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# Diamond-Forming Media in the System Eclogite–Carbonatite–Sulfide–Carbon: Experiments at 6.0–8.5 GPa

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**Abstract**—Processes of diamond crystallization were experimentally studied in the model system eclogite–carbonatite–sulfide–carbon at pressures of 6.0–8.5 GPa. Diamond was synthesized for the first time in the sulfide–carbon and the eclogite–sulfide–carbon systems. Sulfide–carbon melts were produced in experiments with mixtures of graphite with chalcopyrite, pyrrhotite, and pentlandite, which are associated with both diamond and mantle peridotites and eclogites. The investigation of the eclogite–carbonatite–carbon system showed that carbonatite melts dissolved eclogitic minerals along with carbon (graphite) producing carbonate–silicate–carbon liquids. This can result in diamond crystallization together with silicate minerals and entrapment of cogenetic silicate inclusions in diamonds. According to experimental and mineralogical data, natural diamond-forming media are carbonate–silicate–carbon melts with varying chemical characteristics. They contain diverse admixtures, including sulfides. Residual melts enriched in sulfides form during the fractional crystallization of silicates and carbonates. This promotes the entrapment of sulfide inclusions by growing diamond crystals. Sulfide melts are efficient media for diamond growth. These processes are important for the genesis of diamond-bearing eclogites.

## INTRODUCTION

Sulfides are common primary inclusions in diamonds from kimberlites (Efimova *et al.*, 1983). In addition, sulfides were identified in mineral assemblages of mantle peridotites, eclogites, and clinopyroxenites (Sobolev and Vakhrushev, 1967; Desborough and Czamanske, 1973). Strongly compressed sulfide phases are often included directly in the growth centers of natural diamond monocrystals (Bulanova *et al.*, 1979; Bulanova, 1993). Based on these findings, sulfide materials were proposed as diamond-forming media (Bulanova, 1995; Bulanova *et al.*, 1998). This suggestion was supported by the sulfide coats or films that were found in paragenetic contact with diamonds from eclogites (Bulanova *et al.*, 1990; Spetsius, 1999). Successful diamond synthesis in mixed sulfide–carbon melts (Litvin *et al.*, 2002; Butvina *et al.*, 2002) provided a solid argument in favor of the possible participation of sulfide parent media in diamond formation under mantle conditions. Moreover, the carbonate–silicate or carbonatite model of the chemical composition of parent media for natural diamond growth has recently received strong support from experimental (Litvin *et al.*, 1997, 1999; Sokol *et al.*, 1998; Litvin and Zharikov, 1999, 2000; Pal'yanov *et al.*, 2001, 2002; Shatsky *et al.*, 2002) and mineralogical studies (Schrauder and Navon, 1994; Navon, 1999; Izraeli *et al.*, 2001). There is now compelling evidence that carbonatite and sulfide media are favorable for diamond formation, and their real participation in the genesis of natural diamonds is firmly established. Diamond synthesis experiments at 7.0–7.7 GPa and 1800–2200°C in the silicate–carbonate–carbon melts of natural kimberlites (Arima *et al.,* 1993) demonstrated the possibility of episodic diamond crystallization (within the *P*–*T* field of diamond stability) from transporting kimberlite media, if they are molten and oversaturated in carbon with respect to diamond.

According to the available experimental data (e.g., Borzdov *et al.,* 1999), silicate melts are not productive with respect to diamond formation. Arima *et al.* (1993) reported the "crystallization of diamond from a silicate melt of kimberlite composition," but in fact their diamonds crystallized from silicate–carbonate kimberlite melts, which is demonstrated by the analyses of quench products. A key factor of diamond formation is the presence of carbonate compounds in such melts. However, it is evident that silicate minerals, rocks, and melts take part in the genesis of diamond; they form the mantle environment where diamond-forming processes occur and participate in the diamond-forming medium. This is suggested by the presence in diamonds of primary mineral inclusions representing two major assemblages of diamond-bearing rocks, peridotite and eclogite (Sobolev, 1974).

