsequent study of the trace-element partition in diamond-forming mantle systems was aimed at the multicomponent peridotite–carbonatite and eclogite–carbonatite systems. The bulk composition of the starting carbonate–silicate mixtures (wt.%) in terms of the oxides of elements was as follows:

Per<sub>30</sub>Carb<sub>70</sub> (sample 2440): SiO<sub>2</sub>, 13.52; Al<sub>2</sub>O<sub>3</sub>, 1.04; FeO, 15.08; CaO, 22.84; MgO, 12.41; Na<sub>2</sub>O, 0.11; CO<sub>2</sub><sup>\*</sup>, 35.01; Ecl<sub>60</sub>Carb<sub>40</sub> (sample 2233): SiO<sub>2</sub>, 32.73; Al<sub>2</sub>O<sub>3</sub>, 9.49; FeO, 16.53; CaO, 10.70; MgO, 10.07; Na<sub>2</sub>O, 0.72; CO<sub>2</sub><sup>\*</sup>, 19.76; Ecl<sub>60</sub>Dol<sub>40</sub> (sample 2306): SiO<sub>2</sub>, 33.78; Al<sub>2</sub>O<sub>3</sub>, 8.51; FeO, 8.61; CaO, 14.06; MgO, 13.87; Na<sub>2</sub>O, 1.25; CO<sub>2</sub><sup>\*</sup>, 19.93. CO<sub>2</sub><sup>\*</sup> is the value calculated from the difference between the analytical total and the total of the rest of the oxides. The compositions of the peridotite and eclogite phases used in the experiments have natural prototypes—garnet lherzolite (Mathias et al., 1970) and eclogite (Sobolev, 1977), respectively. According to the experimental data (Bobrov and Litvin, 2009; Litvin et al., 2005), the carbonate–silicate melts of the systems under study are efficient for the formation of diamond and paragenetic minerals and melts.

A series of experiments was performed using an apparatus of the “anvil-with-hole” type (Institute of Experimental Mineralogy) at 7.0–8.5 GPa (which corresponds to conditions of

diamond stability) to study the mineral–melt and mineral–mineral equilibrium partition of trace elements in the peridotite–carbonatite and eclogite–carbonatite systems. A mixture of trace elements, 30 mg of each compound (oxides of Cs, Th, U, Ta, Nb, La, Ce, Pb, Pr, Nd, Zr, Hf, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, and Sc; RbCl; and strontium and barium carbonates) was prepared and homogenized by long-lasting rubbing with alcohol, dried, and added to a carbonate–silicate mixture in the ratios 98.6:1.4 and 99:1 for the eclogite–carbonatite and peridotite–carbonatite systems, respectively. The starting carbonate–silicate and trace-element mixtures were brought together, thoroughly homogenized for 1 h, and dried at 105 °C for several days. The relationships of the components in the starting materials corresponded to  $[(\text{Ol}_{60}\text{OPx}_{16}\text{CPx}_{12}\text{Grt}_{12})_{30}\text{Carb}_{70}]_{99}\text{TE}_1$  for the peridotite–carbonatite and to  $[(\text{CPx}_{52-64}\text{Grt}_{28-40}(\text{SiO}_2)_{20})_{59.3}\text{Carb}_{39.3}]_{98.6}\text{TE}_{1.4}$  for the eclogite–carbonatite systems. The mineral relationships were corrected to obtain large enough garnet grains together with olivine and/or clinopyroxene. Carbonate corresponded to dolomite ( $\text{CaCO}_3$ )<sub>50</sub>( $\text{MgCO}_3$ )<sub>50</sub> and triple carbonate ( $\text{CaCO}_3$ )<sub>33.33</sub>( $\text{MgCO}_3$ )<sub>33.33</sub>( $\text{FeCO}_3$ )<sub>33.33</sub>. The experimental cell (Kuzyura et al., 2010; Litvin, 1991) with a 30-mm outer diameter is made of lithographic limestone (Algeti River gorge, Georgia). A graphite rod, 7.2 mm high and 6 mm in diameter, is placed in the cell. The rod, which is also a heater, has a hole 2 × 2 mm in size for the sample, and the starting mixture is placed into this hole. The collar between cell and graphite heater with an 8-mm outer and 6-mm inner diameters, made of a compressed MgO–BN mixture (3 : 1), served as a heat insulator. The temperature distribution in the strongly compressed samples was quite uniform (within ±20 °C) because of their small sizes and central position within the heater. Pressure and temperature were preliminarily calibrated using Bi, Tl, and Ba sensors and the Pt<sub>70</sub>Rh<sub>30</sub>/Pt<sub>94</sub>Rh<sub>06</sub> thermocouple, respectively, with correction of pressure along the curve of the graphite–diamond equilibrium. The accuracy of determination of pressure and temperature is estimated at ±0.1 GPa and ±20 °C (Kuzyura et al., 2010; Litvin, 1991). After quenching at a rate of ~300 °C/s, the samples were pulled out and polished. The experimental samples were examined using a CamScan M2300 SEM (VEGA TS 5130MM), and the overall compositions of the phases were analyzed using a Link INCA Energy energy-dispersive microprobe at the Institute of Experimental Mineralogy (with the participation of A.N. Nekrasov, K.V. Van, and A.A. Viryus). The accelerating voltage was 15 kV. The trace elements in the same samples (after the removal of carbon dusting) were determined by LA-ICP-MS at the Science Facilities Department of the Natural History Museum, London, using a Thermo Elemental PQ3 +S ICP-MS with a New Wave UP213AI laser ( $\lambda = 213$  nm) and an Agilent 7500cs ICP-MS with a New Wave UP193FX laser ( $\lambda = 193$  nm). The operation modes of the lasers ensured a radiation density of 3 J/cm<sup>2</sup> and a pulse frequency of 10 Hz. The mass-spectrometry data were recorded with a temporal resolution of 10 ms. Homogeneous or fine-grained areas of melt, preferably with no large dendrites (the beam diameter was 40–50 μm), were analyzed along with

isometric grains of minerals: garnet, clinopyroxene, and olivine (minimum crater diameter was 20 μm). Convergence of the data was ensured by external calibration against standards (glass NIST 610 and basalt glass BCR) before and after each series of analyses. Correction for the matrix effect and difference in the masses lost by the samples and standards was made using an internal standard—the Ca content of the phase under study (or Si content if Ca was not detected), preliminarily determined with an electron microprobe.

