EXPERIMENTAL STUDY OF DIAMONDITE FORMATION IN CARBONATE-SILICATE MELTS: A MODEL APPROACH TO NATURAL PROCESSES

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To simulate a natural carbonate-silicate medium parental for both diamondites and their syngenetic mineral inclusions, melanocratic carbonatites of the Chagatai complex, Uzbekistan, were used. The carbonatites are characterized by a high percentage of silicate components and high-pressure eclogitic silicate minerals. The experiments carried out at 7.0–8.5 GPa and 1800 ℃ show that the diamondites formed very quickly in C-enriched carbonate-silicate melts of the Chagatai carbonatites. According to experimental evidence, the mineralogy of the Chagatai carbonatites under *P-T* conditions of diamondite formation is represented by grossular-almandine garnet, diopside-hedenbergite clinopyroxene, and calcite (aragonite) and resembles the mineralogy of diamond-bearing Ca-rich eclogites and grospydites found in kimberlites as mantle xenoliths. The Chagatai carbonatites are quite appropriate as a parental medium to simulate physicochemical processes for the formation of natural diamondites. The most important characteristics of these processes are as follows: quick migration of mobile low-viscosity carbonate-silicate melts into zones of diamondite formation, extremely high "snowballing" rate of diamondite crystallization from a carbonate-silicate melt oversaturated with dissolved carbon, formation of syngenetic inclusions of garnet and clinopyroxene, carbonate and sulfides, etc. inside the pores and cavities of diamondites. Experiments show that the formation of diamondites and their syngenetic inclusions is accompanied by coarse-grained crystallization of eclogitic minerals in the parental media surrounding the growing diamondites.
Syngenesis of diamondites and inclusions, carbonate parental melts, experiment

INTRODUCTION

Natural diamondites are polycrystalline intergrowths of diamond crystals measuring few to tens of micrometers, with pores and caverns which host diamond crystals as well as silicate, oxide, and sulfide minerals (with and without diamonds). A specific feature of diamondites is that they contain garnets chemically similar to garnets of peridotites and eclogites as well as "peridotite" clinopyroxenes, sulfides, and ilmenite, which are chemically similar to the same minerals from primary inclusions in single crystals of diamond; but diamondites contain no inclusions of olivine, the commonest mineral of the mantle [1]. Carbonates were not found in diamondites either, but they might have been dissolved by an acid when preparing the rocks for analysis. We suppose that carbonate-rich inclusions should be present in both diamondites and silicates. They are carriers of the most incompatible rare elements, as was shown in [2]. It should also be noted that the concentration ratios of trace elements in silicate minerals of diamondites clearly show that carbonatite melts were involved into the processes of diamondite formation [1, 2]. Support for a possible key role of natural carbonatite media (melts or fluids) in the formation of diamondites came from high-pressure high-temperature experiments on diamond nucleation and

growth in multicomponent carbonate and carbonate-silicate melts with natural chemistry [3, 4]. In these experiments, initial materials were selected so that their compositions corresponded to the compositions of primary fluid-carbonatite (carbonate-silicate) inclusions in diamonds from Botswana [5].

Melanocratic carbonatite rocks (sövites and ringites) from diatremes of the Chagatai trachite-carbonatite complex in Uzbekistan were described as a new type of diamondiferous rocks [6]. Therefore, these carbonatite rocks were used as parental diamond-forming media in high-pressure high-temperature experiments, with graphite as a source of carbon. The diamonds successfully nucleated and grew in carbonate-silicate melts (with dissolved carbon) of the Chagatai carbonatites [7]. Their crystallization with high contents of silicate components is accompanied by the syngenetic formation of grossular-almandine garnet, diopside-hedenbergite clinopyroxene, apatite, calcite (aragonite) and alkaline carbonates, carbides, coesite, pyrrhotite, iron, and gold, Fe-Cr alloys, and some other phases. High-pressure silicate mineralization for the Chagatai carbonatites was studied at 7 GPa [8]. The main minerals are garnet, clinopyroxene, and carbonate (calcite). This assemblage is completely similar to mineral compositions of diamondiferous high-Ca eclogites and grospydites [9]. These features are important and permit the Chagatai carbonatites to be used for modeling the compositions of carbonate-silicate parental media responsible for the formation of natural diamonds, diamondites, and their syngenetic inclusions. Diamondites were successfully synthesized in carbonate-carbon melts under high pressures [10].

The present experimental study was chiefly aimed at synthesizing diamondite in melts of the Chagatai carbonatites and analyzing the phases newly formed in the Chagatai carbonatites under *P-T* conditions of diamond formation.

METHODS

Starting materials were the Chagatai carbonatites, which are biotite-pyroxene-calcite rocks with accessory plagioclase, muscovite, apatite, Ti-magnetite, barite, zircon, and rutile [6]. Chemical compositions of two used rocks are given in Table 1. Under the *P-T* conditions of diamond stability the phase relationships during melting of these rocks are characterized by the formation of clinopyroxene (sp. 23) or garnet (sp. 79) as phases of liquidus at 1730 and 1700 °C, respectively [8]. A three-phase assemblage of clinopyroxene, garnet, and melt forms at 1620 °C. The complete crystallization of the Chagatai rocks is controlled by quasi-nonvariant eutectics composed of clinopyroxene, garnet, calcite, and melt, at 1510–1480 °C. The subsolidus assemblage consists of clinopyroxene, garnet, and Ca-carbonate. Before using, the Chagatai rocks were powdered. The source of carbon was spectrally pure synthetic graphite.

High-pressure technique. High pressures of 7.0–8.5 GPa and temperatures of 1500–2000 °C were created using an "anvil-with-hole" device with a cell made of lithographic stone and pyrophyllite [11, 12]. To synthesize diamondite, a resistive heater was devised, in the form of a tube 5 mm in outer diameter and 3 mm in inner diameter (with the wall 1 mm thick) and 7.5 mm in length. Phase transformations in the Chagatai carbonatite were studied using pressed blocks 2 mm in diameter and 2 mm long, which were placed in cavities inside a graphite rod 6 mm in diameter and 7.5 mm long, which also served as a resistive heater. This permitted us to vary the temperature distribution in the specimen by changing the position of cavity along the axis of the rod heater. Pressure at room temperature was determined by usual calibration procedure with the use of standard polymorphous transformations in bismuth at 2.55, 2.7, and 7.7 GPa. Temperature was measured by a $Pt_{70}Rh_{30}/Pt_{94}Rh_{06}$ thermocouple in calibrating experiments. Pressure in the specimen at known high temperatures was corrected along the *P-T* curve of diamond-graphite equilibrium [13].

Diamondite was synthesized in a graphite heater, which was simultaneously the source of carbon. The graphite tube heater (carbon source) is devised in such a fashion that, when mounted for experiment, it is completely surrounded by pressed carbonatite powder (Fig. 1).

Table 1

Chemical Compositions of the Chagatai Carbonatites Used in Experiments

Sp.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	CO_2	SO_3	Total
23	22.19	0.60	5.36	14.97	2.87	0.25	2.80	26.64	1.62	1.32	0.49	0.26	18.70	0.01	98.08
79	18.20	0.65	6.24	14.37	4.20	0.23	3.65	29.40	0.29	0.89	0.43	0.46	20.90	0.13	100.04

Note. Chemical analyses were performed at the Institute for Mineral Resources, Tashkent.
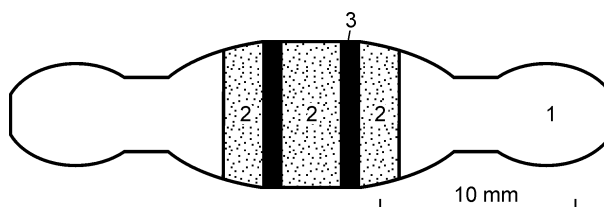
**Fig. 1. Schematic experimental assemblage in a HP-HT device of the "anvil-with-hole" type.
1 — cell made of the Algeti limestone, Georgia, 2 — pressed powder of the Chagatai carbona-
tite, 3 — graphite heater, which serves simultaneously as a source of carbon for diamondite.**

Analyses. The obtained experimental specimens have been analyzed by optical microscopy, scanning electron microscopy (SEM), and electron microprobe in Vienna, Austria, Budapest, Hungary, and Chernogolovka, Russia. At the Institute of Experimental Mineralogy of the RAS in Chernogolovka, a Tescan Vega electron microscope with a Link analyzer was used. Microprobe analyses of garnet and clinopyroxenes were carried out using JEOL superprobe electron microscopes (Laboratory of Geochemical Studies, National Academy of Sciences of Hungary, Budapest) and ARL SEMQ (Natural History Museum, Vienna). Operating conditions for analyses of standard minerals were 15 kV accelerating voltage and 15 nA excitation current. Correction procedures were standard.