The elucidation of relationships between silicate, carbonate, and sulfide components during diamond formation is of key importance for the deciphering of the complicated physical and chemical conditions of dia-

**Table 1.** Chemical compositions (wt %) of starting silicate minerals from bimineralic eclogite sample U–2340 from the Udachnaya pipe, Yakutia (data by Z.V. Spetsius) and the calculated composition of the experimental mixture garnet : clinopyroxene = 50 : 50 (wt %)

| Component | Garnet | Clinopyroxene | Mixture |
|---|---|---|---|
| $SiO_2$ | 39.04 | 55.04 | 47.04 |
| $TiO_2$ | 0.64 | 0.38 | 0.51 |
| $Al_2O_3$ | 20.98 | 4.95 | 12.97 |
| $Cr_2O_3$ | 0.03 | 0.01 | 0.02 |
| FeO | 21.79 | 7.50 | 14.64 |
| MgO | 8.52 | 11.64 | 10.08 |
| MnO | 0.44 | 0.04 | 0.24 |
| CaO | 8.47 | 17.90 | 13.19 |
| $Na_2O$ | 0.09 | 2.48 | 1.28 |
| $K_2O$ | 0.00 | 0.06 | 0.03 |
| Total | 100.00 | 100.00 | 100.00 |

**Table 2.** Starting carbonatite mixture of the model carbonatite composition according to Litvin and Zharikov (2000)

| Component | Mixture |
|---|---|
| $K_2CO_3$ | 27.21 |
| $Na_2CO_3$ | 2.89 |
| $CaCO_3$ | 26.91 |
| $MgCO_3$ | 17.35 |
| $FeCO_3$ | 25.63 |
| Total | 99.99 |

**Table 3.** Chemical compositions of natural sulfide minerals from bimineralic eclogite sample U–2340 from the Udachnaya pipe, Yakutia (data by Z.V. Spetsius), which were taken as prototypes, and the calculated compositions of the starting pyrrhotite–chalcopyrite (50 : 50, wt %) and chalcopyrite–pentlandite (50 : 50, wt %) mixtures

| Element | Pyrrhotite | Chalcopyrite | Pyrrhotite + chalcopyrite | Pentlandite + chalcopyrite |
|---|---|---|---|---|
| Fe | 62.64 | 31.40 | 35 | 25 |
| Ni | 0.35 | 4.25 | | 10 |
| Co | 0.04 | 0.28 | | |
| Cu | 0.02 | 29.44 | 17 | 17 |
| S | 35.06 | 31.53 | 48 | 48 |
| Total | 98.01 | 96.92 | 100 | 100 |

mond genesis and formation of diamondiferous rocks. Experimental studies at high pressures and temperatures are crucial for the solution of this problem.

The purpose of this paper is experimental modeling of diamond formation for several variants of the chemical composition of parental medium in the eclogite assemblage. The subject of our study is the model multicomponent system eclogite–carbonatite–sulfide–carbon, whose composition was taken in accordance with the compositions of natural prototypes.

## EXPERIMENTAL METHODS

Starting mixtures of eclogite compositions were prepared from clinopyroxene and garnet from a diamondiferous eclogite of the Udachnaya pipe (Table 1), which were mixed in a weight proportion of 1 : 1 and ground in a tungsten carbide (VK6) mortar. The model carbonatite is a mixture of K, Na, Ca, Mg, and Fe carbonates (Table 2) corresponding to the major-component composition of the end-member carbonatite for primary fluid-bearing multiphase inclusions in diamonds from the Jwaneng pipe, Botswana (Schrauder and Navon, 1994; Litvin and Zharikov, 2000). Starting sulfide compositions (Table 3) were selected taking into account that phases of the Fe–Ni–Cu–S system are predominant among mantle sulfides associating with diamond. Pyrrhotite, pentlandite, and chalcopyrite are most common as sulfide inclusions in diamonds. Mixtures of sulfide powders were prepared from natural pyrrhotite $Fe_{1-x}S$ (with small admixtures of Cu, Ni, Co, Mn, and Zn), pentlandite $(Fe, Ni)_9S_8$ (containing about 2 wt % Co), and chalcopyrite $CuFeS_2$ (with trace amounts of Ag and Au). Two mixtures were prepared: (1) from equal masses of chalcopyrite and pyrrhotite and (2) from equal masses of chalcopyrite and pentlandite. Table 1 shows the compositions of starting mixtures. Ultrapure graphite (powder with a grain size of 0.5 mm; 40 wt % in all the systems) was used as a carbon source.