## Results

The major- and trace-element contents of the experimental phases are shown in Table 1. We present the results for the most representative samples, in which the grains of newly formed silicate minerals are at a contact with melt. The products of the experiments include pyrope–almandine–grossular garnets Prp<sub>0.76-0.83</sub>Gros<sub>0.12-0.16</sub>Alm<sub>0.02-0.12</sub> and Prp<sub>0.13-0.71</sub>Gros<sub>0.25-0.77</sub>Alm<sub>0.03-0.60</sub> for the eclogite–carbonatite and peridotite–carbonatite systems, respectively, as well as hedenbergite–diopside clinopyroxene with an aegirine component (0.40–4.72 wt.% Na<sub>2</sub>O), olivine Fo<sub>0.85-0.98</sub>, a mixture of carbonates, and the carbonate–silicate quenching melt (Fig. 1, Table 1). The formation of several olivine crystals was detected in sample 2306; their compositions are also presented in Table 1; i.e., the sample can be assigned to olivine eclogites, which rarely occur in kimberlite-hosted mantle xenoliths (Dawson, 1980). The garnet and clinopyroxene crystals were up to 200 μm in size, and the olivine crystals, up to 150 μm. Completely miscible carbonate–silicate melts were formed in the experiments. These melts transformed into fine-grained solid substances with a dendritic texture (as in experiments on “carbonate” synthesis of diamonds) during the quenching, whereas the melts of the Chagatai (Uzbekistan) natural melanocratic carbonatites were quenched into dense homogeneous glass (Kuzyura et al., 2010). Nevertheless, areas of quenching glass are also observed in the systems under study. The typical quenching substances of the carbonate–silicate melts of the peridotite–carbonatite and eclogite–carbonatite systems consist of small carbonate crystals with interstitial oxides and silicates. The melts (from carbonatitic to dolomitic) contain 41–54 wt.% CO<sub>2</sub>. The Mg# value (Mg/(Mg + Fe)) of the quenching melts is 0.85–0.98. The garnet, clinopyroxene, and olivine crystals in the samples are usually surrounded by carbonate–silicate melt. Sometimes, owing to gravity and the low viscosity of the melt, large crystals fractionate and separate from the carbonate–silicate parental melts, which causes the formation of their accumulations.

The trace-element contents of the experimental phases are shown in Table 1. Note that the peridotite–carbonatite system is characterized by more intense (by two to ten times) accumulation of heavy trace elements in garnet than the eclogite–carbonatite system; on the contrary, clinopyroxene in the peridotite–carbonatite system has somewhat lower trace-element contents than that in the eclogite–carbonatite system