RESULTS

Diamondite synthesis. Carbonatite specimens 23 and 79 were used as starting materials for obtaining experimental specimens 979 and 1012, respectively. The experiments carried out at 7.0–8.5 GPa and 1800 °C show that the heater graphite in contact with carbonatite has intensely transformed into diamondite for 3–5 s to form a diamond tube (Fig. 2). Rapid "snowballing" crystallization results in the formation of dense polycrystalline diamond intergrowths of the kind of natural diamondites, composed of intimately intergrown octahedral microcrysts of diamond measuring 1 to 500 μm (Fig. 3). The estimated density of nucleation of these "carbonatite-synthetic" diamondites is close to $1 \cdot 10^5$ nuclei in 1 mm^3 (for comparison: nucleation density in the case of spontaneous
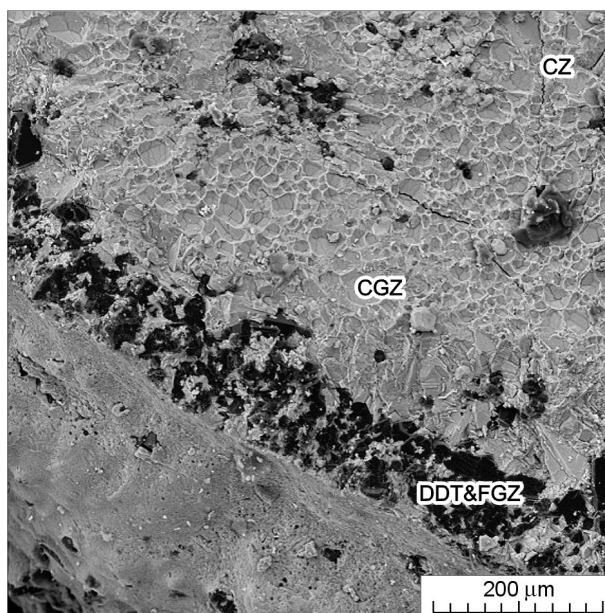
**Fig. 2. SEM image of experimental sp. 1012 after recrystallization of heater's
graphite into diamondite. Hereafter, CZ — central zone, CGZ — coarse-
grained zone, FGZ — fine-grained zone, DDT — diamondite.**
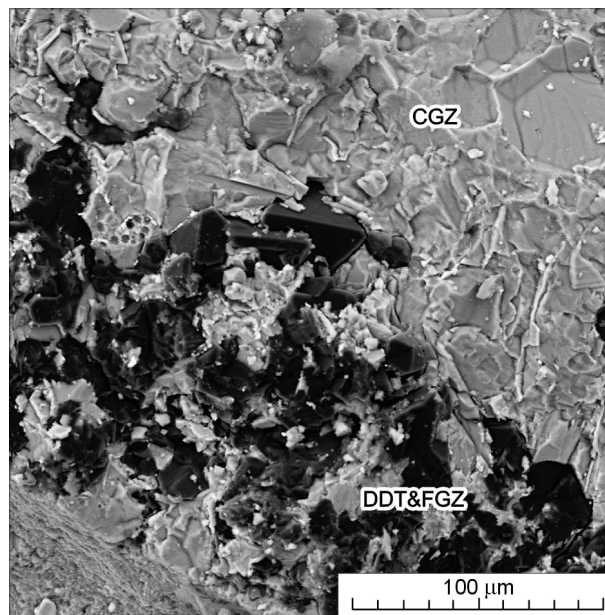
Fig. 3. SEM image of a diamondite belt (sp. 1012) that shows spatial relationships between the parental carbonatite medium and diamond crystallites after quenching. Symbols follow Fig. 2.

diamond nucleation in carbonatite melts with dissolved carbon is about $(3-5) \cdot 10^2$ nuclei in 1 mm^3 [14]. The experimental conditions were kept the same during 40 min to promote better conditions for the growth of syngenetic minerals in carbonate-silicate melts. Carbon was dissolved in a carbonate-silicate melt and migrated to the core of the specimen, and some octahedral diamond crystals could form simultaneously with spherules of metastable graphite rather far from the zone of diamondite formation and carbon source (Fig. 4). Occasionally, single crystals of plate-habit graphite formed. No signs of carbonate-silicate liquid immiscibility have been observed in melts of the Chagatai carbonatites (in quenching products after high-pressure experiments).

Formation of high-pressure minerals in parental carbonatite. Of the greatest importance is the mineralogical composition of experimental specimens in the zone of diamondite formation (Figs. 5–7). The specimens were split across, and actually the diamondite surfaces shown in the figures are inner parts of the diamondite specimens. The initial ("parental") carbonatite was transformed into an assemblage of garnet, clinopyroxene, and carbonate, whose compositions are given in Table 2. These minerals form a fine-grained mass, which is dominated by carbonate phase and is produced by quenching of a carbonatite-rich melt. This melt is responsible for diamondite formation and is also present within diamondites in the form of disperse solidified material (see Fig. 5). This well illustrates how silicates, carbonates, and other primary inclusions can syngenetically intergrow with diamonds within diamondites when the latter crystallize from parental carbonate-silicate melts under the experimental or natural conditions. A band of coarse-crystalline garnet-clinopyroxene eclogite rock with a subordinate amount of carbonate forms in the zone of inner contact with the diamondite ring (Figs. 6 and 7).

Study of phase transformations of parental Chagatai carbonatites under *P-T* conditions of diamond stability. It is interesting to estimate physicochemical behavior of the Chagatai carbonatite as a parental medium for diamondite formation for the same experimental conditions under which the diamondites themselves were formed. The Chagatai carbonatite (sp. 23) is a biotite-pyroxene-calcite rock with accessory plagioclase, apatite, Ti-magnetite, barite, zircon, and rutile (for chemical composition see Table 1). Experimental determination of phase relationships in the rock (sp. 23) shows that clinopyroxene is a liquidus phase at 7 GPa and 1730 °C, an assemblage of clinopyroxene and garnet forms at 1620 °C, and complete crystallization is controlled by the quasi-nonvariant eutectic assemblage clinopyroxene + garnet + calcite + melt (at 1480–1510 °C). Subsolidus equilibrium relationships are represented by the assemblage clinopyroxene + garnet + calcite [8]. Experimental data obtained at high pressures for carbonatite sp. 23 under conditions of temperature gradient and under isothermal conditions are given in Table 3.