The starting mixtures were packed in graphite capsules, 7.2 mm in length and 4 mm in diameter (wall thickness of 0.5 mm), and closed by graphite plugs, 1 mm thick. Monocrystalline seeds of cuboctahedral synthetic diamonds (synthesized in Ni–Mn–C melts), 0.6 mm in size, were placed in the center of capsules together with the starting mixtures. The spontaneous crystallization of diamonds occurred also without seeds in the labile oversaturated carbonate–silicate–carbon and sulfide–carbon melts. The seeds therefore had no significance for the initiating of spontaneous diamond nucleation. The seeds were used only to check the physicochemical conditions of diamond crystallization from the effects of growth and dissolution or the absence of changes. The capsules were placed in the central hole of a high-pressure cell, which was manufactured from lithographic limestone. The graphite capsules served as heating elements. A thermal gradient of about 50°C/mm existed within samples during experiments. The temperature decreased from the boundary of the central zone of the cylindrical sample (where temperature varied within ±15°C) toward its ends. Sev-

**Table 4.** Conditions and results of the diamond synthesis experiments in the eclogite–carbonatite–sulfide–carbon system

| Sample number | Capsule | Composition of the system, wt % | | | | Run conditions | | | Diamond synthesis |
|---|---|---|---|---|---|---|---|---|---|
| | | Graphite | Carbonate | Silicate | Sulfide | $P$, GPa | $T$, °C | $\tau$, min | |
| 1033 | Graphite | 40 | 60 | – | – | 6 | 1500 | 20 | + |
| 654 | Graphite | 40 | 60 | – | – | 8 | 1300 | 30 | + |
| 655 | Graphite | 40 | 15 | – | 45 | 8 | 1300 | 30 | – |
| 656 | Graphite | 40 | 30 | 30 | – | 8 | 1350 | 60 | + |
| 657 | Graphite | 40 | 15 | 30 | 15 | 8 | 1500 | 30 | + |
| 658 | Graphite | 40 | – | 45 | 15 | 8 | 1620 | 40 | + |
| 667 | Graphite | 40 | – | – | 60 | 8 | 1700 | 70 | + |
| 668 | Graphite | 40 | – | 45 | 15 | 8 | 1650 | 24 | + |
| 693 | Graphite | 40 | – | – | 60 | 7.5 | 1650 | 80 | + |
| 694 | Graphite | 40 | – | – | 60 | 7 | 1650 | 150 | + |
| 697 | Graphite | 40 | – | – | 60 | 7 | 1500 | 180 | + |
| 698 | Graphite | 40 | – | – | 60 | 7 | 1800 | 40 | + |
| 696 | Graphite | 40 | – | – | 60 ($Ag_2S$) | 8 | 1620 | 30 | + |
| 1/860 | PtRh | – | – | 50 | 50 | 8 | 1500 | 60 | – |
| 1/861 | PtRh | – | 50 | 50 | – | 8.5 | 1790 | 60 | – |
| 2/980 | PtRh | – | – | 50 | 50 | 7 | 1600 | 40 | – |
| 1/862 | PtRh | – | 50 | 50 | – | 7 | 1980 | 50 | – |
| 2/985 | PtRh | – | 50 | – | 50 | 7 | 1500 | 40 | – |
| 2/986 | PtRh | – | – | 50 | 50 | 7 | 1840 | 10 | – |
| 2/987 | PtRh | – | 50 | – | 50 | 7 | 1640 | 15 | – |
| 2/988 | PtRh | – | 50 | 50 | – | 7 | 1600 | 20 | – |
| 2/989 | PtRh | – | 50 | 50 | – | 7 | 1510 | 15 | – |
| 2/990 | PtRh | – | 50 | – | 50 | 7 | 1500 | 30 | – |
| 2/991 | PtRh | – | – | 50 | 50 | 7 | 1500 | 30 | – |

Note: $P$, $T$, and $\tau$ are the pressure, temperature, and run duration, respectively. In all cases, the compositions of silicate phases practically did not change after the experiments; some typical analyses are given in Table 5.

eral experiments were conducted under quasi-isothermal conditions (within ±10°C) using hermetically welded Pt and $Pt_{60}Rh_{40}$ capsules. The experiments were carried out using a high-pressure apparatus of the anvil-with-hole–toroid type. Experimental pressure was calibrated using "point" Bi–Tl pressure sensors installed in the geometrical center of the heater. The juncture of the $Pt_{70}Rh_{30}/Pt_{94}Rh_{06}$ thermocouple was situated in the same place during experiments. Pressure and temperature were controlled with an accuracy of ±0.1 GPa and ±15°C. The apparatus and experimental procedures were described in detail by Litvin (1991).