Table 1. Major (wt.%) and trace (ppm) elements in experimental phases

Component	Eclogite–carbonatite system								Peridotite–carbonatite system			
	Sample 2233			Sample 2306					Sample 2440			
	[[Cpx <sub>64</sub> Grt <sub>16</sub> (SiO <sub>2</sub> ) <sub>20</sub> ] <sub>59.3</sub> Carb <sub>39.3</sub> ] <sub>98.6</sub> TE <sub>1.4</sub> <sup>1</sup>			[[Cpx <sub>52</sub> Grt <sub>28</sub> (SiO <sub>2</sub> ) <sub>20</sub> ] <sub>59.3</sub> Dol <sub>39.3</sub> ] <sub>98.6</sub> TE <sub>1.4</sub> <sup>1</sup>					[Ol <sub>60</sub> Op <sub>16</sub> Cpx <sub>12</sub> Grt <sub>12</sub> ] <sub>30</sub> Carb <sub>70</sub> ] <sub>99</sub> TE <sub>1</sub> <sup>1</sup>			
	1510 °C			1600 °C					1460 °C			
	8.5 GPa			8.5 GPa					7.0 GPa			
	60 min <sup>2</sup>			155 min <sup>2</sup>					180 min <sup>2</sup>			
	Grt (n = 4)	Cpx (n = 4)	L (n = 3)	Grt (n = 6)	Cpx (n = 4)	Ol (n = 4)	L (n = 4)	Grt (n = 3)	Cpx (n = 2)	Ol (n = 3)	L (n = 3)	
SiO <sub>2</sub>	43.48	56.48	43.08	44.55	55.36	41.23	11.46	43.31	54.02	40.02	13.03	
TiO <sub>2</sub>	0.09	0.03	0.55	0.10	0.04	0.07	0.02	–	–	–	–	
MnO	0.03	0.04	0.06	0.08	0.06	0.05	0.04	0.00	0.00	–	–	
Al <sub>2</sub> O <sub>3</sub>	22.20	8.63	6.35	21.04	4.06	0.34	1.80	23.60	2.73	0.00	2.71	
Cr <sub>2</sub> O <sub>3</sub>	0.12	0.09	0.03	0.11	0.04	0.01	0.04	–	–	–	–	
FeO	7.62	3.24	3.13	2.80	0.99	1.92	1.18	2.61	0.71	14.35	1.70	
Na <sub>2</sub> O	0.44	4.72	3.99	0.34	1.83	0.11	0.61	0.00	0.58	0.00	0.46	
MgO	21.19	13.80	9.85	23.79	19.02	55.19	41.56	20.57	18.15	45.63	17.30	
CaO	4.78	12.60	10.82	6.50	18.64	0.16	8.30	9.90	23.81	0.00	21.84	
K <sub>2</sub> O	0.05	0.36	2.59	0.04	0.05	0.04	1.36	0.00	0.00	0.00	0.00	
Total	100.00	100.00	80.45	99.67	100.71	99.29	66.65	100.00	100.00	100.00	57.04	
Sc	543.00	129.00	120.00	764.00	83.80	66.00	61.70	1240.00	69.70	62.50	21.35	
Rb	1.09	11.30	94.65	1.42	40.45	16.60	213.00	0.89	1.40	1.25	99.50	
Sr	1.11	71.20	138.50	2.15	99.55	48.80	244.00	0.90	43.90	1.26	113.00	
Y	694.00	134.00	188.50	340.00	73.65	43.30	117.00	1002.50	22.95	33.40	67.85	
Zr	112.90	23.70	54.55	227.00	24.25	20.00	122.00	363.50	3.57	10.62	54.40	
Nb	1.41	18.60	148.00	2.44	18.46	13.30	122.00	2.82	1.62	2.22	51.40	
Cs	0.36	14.70	83.80	2.17	28.90	22.40	141.00	0.20	1.15	0.88	87.05	
Ba	0.00	28.60	218.50	0.00	86.05	28.40	354.00	2.77	17.45	11.30	374.00	
La	0.20	19.10	139.00	0.42	30.60	15.20	107.00	0.17	3.75	0.53	61.65	
Ce	1.05	32.20	163.00	2.09	53.10	24.40	126.00	0.66	6.30	0.88	65.80	
Pr	3.15	37.20	159.50	4.32	50.70	23.70	108.00	2.35	9.21	0.76	63.90	
Nd	8.44	43.60	145.50	9.71	20.70	26.70	104.00	6.49	11.95	1.04	66.20	
Sm	42.15	72.20	159.50	36.80	60.60	33.10	104.00	48.75	18.65	2.81	73.25	
Eu	77.75	89.50	171.50	82.20	72.80	38.90	105.00	100.15	22.75	4.07	69.55	
Gd	146.00	109.00	185.00	116.00	71.40	37.10	107.00	192.00	23.55	8.56	74.85	
Tb	275.50	124.00	190.00	193.00	74.45	40.50	112.00	387.00	26.15	14.80	74.55	
Dy	471.50	141.00	199.00	293.00	77.90	47.10	116.00	687.50	28.55	25.05	72.90	
Ho	349.50	70.90	97.55	179.00	36.25	23.00	57.70	492.50	12.60	16.90	31.90	
Er	1040.50	154.00	204.50	468.00	83.90	52.30	120.00	1500.00	25.45	49.85	70.70	
Tm	1410.00	161.00	209.00	534.00	83.40	56.20	127.00	2120.00	25.20	66.25	68.90	
Yb	1890.00	174.00	224.00	630.00	82.45	58.50	123.00	2765.00	23.75	78.70	65.15	
Lu	2230.00	163.00	205.00	638.00	74.60	58.80	126.00	3070.00	20.35	91.60	59.00	
Hf	108.40	47.90	97.80	267.00	29.40	24.50	127.00	313.50	8.32	11.05	56.85	
Ta	4.49	25.00	177.50	6.67	28.05	15.30	154.00	15.39	2.33	4.84	87.05	
Pb	0.00	31.90	133.00	1.70	33.70	19.60	136.00	0.54	7.94	2.67	77.25	

Note. *n*, Number of analytical points (for minerals) or areas (for melts).

<sup>1</sup> Starting composition.

<sup>2</sup> Time of exposure.