Specimen 1/881 was under the conditions of a considerable axial temperature gradient; parenthesized
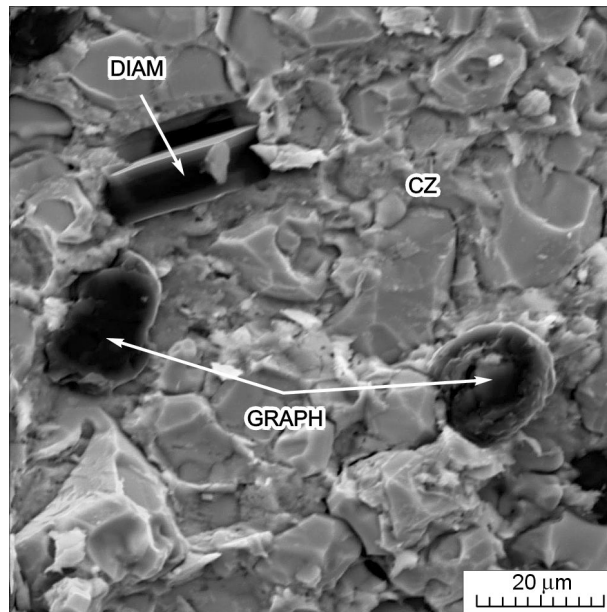
Fig. 4. SEM image of the central part of sp. 979: diamond crystals and graphite spherules. DIAM — diamond, GRAPH — graphite.
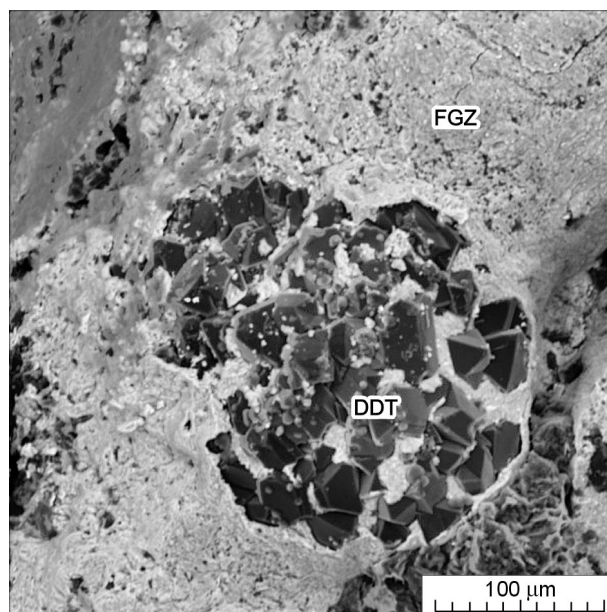

Fig. 5. SEM image of sp. 979 that shows fine-crystalline carbonate-enriched matter in the zone of diamondite formation (diamondite is partly exposed) after quenching. Symbols follow Fig. 2.

temperatures (Table 3) are estimated from the known phase diagram [8]. The complete melting of carbonatite is observed in the high-temperature zone of the specimen (1730–1815 °C). On quenching, carbonate-silicate glass forms (Figs. 8 and 9), chiefly homogeneous, with dendritic quenching crystallization observed only near the liquidus temperature. The liquidus conditions correspond to the sharp rounded boundary (see Fig. 8, *a*). Importantly, there are no signs of carbonate-silicate liquid immiscibility for the Chagatai carbonatite provided the state of complete
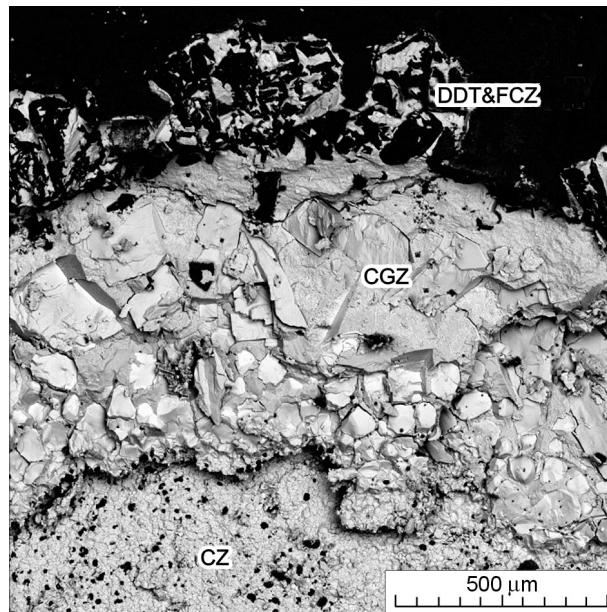
Fig. 6. SEM image of sp. 979 that shows a coarse-grained "belt" of garnet and clinopyroxene minerals with a small amount of carbonate phase in the zone of contact with diamondite. Symbols follow Fig. 2.
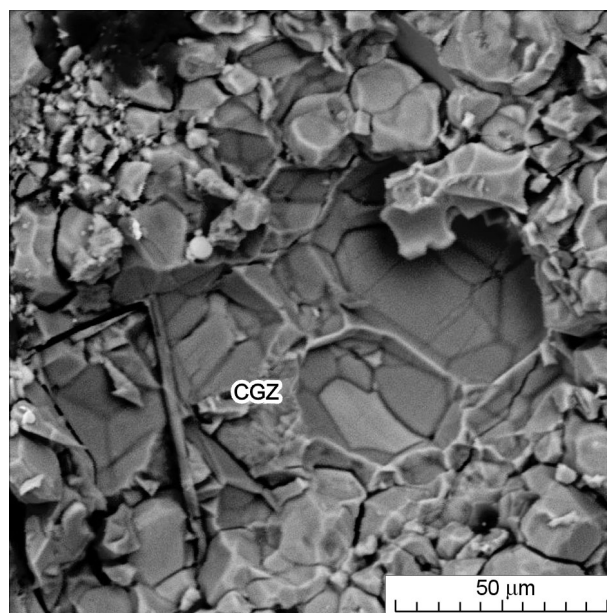
Fig. 7. SEM image of sp. 1012 in the zone of coarse-grained crystallization of garnet and clinopyroxene (eclogite belt).

melting at 7 GPa. This effect is important for characterizing not only diamond-forming carbonate-silicate melts but also mantle carbonatite magmas, as it shows that carbonate and silicate melts can mix at the *P-T* conditions of diamond stability. One more specific feature of multicomponent parental melts is observed in the same specimen during the diamond formation, namely liquid immiscibility of carbonate-silicate and sulfide melts (for detail see [15]). Temperature distribution in specimens 1/882 (Fig. 10), 1/883 (Fig. 11), 1/884 (Figs. 12 and 13) is virtually uniform.

Table 2

Compositions of Syngenetic Minerals in Diamondite of Experimental sp. 979 (starting carbonatite sp. 23)

Oxide	Gt1	Gt1	Gt2	Gt3	Cpx1	Cpx2	Cpx3	Crb1	Crb1*	Crb2	Crb2	Crb3
SiO_2	36.6	34.7	40.3	39.3	52.1	52.2	45.3	1.57	0.89	9.6	6.5	14.8
TiO_2	0.49	0.50	0.89	0.42	0.52	0.15	0.39	0.31	0.47	0.54	0.53	1.44
Al_2O_3	19.6	18.2	20.1	21.0	3.80	5.5	6.8	0.61	0.05	5.4	4.1	1.50
Cr_2O_3	0.11	<0.02	<0.02	<0.02	<0.02	<0.02	0.06	<0.02	<0.02	<0.02	<0.02	0.11
FeO	15.2	17.2	14.6	12.7	16.0	14.9	12.6	17.6	2.20	16.4	13.9	18.5
MnO	0.45	0.43	0.39	0.33	0.24	0.04	0.06	0.48	0.22	0.49	0.39	0.30
MgO	2.40	2.43	2.88	2.97	6.1	6.1	6.2	2.56	0.76	1.31	2.30	2.12
CaO	24.7	26.0	20.6	20.6	17.2	17.2	21.9	32.0	1.51	26.3	25.3	22.8
Na_2O	0.28	0.20	0.20	1.54	3.67	3.86	5.4	5.7	14.3	1.42	5.8	1.35
K_2O	0.02	0.12	<0.02	0.80	0.14	0.14	1.09	5.0	15.5	2.46	3.68	0.80
P_2O_5	0.11	0.06	<0.02	0.24	0.22	<0.02	0.24	3.86	5.2	1.16	2.42	0.21
Total	99.96	99.84	99.96	99.90	99.99	100.09	100.04	69.69	41.11	65.08	64.92	63.93

Note. Gt — Garnet, Cpx — clinopyroxene, Crb — carbonate; numbers at mineral symbols stand for different zones of specimen:
1 — central part, 2 — coarse-grained belt near diamondite, 3 — diamondite and fine-grained material.
* Microprobe analysis over an area of 36×36 μm^2.