The experimental samples were analyzed by the methods of scanning electron microscopy and microprobe analysis using CamScan electron microscope equipped with a Link AN 10/85S energy dispersive system at the Department of Petrology, Moscow State University (analyst E.V. Guseva). Phases were analyzed at an accelerating voltage of 15 kV and an electron beam diameter of 3 μm. All analyses were automatically recalculated to 100%.

## EXPERIMENTAL RESULTS

Experimental conditions and results are shown in Table 4. The experiments in the carbonate–carbon system were performed for control purposes and reproduced the results of our previous experiments (Litvin and Zharikov, 2000). Figure 1 shows diamond (*Diam*) crystals *in situ* in the multicomponent carbonatite–carbon melt–solution.[1] After solidification during cooling, this melt transformed into a loose white carbonate matrix with flakelike, featherlike, and, occasionally, spherical aggregates. The carbonate material is a fine-grained mixture of carbonate phases, including $CaCO_3$, $MgCO_3$, $FeCO_3$, $K_2Ca(CO_3)_2$, etc. This means that

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[1] Mineral abbreviations: *Carb*—carbonate, *Cpx*—clinopyroxene, *Diam*—diamond, *Grt*—garnet, and *Sulf*—sulfide.

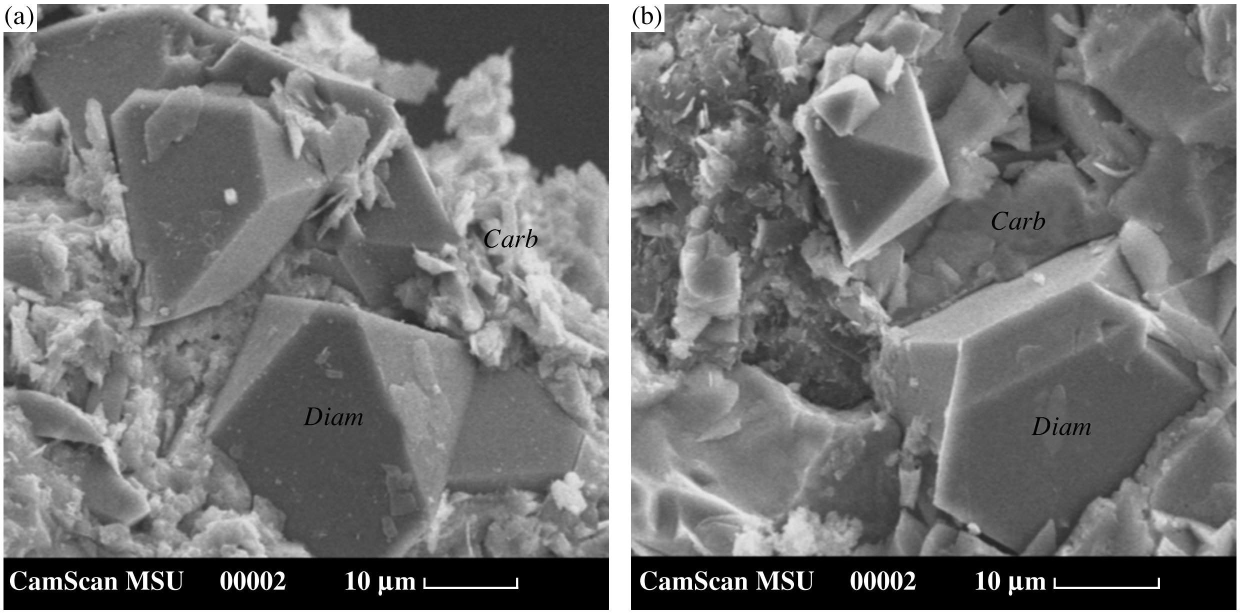


**Fig. 1.** Diamonds in the solidified melts of the carbonatite–carbon system (run 654, duration 30 min). (a) Octahedral crystals and (b) spinel twins.