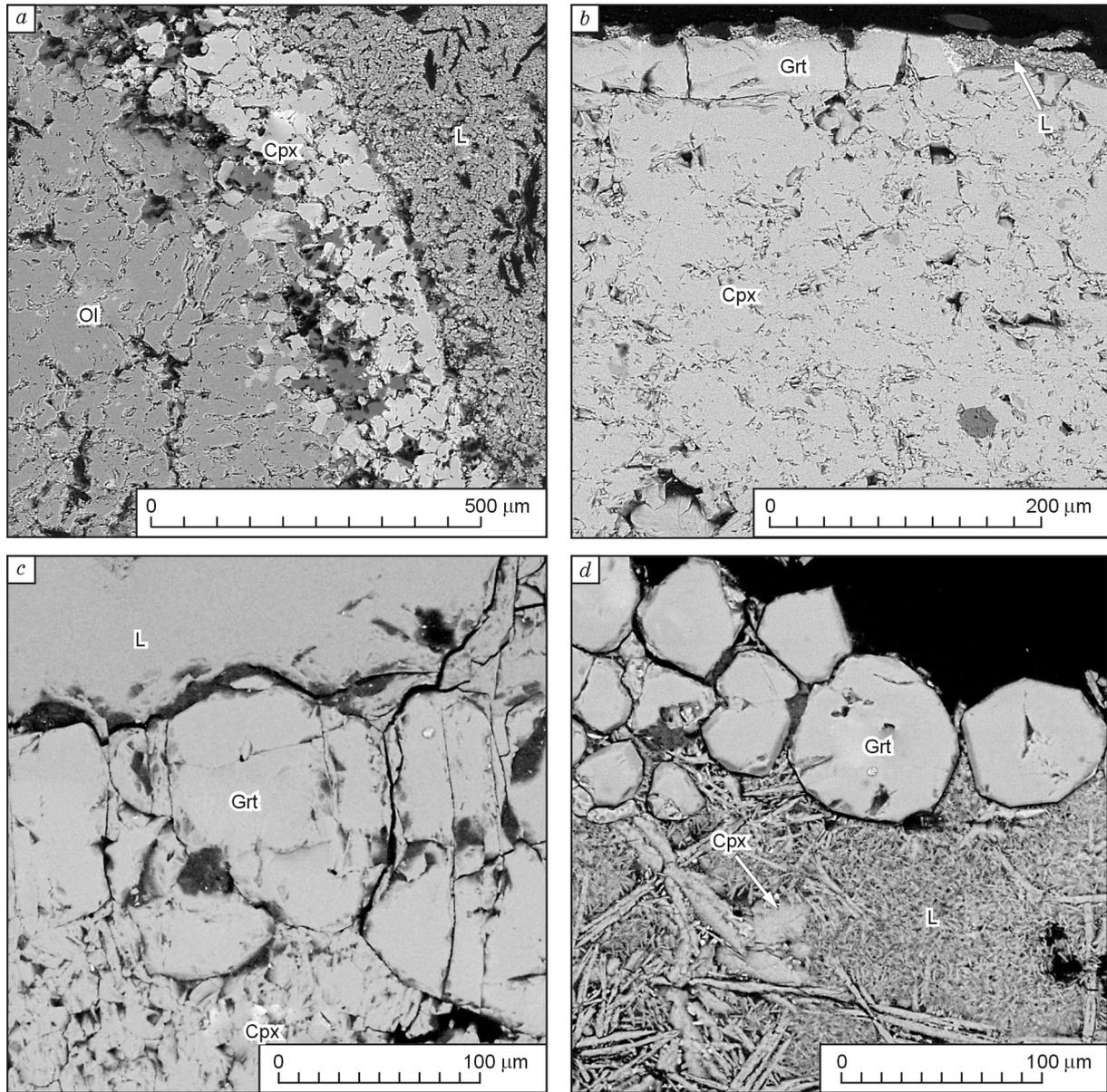


Fig. 1. Equilibrium mineral phases and carbonate–silicate melt obtained in experiments with peridotite–carbonatite (*a, b*) and eclogite–carbonatite (*c, d*) systems. Ol, Olivine; Cpx, clinopyroxene; L, carbonate–silicate melt; Grt, garnet.

(by up to one order of magnitude); and the difference in the trace-element contents of olivine is the least conspicuous. It is known from (Lee et al., 1994; Thibault et al., 1992) that the equilibrium conditions in systems with a carbonate component are reached at high rates. The experimental data in (Brey et al., 2008) show that the equilibrium of peridotite with carbonate–silicate melt is reached within the first hours and the melt composition does not change significantly afterward, which is consistent with the conditions of our experiments with exposure times of 60–180 min.

The coefficients of trace-element partition between the minerals (garnet, clinopyroxene, and olivine) and carbonate–silicate melt (Table 2) were calculated based on the relationships of contents in the mineral and melt, in accordance with the terminology in (Beattie et al., 1993). Also, the mineral–

mineral partition coefficients for the Grt–Cpx and Grt–Ol pairs were calculated. Spidergrams (Fig. 2) show the interface partition of trace elements.

Analysis of the spidergram shows that the main participants of the trace-element partition are garnet and melt. The main feature of the obtained partition is different behavior of light trace elements (La, Ce, Pr, Rb, and Ba), on the one hand, and medium and heavy trace elements (Zr, Hf, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu), on the other. The light elements mainly remain in the melt, whereas the heavy ones are distributed into garnet. The crystallization of minerals from the melt causes a redistribution of heavy elements into garnet as it appears on the liquidus and the depletion of the residual melt in these elements. Scandium also accumulates mainly in garnet ( $K_D^{Sc} = 58.08$  for the peridotite–carbonatite and 8.45

Table 2. Partition coefficients of trace elements between minerals and carbonate-silicate melt and between minerals