Table 3

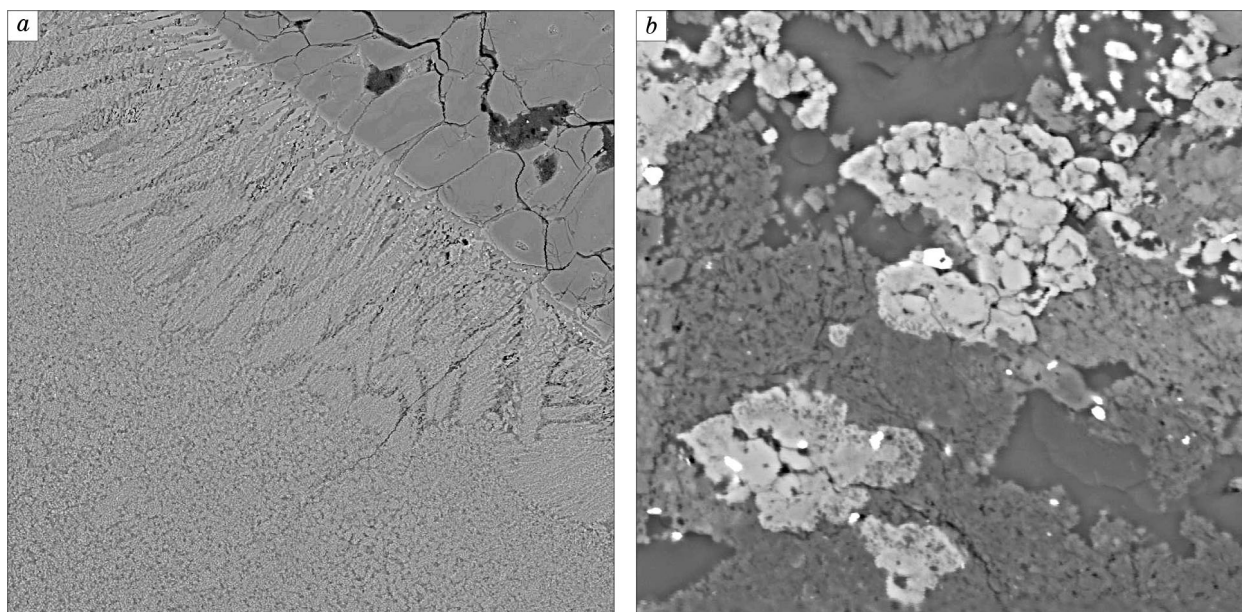**Phase Relationships in Chagatai Carbonatite Rock (sp. 23) at 7 GPa and High Temperatures**

Sp.	T, ℃	Exposure time, min	Phases	Equilibrium association of carbonatites
1/881	1815	20	Gl, Sulf	L
	(1700)		Gl, Cpx	L + Cpx
	(1600)		Gl, Cpx, Gt	L + Cpx + Gt
	(1500)		Gl, Cpx, Gt, Crb	L + Cpx + Gt + Crb
	(1400)		Cpx, Gt, Crb (Calc)	Cpx + Gt + Calc
1/883	1650	45	Gl, Cpx, Gt	L + Cpx + Gt
1/882	1580	80	Gl, Cpx, Gt, Sulf, SiO_2, Carb	L + Cpx + Gt
1/885	1550	210	Gl, Cpx, Gt, Qtz	L + Cpx + Gt + Qtz
1/884	1500	65	Cpx, Gt, Qtz, Carb	Cpx + Gt + Carb + Qtz

Note. Gl — Glass, Gt — garnet, Calc — calcite, Cpx — clinopyroxene, Crb — carbonate, L — liquid, Qtz — quartz, Sulf — sulfide.

Phase compositions. Compositions of carbonate-silicate melts and solid phases for experimental specimens are given in Tables 2 and 4. Content of SiO_2 in the melts coexisting with garnets and clinopyroxenes ranges from 1 to nearly 30 wt.%; amounts of the rest of elements are also variable. As SiO_2 increases in melts of sp. 979, amounts of TiO_2, Al_2O_3, FeO, and MgO decrease, whereas the concentrations of alkalies and P_2O_5 increase. In most cases carbonatite melts in sp. 979 are not uniform and are characterized by subsolidus separation into Ca- and alkali-enriched portions. The quenched melts in sp. 1/881 and 1/883 have alkali-enriched carbonatite compositions and are obviously homogeneous. These specimens are distinguished by chemical compositions of melts, which are richer in SiO_2 in sp. 1/883 than in sp. 1/881. In both cases the melts are enriched in CaO (~29 wt.%), FeO (~9.5), and Na_2O (~2.5) and depleted in Al_2O_3 (4–6) and MgO (2–3 wt.%).
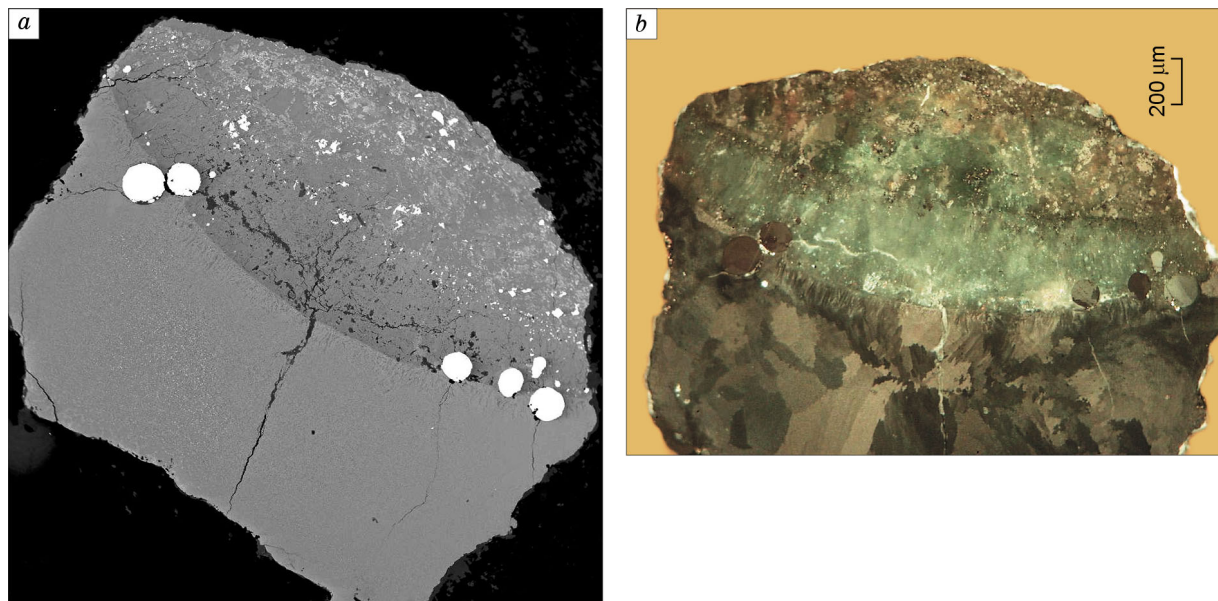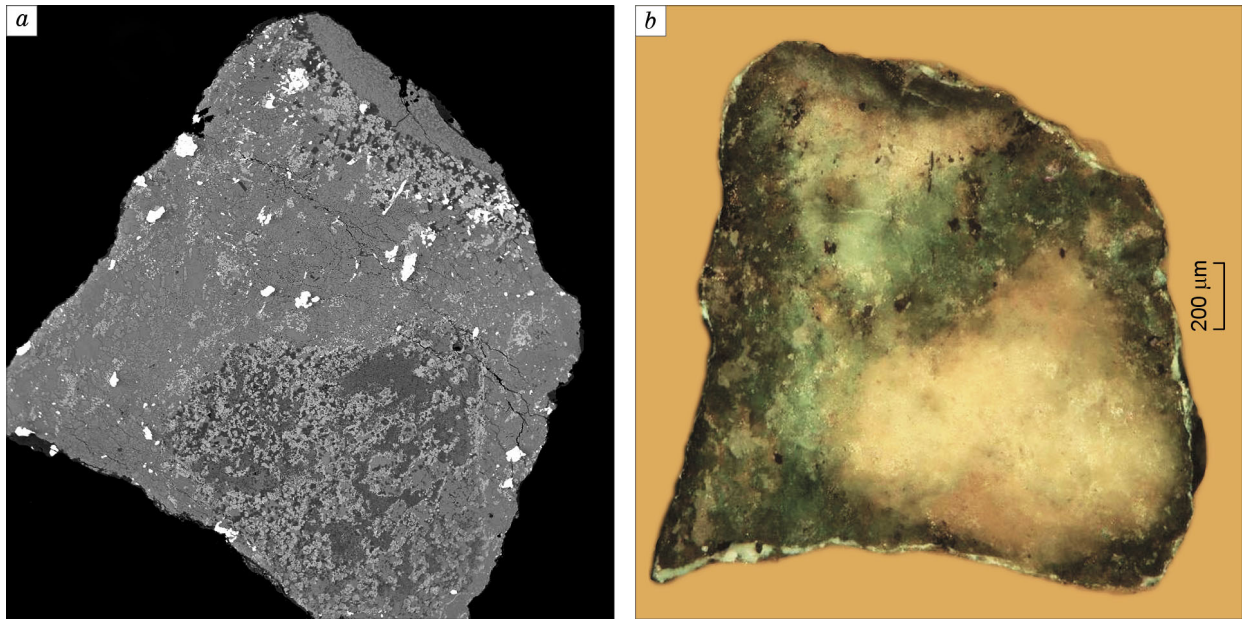
Fig. 8. Experimental specimen 1/881 of the Chagatai carbonatite. The melt-pyroxenite contact formed on quenching (center), sulfide immiscible melts (white) and eclogite garnet-clinopyroxene assemblage (upper part). *a* **— BSE image;** *b* **— under microscope with crossed polars.**
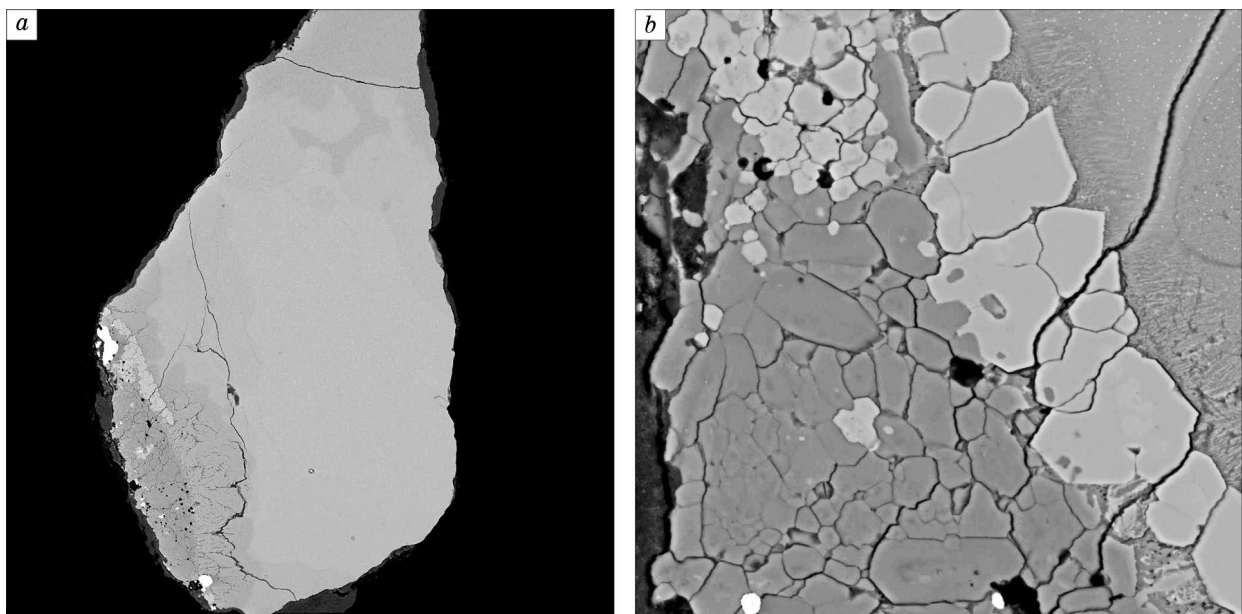