heating under pressure did not result in carbonate decomposition and formation of corresponding oxides and carbon dioxide. These phases produced a multicomponent carbonate (carbonatite) melt without decomposition upon heating up to or above the eutectic temperature. The congruent melting of carbonates is the first important effect of high pressure. High pressures provided the thermodynamic conditions of diamond stability on the phase diagram of carbon (Kennedy and Kennedy, 1976). A very important consequence of high pressure is an increase of carbon solubility in the carbonatite melt, which provided the possibility of formation of labile solutions oversaturated with respect to diamond. These solutions allowed spontaneous nucleation with a density of above 1000 nuclei per 1 mm$^3$ of melt–solution and diamond growth with a linear rate of at least 0.1 mm/min. Although carbon (graphite) is a strong reducer, both solid and liquid carbonate compounds may coexist with it. The redox potential of the system and the stability of major components of the process are controlled by the buffer mixture formed by reactants, carbon and carbonates. In carbonate–carbon melt–solutions, diamonds crystallized as octahedra with flattened faces, spinel twins, and intergrowths oriented parallel to the octahedral planes. Cubic faces did not develop.

Carbonate–carbon melt–solution forms initially in the eclogite–carbonatite–carbon system upon heating. Similar to the carbonatite–carbon system, rapid spontaneous diamond crystallization occurs at the contact of the melt with graphite. Refractory eclogite minerals do not melt but dissolve in carbonatite melt along the contacts. They loose flat faces and become rounded (Fig. 2). It is important to note that the dissolution of eclogite minerals (in this case, eclogite serves as a host rock) produces carbonate–silicate–carbon melts, although the processes of silicate phase dissolution in carbonatite melts under experimental conditions are kinetically slow compared with diamond formation. This is related to the formation of labile carbon-oversaturated solutions at the contact of graphite and carbonates, whereas the contacts of silicate minerals and carbonatite melts are beyond the zone of diamond formation during carbonate melting. Silicate minerals continue to dissolve during experiments and form carbonate–silicate melts, which penetrate the zones of diamond formation at the contact with graphite. Carbonate–silicate melts are efficient diamond-forming media and can participate in diamond growth under conditions of spontaneous nucleation or on seeds.

The experiments on diamond synthesis in the sulfide–carbon system showed its spontaneous crystallization and growth of new diamond layers from sulfide melt on the seed crystals of diamond synthesized in metallic melts (Fig. 3). The spontaneous crystallization of new sulfide-synthetic diamond produced octahedral crystals with flat faces and occurred with high rates: within 1–2 min from the beginning of nucleation, numerous monocrystals, 10–80 µm in size, and their intergrowths were formed. Similar to carbonate-synthetic diamonds, the layer growth of newly formed sulfide-synthetic diamonds on the (111) octahedral faces of metal-synthetic diamond seeds resulted in formation of smooth faces. Diamond growth on the (100) cubic faces produced rough faces formed by layers of closely packed octahedral micropyramids. The structure of sulfide material in contact with diamonds suggests that it was molten during diamond synthesis and solidified