Component	$K_D(\text{Grt-L})$			$K_D(\text{Cpx-L})$			$K_D(\text{Ol-L})$		$K_D(\text{Grt-Cpx})$		$K_D(\text{Grt-Ol})$	
	PC	EC	Sample 1638*	PC	EC	Sample 1638*	PC	EC	PC	EC	PC	EC
Rb	0.01	0.01	0.12	0.01	0.15	0.01	0.11	0.06	0.43	0.03	0.02	0.05
Cs	0.00	0.01	0.10	0.01	0.19	0.00	0.23	0.04	0.09	0.05	0.01	0.05
Pb	0.01	0.01	0.10	0.10	0.24	0.02	0.21	0.10	0.05	0.02	0.01	0.05
Ba	0.01	0.00	0.11	0.05	0.19	0.01	0.12	0.12	0.11	0.00	0.01	0.01
Th	0.00	0.00	0.16	0.00	0.00	0.02	0.20	0.13	1.50	0.38	0.50	0.18
U	0.00	0.00	0.25	0.00	0.00	0.02	0.43	0.44	2.00	0.65	1.00	1.00
Nb	0.05	0.01	0.17	0.03	0.14	0.01	0.16	0.06	1.14	0.08	0.10	0.10
Ta	0.18	0.03	0.16	0.03	0.16	0.02	0.14	0.06	4.34	0.14	0.29	0.24
La	0.00	0.00	0.12	0.06	0.21	0.01	0.20	0.07	0.03	0.01	0.00	0.02
Ce	0.01	0.01	0.15	0.10	0.31	0.02	0.28	0.08	0.07	0.02	0.01	0.05
Sr	0.01	0.01	0.06	0.39	0.46	0.05	0.29	0.07	0.01	0.01	0.01	0.02
Pr	0.04	0.03	0.22	0.14	0.35	0.02	0.32	0.07	0.17	0.04	0.05	0.10
Nd	0.10	0.08	0.32	0.18	0.25	0.02	0.37	0.07	0.36	0.10	0.15	0.20
Zr	6.68	1.97	0.85	0.07	0.32	0.09	0.24	0.14	67.97	5.10	5.04	6.11
Hf	5.51	1.61	0.95	0.15	0.36	0.20	0.28	0.14	25.17	4.43	4.16	5.88
Sm	0.67	0.31	0.71	0.25	0.52	0.04	0.46	0.07	1.75	0.31	0.94	0.60
Eu	1.44	0.62	0.85	0.33	0.61	0.04	0.53	0.08	2.94	0.54	1.85	1.14
Gd	2.57	0.94	1.25	0.31	0.63	0.04	0.50	0.10	5.45	0.80	2.68	1.68
Tb	5.19	1.59	1.58	0.35	0.66	0.05	0.52	0.13	9.92	1.09	4.14	2.58
Dy	9.43	2.45	1.92	0.39	0.69	0.06	0.58	0.18	16.14	1.86	5.31	3.35
Y	14.78	3.29	2.48	0.34	0.67	0.06	0.53	0.22	29.40	2.35	6.79	4.23
Ho	15.44	3.34	2.25	0.39	0.68	0.06	0.57	0.24	26.26	2.46	6.54	4.19
Er	21.22	4.49	2.54	0.36	0.73	0.07	0.63	0.29	39.55	2.96	7.42	4.82
Tm	30.77	5.48	2.66	0.37	0.71	0.08	0.64	0.38	56.66	3.46	8.28	5.12
Yb	42.44	6.78	2.81	0.36	0.72	0.08	0.68	0.48	78.30	4.18	9.36	5.80
Lu	52.03	7.97	2.90	0.34	0.69	0.09	0.67	0.59	101.36	4.79	9.24	5.84
Sc	58.08	8.45	3.01	3.26	1.22	1.47	1.54	1.43	11.98	3.98	4.34	6.25

Note. PC, Peridotite-carbonatite system; EC, eclogite-carbonatite system (generalized).

\* Sample from (Kuzyura et al., 2010).

for the eclogite–carbonatite systems); the structure of olivine and clinopyroxene includes less Sc ( $K_D^{\text{Sc}}_{\text{Ol}} = 1.54$  and  $1.43$ , and  $K_D^{\text{Sc}}_{\text{Cpx}} = 3.26$  and  $1.22$  for the peridotite–carbonatite and eclogite–carbonatite systems, respectively). Note that all the  $K_D^{\text{TE}}$  in clinopyroxene and olivine are less than unity, except  $K_D^{\text{Sc}}$ . This shows that the minerals (except Sc) do not take part in the trace-element partition; i.e., they are of limited importance in the trace-element geochemistry.

## Discussion and applications to natural conditions

There are no reliable data on the trace-element partition between peridotitic and eclogitic minerals, on the one hand, and the carbonate–silicate parental melts of natural diamonds, on the other. This is because of the scarcity of mineralogical data on the fragments of parental melts trapped together with minerals which are paragenetic with diamond, i.e., on the pairs

mineral–solidified parental melt (Tomlinson et al., 2009). As stated above, the determination of a limited number of trace elements in the phases of a solidified carbonatitic melt is complicated by the small sizes of the carbonate phases and their being part of a multiphase fluid association in inclusions.

Direct experimental determination of trace elements in coexisting phases (paragenetic minerals and solidified carbonate–silicate parental melts) and, therefore, calculations of the trace-element partition coefficients for the representative phases of the diamond-forming carbonate–silicate systems became possible owing to physicochemical experiment. Such data can ensure a reliable interpretation of the trace-element contents of peridotitic and eclogitic mineral inclusions in natural diamonds and a more detailed interpretation of real diamond formation based on their geochemical background.

Spidergrams (Fig. 2) show experimentally determined interface partition coefficients of trace elements  $K_D^{\text{TE}}$  in the diamond-forming peridotite–carbonatite and eclogite–carbonate