Fig. 9. Experimental specimen 1/881 of the Chagatai carbonatite. *a* **— View of liquidus relationships of clinopyroxenite (upper right) at the contact with carbonatite liquid after quenching. BSE image. Width of the image is 250** μm. *b* **— Details of phase relationships of the assemblage garnet (light-gray)-clinopyroxene (gray)-carbonate (dark-gray). Image is 77** μm **wide.**

Garnets in sp. 979 are rich in CaO and contain variable amounts of FeO and CaO from 12.7 to 17.2 and from 20.6 to 26 wt.%, respectively. These garnets contain Na (0.2–0.28 wt.% Na_2O) and possibly some K. Clinopyroxenes are also chemically nonuniform: Contents of FeO, CaO, and Na_2O are within 12.6–16, 17.2–21.9, and 3.7–5.4 wt.%, respectively. Clinopyroxenes contain some amounts of Al_2O_3 (3.8–6.8 wt.%) and K_2O (0.14–1.09 wt.%).
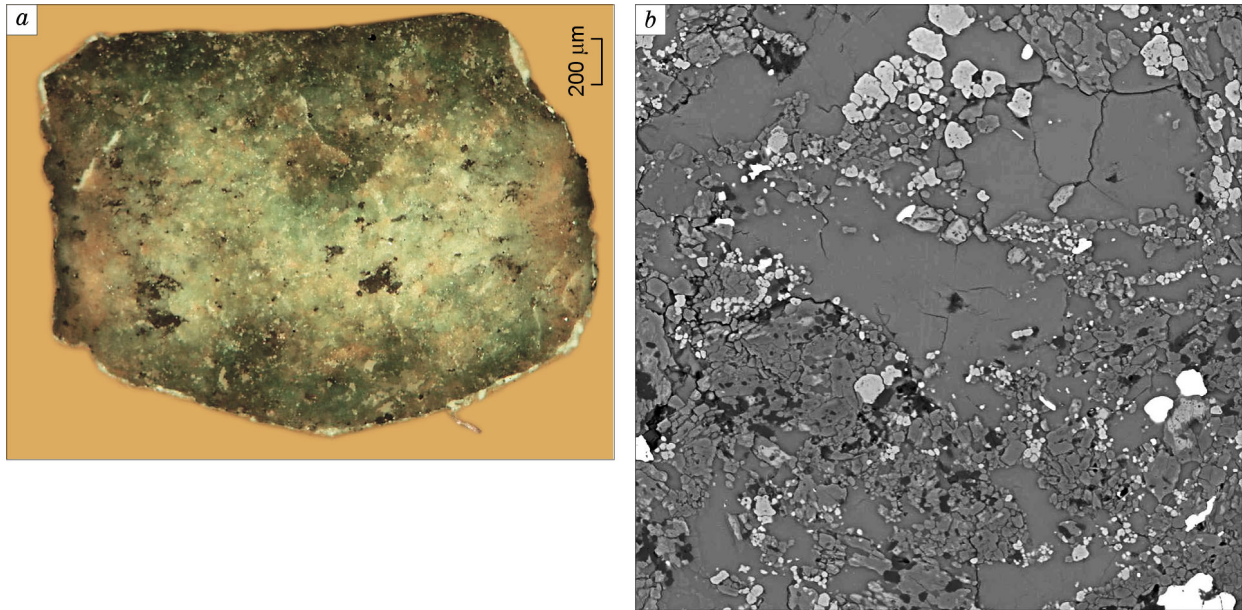
Fig. 10. Experimental specimen 1/882 of the Chagatai carbonatite. Irregular distribution of phases. Garnet-and carbonate-enriched nests (dark-gray spots at the bottom and in the uppermost part in panel *a* in the clinopyroxene-enriched matrix. Sulfides (white in panel *a*) are not segregated like immiscible liquids in sp. 1/881. *a* — BSE image; *b* — under microscope with crossed polars.

Fig. 11. Experimental specimen 1/883 of the Chagatai carbonatite. *a* — Specimen is largely uniform and monocrystalline (quenched melt), *b* — crystalline, composed of garnet (light-gray) and clinopyroxene (gray). BSE image 116 μm wide.

Garnets in sp. 1/881–1/885 are also rich in CaO (17.2–23.3), FeO (12.7–19.8), and TiO_2 (0.22–2.34) and always contain Na_2O (0.04–0.73 wt.%). Clinopyroxenes are enriched in Na_2O (3.8–6.6), Al_2O_3 (4.3–15.0), and FeO (7.2–16.8 wt.%) and also contain variable amounts of K_2O (≤0.27 wt.%).