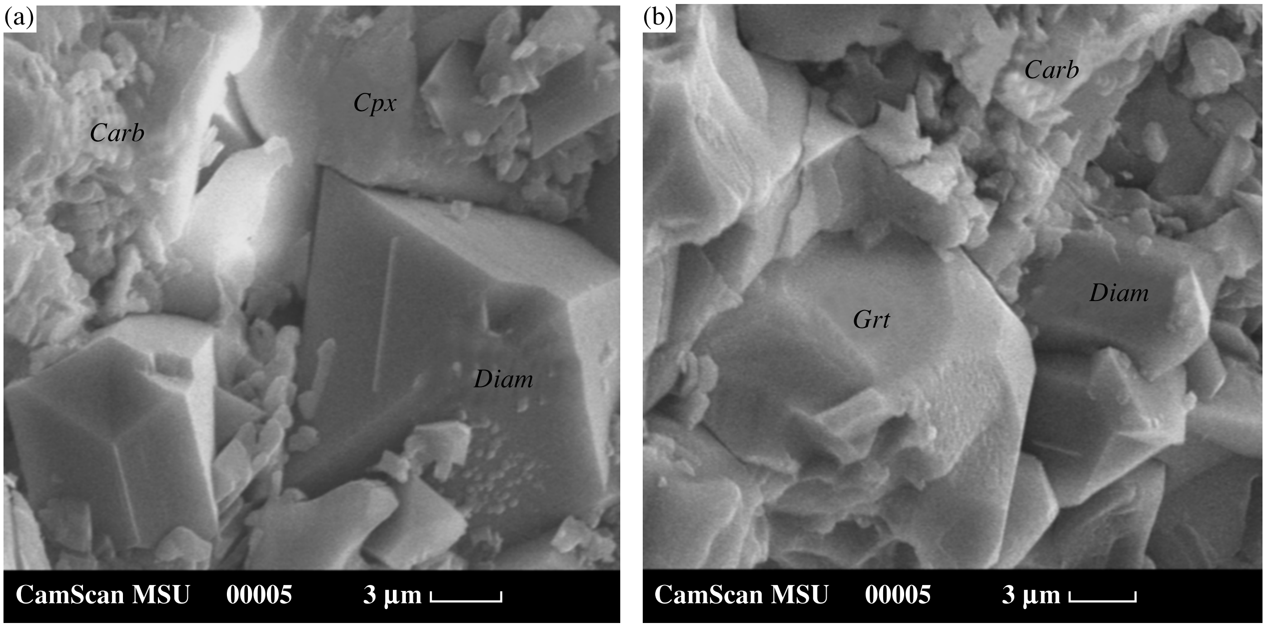
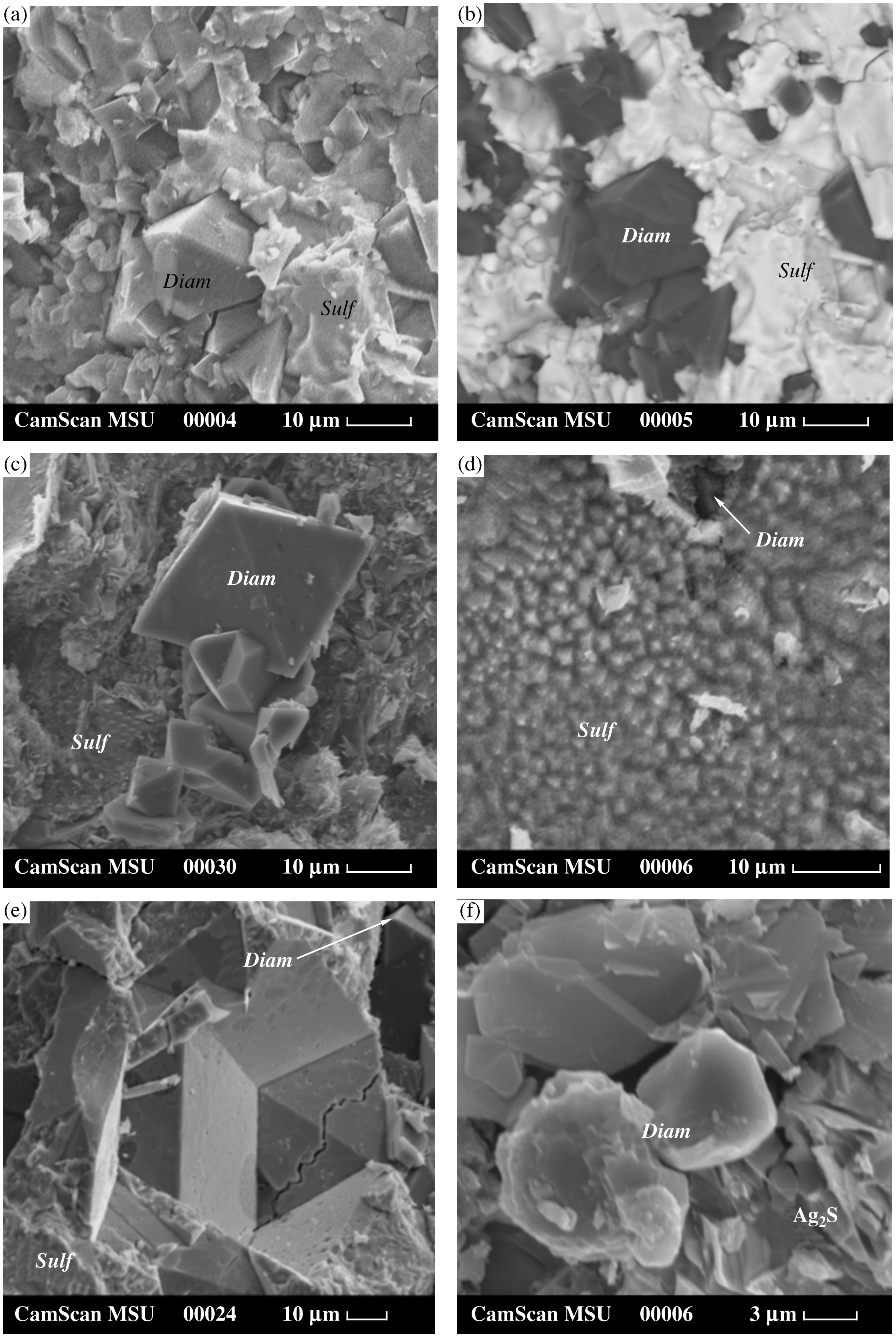