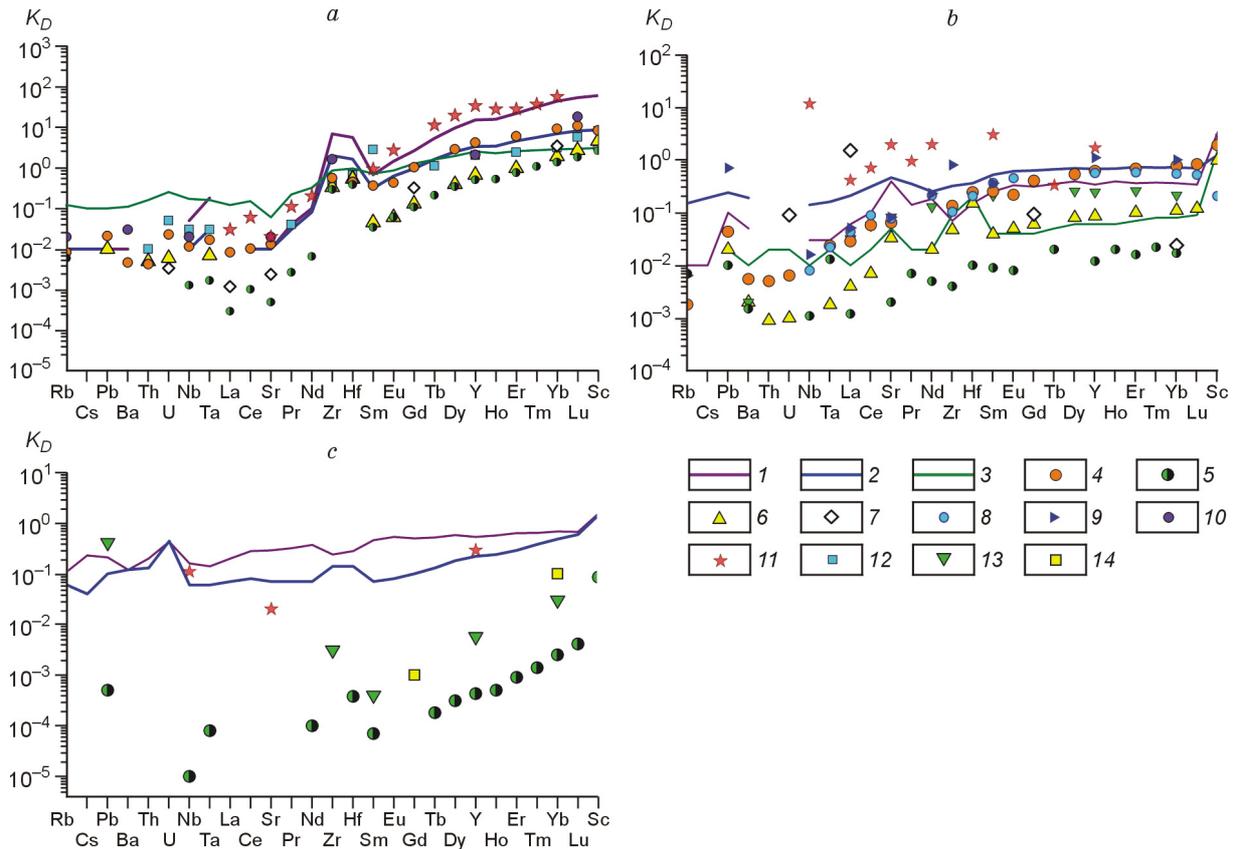


Fig. 2. Spidergrams for trace-element partition between garnet and carbonate–silicate melt (a), clinopyroxene and carbonate–silicate melt (b), and olivine and carbonate–silicate melt (c). 1, 2, present paper: 1, peridotite–carbonatite system; 2, eclogite–carbonatite system; 3, (Kuzyura et al., 2010); 4, (Pertermann et al., 2004); 5, (Girnis et al., 2013); 6, (Dasgupta et al., 2009); 7, (Hammouda et al., 2009); 8, (McDade et al., 2003); 9, (Blundy and Dalton, 2000); 10, (Sweeney et al., 1995); 11, (Tomlinson et al., 2009); 12, (van Westrenen et al., 1999); 13, (Sobolev, 1977); 14, (Brenan and Watson, 1991).

tite systems with the participation of completely miscible carbonate–silicate (carbonatitic) melts. For comparison, the  $K_D^{\text{TE}}$  values for the pairs silicate mineral–silicate melt and silicate mineral–carbonate melt are given, according to literature data (Blundy and Dalton, 2000; Brenan and Watson, 1991; Dasgupta et al., 2009; Girnis et al., 2013; Hammouda et al., 2009; Kuzyura et al., 2010; McDade et al., 2003; Pertermann et al., 2004; Sweeney et al., 1992, 1995; Tomlinson et al., 2009; van Westrenen et al., 1999; Walter et al., 2008).

According to the experimental data, the peridotite–carbonatite and eclogite–carbonatite mantle systems, including diamond-forming systems, show such trends in the mineral–melt partition coefficients  $K_D^{\text{TE}}$  at 7.0–8.5 GPa, with the maximum redistribution into garnet. The garnet–melt pairs show similar partitions between garnet and carbonate–silicate melt (this paper) (Kuzyura et al., 2010), garnet and silicate melt (Pertermann et al., 2004; van Westrenen et al., 1999), and garnet and carbonate melt (Sweeney et al., 1995; Tomlinson et al., 2009). Note that heavy trace elements are concentrated in garnet with the maximum Lu or Sc contents, and the rest are redistributed into the melts.

It should be stressed that the trace-element partition in (Tomlinson et al., 2009) is based on real data on mineral and

multiphase fluid inclusions coexisting in a single inclusion in diamond. The partition coefficients  $K_D^{\text{TE}}$  were calculated for a limited number of elements. The partition coefficients for the Grt–L pair in the case of heavy elements are one to three orders of magnitude higher than all the rest, which agrees with the direct experimental measurements in the present paper.

The  $K_D^{\text{TE}}$  between garnet and carbonate–silicate melt in (Dasgupta et al., 2009; Girnis et al., 2013; Hammouda et al., 2009) are considerably lower (by one to two orders of magnitude) on the y-axis than the coefficients obtained in the present paper.

Also, a difference of one to four orders of magnitude is observed for  $K_D^{\text{TE}}$  between clinopyroxene and different melts as well as olivine and the melts, though the general distribution pattern is preserved. The maximum difference is between the coefficients obtained in this work and in (Girnis et al., 2013). Note the elevated (12.5–30.3 wt.%) water contents of “silica–carbonate” melts associated with solid phases in (Girnis et al., 2013).