Fig. 12. Experimental specimen 1/884 of the Chagatai carbonatite. *a* — Central part is enriched in clinopyroxene (green) and is surrounded by a garnet-enriched assemblage (reddish); under microscope with crossed polars. *b* — Typical textures with garnet (light-gray), clinopyroxene (gray), quartz (dark-gray) and large grains of carbonate (gray). BSE image 208 μm wide.
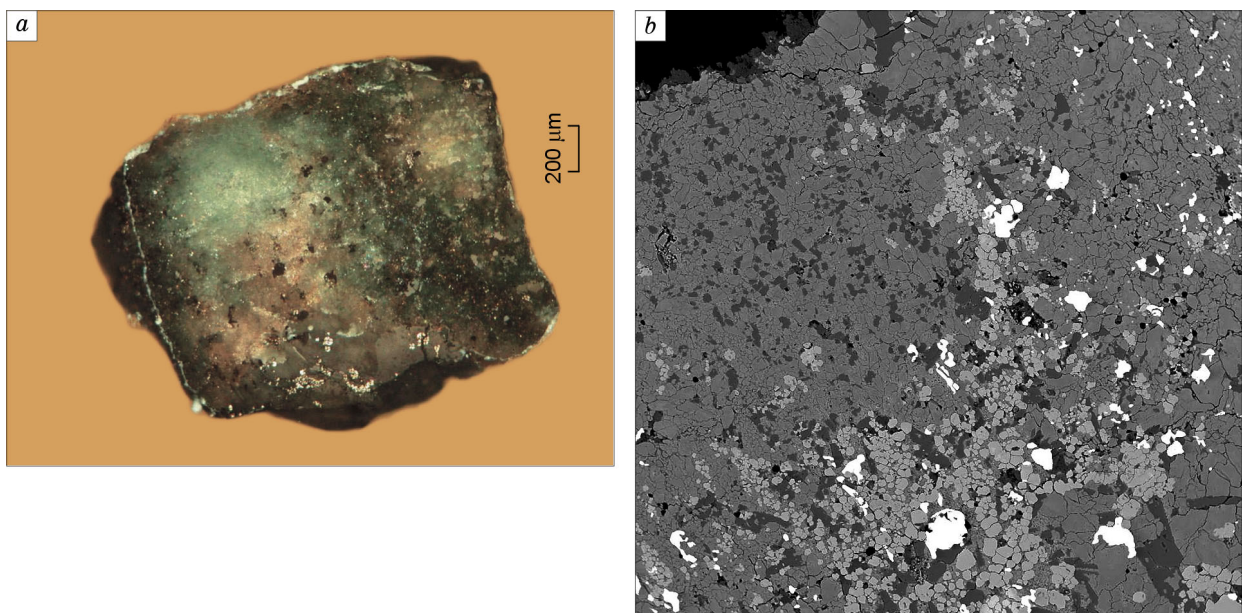
Fig. 13. Experimental specimen 1/884 of the Chagatai carbonatite. *a* — Mineral assemblages are visible, enriched in garnet (reddish) or clinopyroxene (green) or in quenched phase of carbonatite melt (bottom); under microsocpe with crossed polars. *b* — Typical textures with garnet (light-gray), clinopyroxene (gray), and quartz (dark-gray). BSE image 830 μm wide.

APPLICATION TO GENESIS OF NATURAL DIAMONDITES

Physicochemical mechanism of formation of diamonds and diamondites in experimental carbonatite-carbon melts can be defined as follows. Under the conditions of thermodynamic stability of diamond starting graphite

Table 4

Electron Microprobe Analyses of Phases from Experimental Specimens of Chagatai Carbonatites Containing Melts (wt.%)

Oxide	Cpx1	Cpx2	Cpx3	Cpx r	Cpx vr	Gtl	Melt
				Sp. 1/881			
SiO_2	53.0	53.7	52.8	52.6	50.2	38.3	23.0
TiO_2	0.09	0.22	0.86	0.15	0.21	0.22	0.56
Al_2O_3	15.0	14.4	4.31	10.2	3.27	18.5	4.29
Cr_2O_3	<0.02	0.16	0.12	<0.02	0.04	0.09	0.19
FeO	7.4	7.5	13.6	10.7	16.8	18.9	9.4
MnO	0.02	0.12	0.2	0.38	0.49	0.39	0.17
MgO	4.43	5.2	6.4	4.7	5.5	3.27	2.18
CaO	13.2	14.0	16.6	13.6	17.0	19.8	29.5
Na_2O	6.2	5.6	5.0	5.6	3.80	0.04	2.82
K_2O	0.07	<0.02	0.13	0.04	0.07	—	1.50
Total	99.41	100.90	100.04	97.97	97.38	99.51	73.61

	Cpx1	Cpx2	Cpx3	Cpx r	Cpx r	Gt1	Gt2	Gt3
				Sp. 1/882				
SiO_2	53.6	54.2	54.1	53.8	51.7	38.1	39.1	37.7
TiO_2	0.67	0.24	0.18	0.14	0.49	1.09	1.01	1.10
Al_2O_3	12.0	11.1	11.7	9.2	8.2	19.9	19.6	17.8
Cr_2O_3	<0.02	0.05	<0.02	<0.02	<0.02	0.04	0.17	<0.02
FeO	8.9	9.5	9.6	11.2	13.2	14.1	16.3	19.1
MnO	0.07	<0.02	0.39	0.19	0.26	0.21	0.63	0.82
MgO	4.99	4.87	5.1	5.4	5.3	1.69	2.14	2.97
CaO	13.0	13.2	13.6	14.8	15.8	23.3	21.9	19.9
Na_2O	6.1	6.5	5.8	5.5	4.50	0.42	0.27	0.18
K_2O	0.06	0.11	0.18	0.23	0.27	—	—	—
Total	99.39	99.77	100.65	100.46	99.72	98.85	101.12	99.57

Oxide	Cpx1	Cpx2	Cpx3	Gt1	Gt2	Gt3	Melt 1	Melt 2
				Sp. 1/883				
SiO_2	52.0	51.3	52.4	39.2	38.8	39.6	27.4	27.8
TiO_2	0.23	0.38	0.28	0.54	0.51	0.51	0.53	0.61
Al_2O_3	13.4	11.7	11.5	21.3	20.9	21.6	5.9	5.8
Cr_2O_3	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.07
FeO	7.9	9.2	10.2	12.7	13.5	14.7	9.4	9.7
MnO	0.04	0.29	0.12	0.74	0.43	0.35	0.19	0.13
MgO	5.6	5.2	5.1	4.08	3.80	3.13	2.62	2.97
CaO	15.5	15.2	15.3	21.4	21.1	21.6	29.0	28.6
Na_2O	4.98	5.2	5.4	0.36	0.38	0.23	2.37	2.52
K_2O	<0.02	0.12	0.15	—	—	—	0.75	0.82
Total	99.67	98.59	100.45	100.32	99.42	101.72	78.16	79.02

Table 4 **(continued)**

Oxide	Cpx1	Cpx2	Cpx3	Gt1	Gt2	Gt3	Gt4
				Sp. 1/884			
SiO_2	54.9	54.6	53.3	39.3	39.4	38.0	38.0
TiO_2	0.27	0.39	0.61	0.98	0.93	1.65	2.34
Al_2O_3	12.0	11.0	7.4	20.6	20.2	18.3	16.1
Cr_2O_3	<0.02	<0.02	0.06	<0.02	<0.02	<0.02	0.11
FeO	8.4	9.4	12.8	16.5	18.0	19.8	23.3
MnO	0.28	0.07	0.12	0.88	1.00	0.90	0.50
MgO	5.4	5.2	5.4	2.22	2.71	2.41	2.43
CaO	12.7	13.3	15.2	20.0	19.6	19.2	17.2
Na_2O	6.6	6.1	5.1	0.61	0.31	0.10	0.73
K_2O	0.12	0.08	0.02	—	—	—	—
Total	100.67	100.14	100.01	101.09	102.15	100.36	100.71