**Fig. 2.** Diamonds formed in the eclogite–carbonatite–carbon system (run 656, duration 60 min).
Silicate minerals are affected by minor surface dissolution in carbonatite melt: (a) diamonds and clinopyroxenes; (b) diamonds and garnets.

upon cooling. Thin sulfide coats were detected on the diamonds. The electron microprobe investigation of the substance in direct contact with diamonds showed that it consisted of sulfide compounds only. Depending on the composition of starting material, this material was represented by chalcopyrite–pyrrhotite or chalcopyrite–pentlandite assemblages. No evidence for the presence of metallic phases or sulfur was found. This suggests that sulfide compounds were stable during melting and subsequent solidification near the contact and during interaction with solid carbon phases. Such interaction results in the formation of sulfide melt–solutions oversaturated with respect to diamond. Carbon mass transfer from dissolved graphite into the sulfide melt occurs by a diffusion mechanism, although convective melt motion and carbon transfer cannot be excluded. These mechanisms remain to be efficient after nucleation and during diamond growth. In addition, the interaction of graphite, which is a strong reducer, with sulfides does not result in the reduction of metals. This suggests that the system was self-buffered by the sulfide–graphite (diamond) pair at a level providing the stability of sulfides. Metals bound in sulfides cannot be considered as independent catalysts of diamond formation in the sulfide–carbon systems, as is sometimes alleged (Chepurov, 1988; Spetsius, 1999). It should be noted that the term catalyst is often used with no sound justification as a substitute for the term solvent, which is more adequate to the physical sense of diamond-forming processes in carbon solutions in metallic melts (Litvin, 1968). The sulfides used in our experiments included Fe and Ni cations, which are often used for diamond synthesis in the melt–solutions of metal–carbon systems. The fact that sulfide–carbon systems are favorable for diamond synthesis was supported by the successful results of special runs on diamond crystallization in the melts of the silver sulfide–carbon system (Fig. 3). Silver is not considered as a "catalyst," because its melt shows a negligible carbon solubility.

Diamond was not previously synthesized in the sulfide–carbon melt–solutions of the systems studied. Preliminary data on the first successful experiments on diamond synthesis in sulfide–carbon systems were reported by Litvin *et al.* (2002). Earlier attempts to synthesize diamond in sulfide–carbon systems failed (Wentorf, 1966; Chepurov, 1988). The experiments by Chepurov (1988) did not yield diamond in the Fe–S–C system because the pressures were not sufficient for spontaneous nucleation (labile oversaturation of carbon solution in iron sulfide melts with respect to diamond was not reached).

The spontaneous crystallization of diamond and its growth on the seed monocrystals of metal-synthetic diamond occurred in the eclogite–sulfide–carbon system (Fig. 4). The compositions of starting eclogite minerals did not change (Table 5). The experiments showed that silicate minerals are practically insoluble in sulfide melts. This limits the possibility of formation of sulfide–silicate melts (there are suggestions on the generation of such melts in nature, e.g., Spetsius, 1999). It is important that the experiments revealed immiscibility between sulfide melts and both silicate and carbonate melts (Fig. 5) (diamond synthesis in the carbonate–sulfide–carbon system showed that sulfide minerals do not melt and dissolve in carbonate–carbon melt). The effects of sulfide–carbonate liquid immiscibility were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clearly observed in experiments on diamond synthesis in the melts of the carbonate–silicate rocks of the Chagatai massif, Uzbekistan, which contained sulfide admixtures (Litvin *et al.*, 2001).