Thus, despite significant differences in the physical parameters and chemical compositions of coexisting melt phases, the trace-element partitions for carbonate–silicate, carbonate, and silicate melts coincide; i.e., the mineral–melt partition in the carbonate–silicate systems does not depend on temperature,

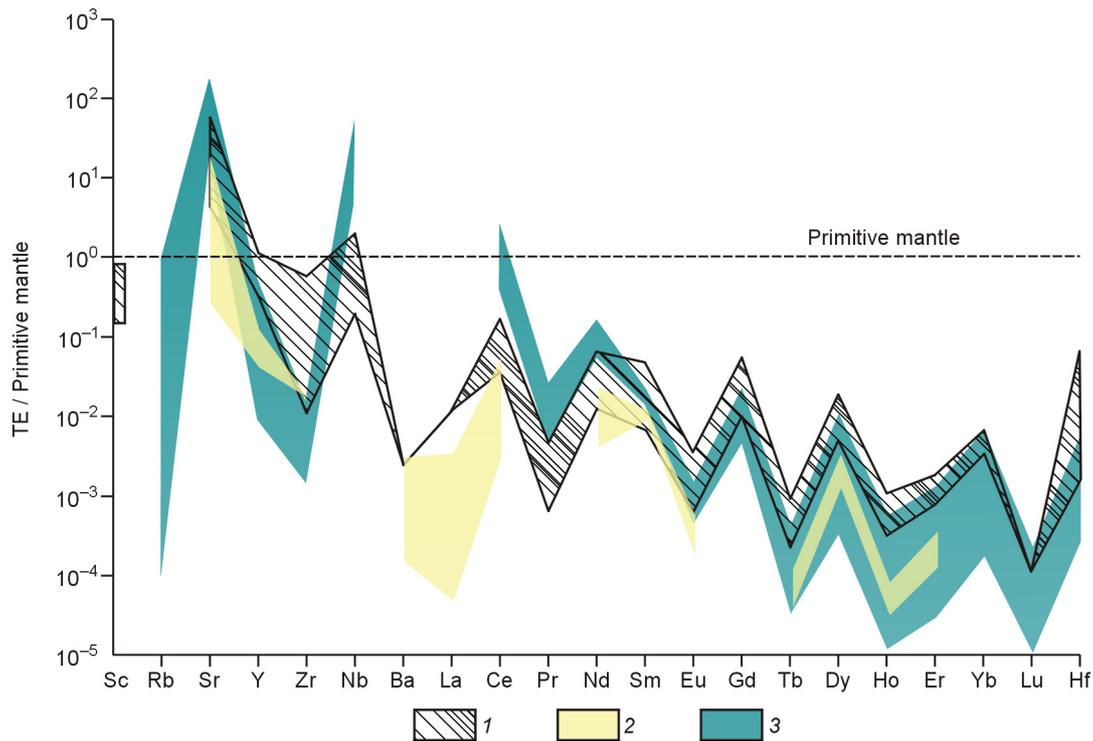


Fig. 3. Spidergram with the fields of experimental and natural melts. The trace-element contents are normalized to the primitive mantle (Lyubetskaya and Korenaga, 2007). 1, peridotite xenoliths, Vitim pipe, Siberia (Ionov, 2004); 2, eclogite xenoliths, Roberts Victor pipe, South Africa (Harte and Kirkley, 1997); 3, inclusions in diamonds, Akwatia pipe, Ghana (Stachel and Harris, 1997).

pressure, or composition of “the partner melt.” The same conclusion was made by A. Girnis et al. (2013). This means that the above-mentioned similarity between the trace-element partitions in mineral–melt pairs containing melts with absolutely different chemical compositions does not permit an unambiguous determination of the chemical nature of “the partner melt” from the trace-element content of the coexisting mineral, e.g., garnet (main phase concentrating trace elements in the cases under consideration).

The experimentally obtained carbonate–silicate melts are diamond-producing provided that the systems are saturated with dissolved carbon. With regard to the concentration barrier of diamond nucleation (Litvin et al., 2008), these melts will be capable of spontaneous nucleation of the diamond phase (melts from samples 2306 and 2440), whereas in sample 2233, the previously formed spontaneous crystals will be capable of growing in the melt. Thus, the products of the experiments model diamond-forming media with silicate minerals which formed in these media.

The geochemical background of diamond-forming processes is interesting for the identification and assessment of the contribution of different mantle sources of trace elements to the formation of carbonatite parental media for diamonds and their paragenetic inclusions. Evidently, the formation of the parental media of most natural diamonds and primary phases as inclusions is determined by, and physicochemically and spatially related to, the general magmatic evolution of mantle matter. A physicochemical experiment and mineralogical analysis of inclusion phases showed that leak-tight primary

inclusions (with signs of residual pressure) in natural diamonds are fragments of heterogeneous diamond-forming media rather than of mantle minerals. This agrees with the idea that the parental media for diamonds and inclusions consisting of completely miscible carbonate–silicate melts make up independent magma chambers in mantle rocks.

It can be presumed that the decisive role in the formation of parental carbonate–silicate melts and their magma chambers is played by interaction between the peridotite substance of the upper mantle and “a metasomatic agent.” The evolution of petrologic and geochemical processes might have proceeded by the following scenario. At the first, metasomatic–magmatic, stage, a mantle metasomatic agent causes a partial carbonatization of mantle peridotite and the generation of carbonate melts (the size of the chamber is determined by the metasomatizing capacity of the agent). At the next, dissolution–magmatic, stage, both the rock-forming (olivine, orthopyroxene, clinopyroxene, and garnet) and accessory minerals of the host peridotites, volatiles, and carbon dissolve in the carbonate melts, which are also penetrated by insoluble phases (sulfides). This results in the formation of the peridotite–carbonatite–carbon parental magmas of diamonds and inclusions. Note that these magmas contain both paragenetic soluble silicate minerals and xenogenic insoluble sulfide minerals or immiscible melts. At the last, fractional-crystallization, stage, natural cooling of the parental magmas in the magma chamber automatically causes syngenetic crystallization of diamond and mineral inclusions (which are the recrystallized minerals of mantle peridotite). Meanwhile, the parental magmas experi-

ence ultrabasic–basic evolution in the regime of fractional crystallization (Litvin, 2013b), which is responsible for a transition from peridotitic to eclogitic parageneses in the assemblage of silicate minerals. This agrees with the general petrochemical trends for ultramafic and mafic mantle rocks and the diamond-bearing assemblages of the peridotitic and eclogitic parageneses (Sobolev, 1977). Volatiles are of limited importance in diamond genesis, because they are not capable of forming stable phases under mantle conditions owing to low concentrations, high chemical activity, and high solubility in magmatic melts.