	Cpx1	Cpx2	Cpx3	Gt1	Gt2	Gt3	Gt4
				Sp. 1/885			
SiO_2	53.2	53.7	54.2	39.4	38.3	37.9	38.0
TiO_2	0.24	<0.02	0.33	1.07	0.60	0.65	1.46
Al_2O_3	13.3	12.6	12.6	20.1	21.0	20.0	18.3
Cr_2O_3	<0.02	0.03	0.07	<0.02	<0.02	<0.02	0.02
FeO	7.2	8.3	9.6	14.5	15.4	16.8	19.4
MnO	0.22	0.23	0.07	0.53	0.43	0.80	0.73
MgO	5.1	5.3	4.8	2.72	2.21	2.52	2.12
CaO	13.5	13.8	13.9	22.2	21.8	20.4	19.5
Na_2O	6.1	6.6	5.6	0.24	0.46	0.27	0.49
K_2O	0.07	0.08	0.06	—	—	—	—
Total	98.93	100.64	101.23	100.76	100.20	99.34	100.02

Note. r — Rare, vr — very rare.

remains as a metastable phase. Under the temperatures exceeding the eutectic melting point of carbonate-silicate systems, this metastable graphite is dissolved in the melt to form carbon solutions in carbonate-silicate melts. Being a thermodynamically metastable phase, graphite is characterized by a higher solubility in carbonatite melts than diamond under the same physical conditions. Therefore, graphite dissolution leads to formation of carbonate-silicate melts, which are naturally oversaturated with respect to diamond. It is the carbon oversaturation of carbonate-silicate-carbon melt that is responsible for the nucleation and growth of diamond crystals [16]. Study of the mechanism of diamondite formation shows that the main driving force of this process is a difference in solubilities of metastable graphite and diamond in a carbonatite melt [10]. The intense dissolution of graphite at the graphite-melt contact and the formation of strongly oversaturated melts of carbon leads to spontaneous nucleation of diamond with a very high density of nuclei distribution (about $1 \cdot 10^5$ nuclei/mm^3) and to a thin polycrystalline nucleation layer at the contact of carbonate melt and graphite. Then two processes run simultaneously: rapid transfer of dissolved carbon to the diamond nucleation layer through a thin (less than 100 µm) film of carbonatite melt and "snowballing" formation of diamondite.

Any up-to-date concept of chemical composition of parental media for nucleation and growth of diamond crystals should take into account a leading role of multicomponent carbonate-silicate melts. These melts efficiently dissolve carbon from mantle sources. It is reasonable to differentiate major and minor (or admixed) components in the composition of parental melts [17]. Carbonate and silicate components make a considerable contribution to

the composition of carbonate-silicate melts. Minor components are diverse: oxides, phosphates, sulfides, halides, carbon oxide, water, etc.

The chemistry of natural parental media providing nucleation and crystallization of diamondites under the conditions of the Earth's mantle is of key importance for understanding the diamondite genesis. The problem of carbon source for diamondites is essential in the geochemical context but it is hardly crucial for diamond formation. The requirement for higher grades of supersaturation by carbon with respect to diamond in parental diamond-forming melts seems to be more important irrespective of what is the source of carbon. Elemental carbon in the form of graphite and amorphous phases is present in mantle xenoliths. Probably, the mantle contains much CO, CO_2, and CH_4, which can be considered potential sources of carbon under strong reduction [19]. The problem of carbon source for the formation of natural diamondites remains at the level of "asthenosphere" or "mantle" carbon [5, 18]. The idea of "asthenosphere" carbon seems to be more preferential. Worthy of note is that, being in intimate contact, the carbonate melt and graphite are chemically stable in the processes of formation of diamond and diamondite under high pressures and temperatures. Carbonate is not subject to reduction, and graphite is not oxidized, i.e., this pair carbonate–solid carbon acts as an oxygen buffer for major components of diamond-forming process.

Carbonate-silicate melts of the Chagatai carbonatites are interesting from the point of view of experimental modeling of parental media for diamondites, as they representatively contain major (carbonates and silicates) as well as the most important secondary (sulfides, oxides, native metals, etc.) components of natural parental media. Their use for experimental synthesis of diamondites permits modeling of the conditions under which diamondites trap syngenetic mineral inclusions (such as garnets and clinopyroxenes of eclogite paragenesis). However, the natural processes of diamondite formation are not restricted to the concentration ratios CaO:FeO:MgO typical of the Chagatai carbonatites. Diamondites were also effectively formed in model carbonatite melts (K_2CO_3 — 27.21, Na_2CO_3 — 2.89, $CaCO_3$ — 26.91, $FeCO_3$ — 25.63, $MgCO_3$ — 17.5 wt.%) [10], and a positive result is anticipated for MgO-rich carbonatite melts, which are now under experimental study.

In experiments, diamondites grow from oversaturated solutions of carbon in a carbonate-silicate melt of the Chagatai carbonatite. The source of carbon is graphite. At high pressures, under the *P-T* conditions of diamond stability, carbonates melt congruently, without decomposition into oxides and carbon dioxide as they do under atmospheric pressure. Carbonate components can completely mix with silicates in carbonate-silicate melts. During experiment, diamond crystallization is accompanied with the formation of syngenetic silicate minerals (garnet and clinopyroxene) from the same carbonate-silicate-carbon melts. Cocrystallization of carbonates (calcite or aragonite) with garnet and clinopyroxene occurs at lower temperatures before the complete solidification of the system at solidus temperature. Correspondingly, primary solid inclusions in diamondites are syngenetic phases, which crystallize together with diamondites from the same carbonatite (carbonate-silicate-carbon) melts. The diamondites formed in the Chagatai carbonate-silicate-carbon melts contain solidified portions of a carbonatite parental melt, including garnet, clinopyroxene, carbonates, and accessory minerals (sulfides, phosphates, native metals, etc.).

Experimental data demonstrate that Ca-eclogite garnet and clinopyroxene are syngenetic with diamonds. These results corroborate that natural diamondites and silicate inclusions in them are genetically related [1, 2, 20]. The high-pressure experimental assemblage for both Chagatai carbonatites (sp. 23 and 79) is similar to Fe-enriched carbonate eclogites composed of clinopyroxene, garnet, and carbonates. The liquidus phase is either garnet (sp. 79) or clinopyroxene (sp. 23). Clinopyroxene in all cases has a composition of Fe-omphacite, which is beyond the compositions observed in natural associations with diamonds [21]. It contains K as it was formed at high pressures [22]. Coexisting garnet is characterized by grossular-almandine compositions, which also are beyond the garnet compositions from natural associations with diamond [23]. Garnet contains Na, which agrees with its high-pressure genesis. Most garnets contain no extra Si as could be expected for the majorite component of solid solutions formed under high pressure [24].

Phase compositions in our experiments are variable and depend on the degree of specimen crystallization. Nevertheless, coexisting garnets and clinopyroxenes give a certain insight into the distribution of major and minor elements among them. The coefficients of distribution of elements among garnet and clinopyroxene in experimental sp. 979 (see Table 2) and natural assemblages [1, 2] are like to those for TiO_2 (D = Grt Cpx ~1), Al_2O_3 ($D \approx 3$–6), MnO ($D \approx 2$–3), and Na_2O ($D \approx 0.02$–0.08). However, the distributions in the cases of FeO ($D \approx 1$ for experimental assemblages as compared with $D \approx 3$ for natural ones), MgO ($D \approx 0.5$ as compared with $D \approx 1.3$) and CaO ($D \approx 1.4$ as compared with $D \approx 0.3$) do not agree.

Coexisting garnets and clinopyroxenes in the experiments with the Chagatai carbonatite sp. 23 chiefly indicate the distribution of elements that does not agree with the distribution revealed in natural associations. For TiO_2 $D = 1$–7 (~1 in natural associations), for Al_2O_3 $D = 1.6$–5.7 (~6 in nature), for FeO (Fe_{tot}) $D = 1.1$–1.9 (~3 in nature), for MnO $D = 0.8$–4.4 (as compared with ~4), for MgO $D = 0.4$–0.9 (as compared with ~1.3), and for

CaO D = 1.2–1.7 (as compared with 0.3 in nature). Though these values are slightly overlapped in some cases, most values for distribution of elements among experimental pairs of minerals are far beyond the values for natural associations. Only for Na_2O the values D = 0.01–0.1 do commensurate the natural ones (D = ~0.02), and as a rule the experimental data for MnO overlap the data for natural associations. Obviously, these discrepancies are a consequence of essentially different chemistry for the Fe- and Ca-enriched Chagatai carbonatites in our experiments and chiefly Mg- and alkali-enriched mantle carbonatites. This necessitates carrying out experiments with primitive carbonatites to obtain more precise answers.

Diamondites contain primary mantle minerals with signatures of peridotite and eclogite parageneses [1]. This shows that the compositions of parental media for diamonds and diamondites are strongly variable and also can form from the matter of mantle ultrabasic rocks. On the other hand, relative contents of carbonate and silicate components in parental carbonatite melts are also variable, which follows from the compositions of primary fluid-carbonatite inclusions in diamonds from Botswana [5]. Supposedly, like single-crystal diamond, diamondite can form in parental carbonate-silicate melts with variable chemical compositions of both major and secondary components. It seems reasonable to state that the principal issue is that the origin of diamondites is owing to the formation of ultimately C-oversaturated solutions in mantle carbonatite (carbonate-silicate) melts.

CONCLUSIONS

The carbonatite composition of parental media responsible for the formation fo diamondites was substantiated by data on geochemistry of trace elements in silicate minerals from natural diamondites [1, 2] and high-pressure high-temperature experiments on crystallization of "carbonate-synthetic" diamondites in carbonate-carbon and carbonate-silicate-carbon melts of natural chemical composition [10, 14]. The natural carbonatites of the Chagatai complex (Uzbekistan) with a high content of silicate components and eclogite silicate mineralogy under high pressures were used to model the carbonate-silicate medium, parental for both diamondites and syngenetic inclusions in them. The experiments at 7 GPa and 1800 °C show that diamondites quickly formed in the carbonate-silicate melts of the Chagatai carbonatites with dissolved carbon. Under the *P-T* conditions of diamondite formation the mineralogy of the Chagatai carbonatite is represented by grossular-almandine garnet, diopside-hedenbergite clinopyroxene and calcite (aragonite) and is similar to the mineralogical composition of diamondiferous Ca-eclogites and grospydites revealed as mantle xenoliths in kimberlites. To estimate the physicochemical behavior of the Chagatai carbonatite as a parental medium for diamondite is important to get an insight into the conditions modeling to a certain degree the process of formation of natural diamondites. The most important characteristics of this process are: rapid transport of mobile low-viscosity carbonate-silicate melt to the zone of diamondite formation; ultimately high "snowballing" rate of diamondite crystallization from a C-oversaturated carbonate-silicate melt; formation of syngenetic inclusions of garnet and clinopyroxene, carbonate and sulfides. Experiments show that the formation of diamondite and syngenetic inclusions of silicates, sulfides, phosphates, and other minerals inside the pores and cavities of diamonds is accompanied by coarse-grained crystallization of similar minerals in the parental medium, which surrounds growing diamondites.

REFERENCES

1. Kurat, G., and G. Dobosi, Garnet and diopside-bearing diamondites (framesites), *Miner. Petrol.*, **69**, 143–159, 2000.

2. Dobosi, G., and G. Kurat, Trace element abundances in garnets and clinopyroxenes from diamondites — a signature of carbonatitic fluids, *Miner. Petrol.*, **76**, 21–38, 2002.

3. Litvin, Yu.A., and V.A. Zharikov, Primary fluid-carbonatite inclusions in a diamond modeled by the system

K_2O–Na_2O–CaO–MgO–FeO–CO_2 as a medium of diamond formation in an experiment at 7–9 GPa, *Dokl. RAN*, **367**, 3, 397–401, 1999.

4. Litvin, Yu.A., and V.A. Zharikov, Experimental modeling of diamond genesis: diamond crystallization in multicomponent carbonate-silicate melts at 5–7 GPa and 1200–1570 °C, *Dokl. Earth Sci.*, **372**, 6, 808–811, 2000.

5. Schrauder, M., and O. Navon, Hydrous and carbonatitic mantle fluids in fibrous diamonds from Jwaneng, Botswana, *Geochim. Cosmochim. Acta*, **58**, 2, 761–771, 1994.

6. Djuraev, A.D., and F.K. Divaev, Melanocratic carbonatites — new type of diamond-bearing rocks, Uzbekistan, in S.J. Stanley (ed.), *Miner. Deposits: Processes to Processing*, 639–642, Balkema, Rotterdam, 1999.

7. Litvin, Yu.A., A.P. Jones, A.D. Bird, F.K. Divaev, and V.A. Zharikov, Crystallization of diamonds and syngenetic minerals in melts of the Chagatai diamondiferous carbonatites, Uzbekistan (experiment at 7.0 GPa), *Dokl. Earth Sci,*, **381**, 4, 528–531, 2001.

8. Bobrov, A.V., Yu.A. Litvin, and F.K. Divaev, Phase relations and diamond synthesis in the carbonate-silicate rocks of the Chagatai complex, Western Uzbekistan: Results of experiments at P = 4–7 GPa and T = 1200–1700 °C, *Geochem. Intern.*, **42**, 1, 39–48, 2002.

9. Sobolev, N.V., *The deep-seated inclusions in kimberlites and the composition of the upper mantle*, 304 pp., American Geophysical Union, Washington, 1977.

10. Litvin, Yu.A., and A.V. Spivak, Diamondites: rapid growth at the contact of graphite and carbonate melts (experiments at 7.5–8.5 GPa), *Dokl. Earth Sci.*, **391**, 5, 673–677, 2003.

11. Litvin, Yu.A., *Physicochemical studies of melting of the mantle-derived matter of the Earth* [in Russian], 312 pp., Nauka, Moscow, 1991.

12. Eremets, M.I., *High Pressure experimental methods*, 390 pp., Oxford University Press, Oxford—New York—Tokyo, 1996.

13. Kennedy, C.S., and G.C. Kennedy, The equilibrium boundary between graphite and diamond, *J. Geophys. Res.*, **8**, 14, 2467–2470, 1976.

14. Spivak, A.V., and Yu.A. Litvin, Diamond syntheses in multicomponent carbonate-carbon melts of natural chemistry: elementary processes and properties, *Diamond and related materials*, **13**, 482–487, 2004.

15. Litvin, Yu.A., V.G. Butvina, Diamondiferous media in the system eclogite-carbonatite-sulfide-carbon from experimental data at 6.0–8.5 GPa, *Petrologiya*, **12**, 4, 426–438, 2004.

16. Litvin, Yu.A., L.T. Chudinovskikh, and V.A. Zharikov, Crystallization of diamond and graphite in mantle alkali-carbonate melts in an experiment at 7–11 GPa, *Dokl. RAN*, **355**, 5, 669–672, 1997.

17. Litvin, Yu.A., Alkali-chloride components in processes of diamond growth under conditions of mantle and high-pressure experiment, *Dokl. Earth Sci.*, **389**, 3, 382–386, 2003.

18. Navon, O., Diamond formation in the Earth's mantle, in J.J. Gurney, J.L. Gurney, M.D. Pascoe, S.H. Richardson (eds.), *Proc. VII Int. Kimberlite conf., red roof design, Cape Town, 1999*, vol. 2, 584–604.

19. Pal'yanov, Yu.N., A.G. Sokol, Yu.M. Borzdov, A.F. Khokhryakov, and N.V. Sobolev, Diamond formation through carbonate-silicate interaction, *Amer. Miner.*, **87**, 1009–1013, 2002.

20. Dobosi, G., and G. Kurat, Silicate-bearing diamondites, in *Abs. Intern. sympos. on evolution of continental lithosphere, origin of diamonds and diamond deposits. Novosibirsk, 2005, June 3—5*, 102–103, Novosibirsk, 2005.

21. Taylor, L.A., and M. Anand, Diamonds: time capsules from the Siberian mantle, *Chemie der Erde*, **64**, 1–74, 2004.

22. Harlow, G.E., K in clinopyroxene at high pressure and temperature: an experimental study, *Amer. Miner.*, **82**, 259–269, 1997.

23. Meyer, H.O.A., Inclusions in diamond, in P.H. Nixon (ed.), *Mantle xenoliths*, 501–523. Wileys, England, 1987.

24. Moore, R.O., and J.J. Gurney, Pyroxene solid solution in garnets included in diamonds, *Nature*, **318**, 553–555, 1985.