The hypothesis of metasomatic agent was put forward by many researchers who studied mantle matter. The formation of carbonate–silicate melts under upper-mantle conditions is considered in (Dalton and Presnall, 1998). The agent is described as carbonatitic melts in (Kogarko, 2006; Wallace and Green, 1988; Yaxley et al., 1998). The formation of such melts might be related to finds of microinclusions of carbonate–silicate melts in diamonds (Klein-BenDavid et al., 2007, 2009; Logvinova et al., 2006, 2008; Navon et al., 1988; Schrauder and Navon, 1994; Shiryaev et al., 2005; Skuzovatov et al., 2011; Zedgenizov et al., 2007, 2009) and the formation of reservoirs of diamond-producing carbonate–silicate melts owing to the primary reprocessing of garnet–lherzolite mantle by metasomatic agents (Litvin, 2011, 2013b).

Thus, the chemical compositions of diamond-producing carbonate–silicate (carbonatitic) magmas in terms of major and trace elements were probably determined by two main sources: mantle peridotite and metasomatic agents. The resulting trace-element geochemical background is closely related to, accompanies, and adapts to the physicochemical evolution and differentiation of parental media with the formation of diamonds and all syngenetic minerals, not excluding inclusion minerals, owing to mechanisms of interface trace-element partition.

Experimental determination of the interface partition coefficients of trace elements in carbonate–silicate parental media for diamonds and paragenetic inclusions permits determining trace elements which were initially related to both mantle peridotite sources and metasomatic agents and then involved in the formation of diamonds and parental magma chambers. The trace-element contents of the chambers of diamond-producing carbonatitic melts were calculated based on (1) mineralogical data on the trace-element contents of peridotitic and eclogitic minerals included in diamonds and in diamond-bearing xenoliths of some kimberlite pipes (Harte and Kirkley, 1997; Ionov, 2004; Stachel and Harris, 1997) and (2) the mineral–parental melt partition coefficients  $K_D^{TE}$  experimentally determined in the present work. The results obtained are shown on a spidergram (Fig. 3) as fields of model melts. The elements on the  $x$ -axis are placed in the order of increasing charge.

The trace-element contents of experimental mineral phases and primary inclusions of silicate minerals in diamonds of the Akwatia kimberlite pipe, Ghana, were compared with those of minerals in diamond-bearing xenoliths of the Roberts Victor and Vitim pipes. The parental melts of the diamonds and

inclusion phases are considerably depleted in medium (Ba, La, Ce, Pr, Nd, Sm, Eu, and Gd) and heavy (Tb, Dy, Ho, Er, Yb, Lu, and Hf) trace elements compared to the primitive peridotite. On the other hand, they are enriched in light (Rb and Sr) trace elements, heavy Zr and Nb, rare-earth Y, and transition Sc, but the contents of these elements in the melts are one to four orders of magnitude lower than those in the primitive-mantle peridotite (Lyubetskaya and Korenaga, 2007). The trace elements are mainly the rare-earth components of peridotite mantle. Note the elevated contents of Sr, Nb, and Ce in the calculated parental melts, probably owing to the participation of a metasomatic agent. The field of melts from real diamond inclusions (Akwatia kimberlite pipe, Ghana) is shown on a spidergram (Stachel and Harris, 1997). These melts are highly enriched in Sr, Nb, and Ce, which were, most likely, supplied by a metasomatic agent. Their low position on the spidergram suggests the zero tendency of the contents of di- to pentavalent elements (HREE and HFSE). This means that such a melt might have been at equilibrium with a representative garnet phase (in an eclogitic assemblage), which most of these elements were redistributed into. Conversely, less garnet was at equilibrium with the parental melt of the diamond-bearing peridotite xenolith from the Vitim pipe (Fig. 3), which testifies to the formation of a peridotitic assemblage.

## Conclusions

At 7.0–8.5 GPa, we carried out direct experimental determinations of the trace-element contents of coexisting olivine, garnet, and clinopyroxene, on the one hand, and those of completely miscible carbonate–silicate melts, on the other, for the peridotite–carbonatite and eclogite–carbonatite multicomponent diamond-forming systems. This permitted calculating the equilibrium interface partition coefficients  $K_D^{TE}$  for Rb, Ba, Ta, Nb, La, Ce, Pb, Pr, Sr, Nd, Zr, Hf, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, and Sc and for real diamond-forming conditions. An important role in interface partition belongs to garnet, which heavy trace elements are distributed into, whereas light elements are distributed into carbonate–silicate melts. Spidergrams for trace-element partition have been constructed, whose interpretation reveals a group of trace elements supplied to the parental media together with the main components of mantle peridotite. On the other hand, Sr, Nb, and Ce were supplied to the parental magmas, most likely, by the components of a metasomatic agent. This suggests that the carbonate–silicate (carbonatitic) parental media for diamonds and syngenetic inclusions were formed by the interaction between the metasomatic agent and mantle peridotite matter with the subsequent ultrabasic–basic evolution of the parental magmas.

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