Both diamond-forming media, i.e., carbonatite (carbonate–silicate) and sulfide ones, are present in the eclogite–carbonatite–sulfide–carbon system. Spontaneous crystallization resulted in the formation of octahedral crystals and spinel twins (Fig. 6). Relicts of starting sulfide crystals were found in the run products. This fact implies that the melting temperatures of sulfide compounds were not reached. This allows us to suggest that carbonatite melts were responsible for diamond crystallization, and the processes proceeded via the scenario described above for the eclogite–carbonatite–carbon system.

**Table 5.** Typical analyses of silicate minerals from the experimental products (wt %)

| Component | Garnet | Clinopyroxene |
|---|---|---|
| $SiO_2$ | 38.87 | 54.39 |
| $TiO_2$ | 0.63 | 0.42 |
| $Al_2O_3$ | 21.19 | 5.09 |
| $Cr_2O_3$ | 0.04 | 0.00 |
| FeO | 22.02 | 7.81 |
| MnO | 0.34 | 11.66 |
| MgO | 8.39 | 17.32 |
| CaO | 8.23 | 3.31 |
| $Na_2O$ | 0.29 | 0.00 |
| Total | 100.00 | 100.00 |

## DISCUSSION

The experimental study of diamond crystallization at 6.0–8.5 GPa in the melts of the eclogite–carbonatite–sulfide–carbon system shows that the diamond-forming media in this system are carbonate, carbonate–silicate, and sulfide melts containing dissolved carbon. The available experimental data suggest that (1) silicate melts are not efficient as carbon (graphite and diamond) solvents and, therefore, cannot serve as parental media for the crystallization of natural diamonds; (2) carbon solubility in simple and multicomponent carbonate and carbonate–silicate melts is sufficiently high to provide labile oversaturation of carbonate–carbon melt–solutions, which is a key condition for the spontaneous nucleation and extensive crystallization of diamond; and (3) carbon solubility in simple and multicomponent sulfide melts is sufficiently high to provide labile oversaturation with respect to diamond and its spontaneous nucleation and extensive crystallization in sulfide–carbon melt–solutions.

The results of this and published experimental studies together with the mineralogical and geochemical evidence on primary (cogenetic) silicate, sulfide, carbonate, and fluid-bearing multiphase inclusions in natural diamonds from kimberlites allow us to estimate the major characteristics of the chemical and phase compositions of natural diamond-forming media. The natural parental media are multicomponent carbonate–silicate melts, containing major and trace elements and dissolved carbon in a state of labile oversaturation with respect to diamond (Litvin, 2003). The abundances of both major (carbonates and silicates) and minor (sulfides, oxides, chlorides, phosphates, carbon dioxide, water, *etc.*) components are variable, but a key role in the diamond formation belongs to the carbonate components (mostly in carbonate–silicate–carbon melt–solutions).

Sulfides are relatively common accessory minerals in the Earth's mantle. They can be involved as admixtures into the carbonate–silicate melts that are formed within mantle peridotites. The subsequent evolution of the multicomponent carbonate–silicate melts can be controlled by the processes of fractional crystallization of silicate and carbonate minerals. This process results in an increase in the concentration of sulfide and other components, especially at the latest stages of crystallization. It cannot be excluded that changes in the concentrations of silicate components related to this evolution will result in a gradual transition from peridotite to eclogite mineral assemblages during fractional crystallization (Litvin, 1991). It should be noted that sulfide substances are accumulated in the residual carbonate–silicate melts formed by the fractional crystallization of silicate and carbonate minerals probably as immiscible sulfide melts. Sulfide minerals, if they form, become involved in fractionation processes. The immiscibility of sulfide and carbonate–silicate melts can result in considerable accumulation of sulfide components in the carbonate–silicate media. In such a case, their concentrations may increase to the level of major carbonate and silicate components. Diamonds may trap both sulfide melt and solid sulfide inclusions. The formation of a central sulfide inclusion probably requires the appearance of a diamond seed at the contact between carbonate–silicate and sulfide melts and subsequent overgrow-

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**Fig. 3.** Diamond crystallization in the melts of the sulfide–carbon system (duration 30–180 min): (a), (b) diamonds in quenched paternal sulfide–carbon melts (run 667, duration 70 min), (a) secondary and (b) back-scattered electron images; (c) intergrowth of octahedral crystals and spinel twins of diamond (run 697, duration 180 min); (d) numerous diamond micropyramids overgrowing the cubic face of metal-synthetic diamond in the oversaturated sulfide–carbon melts, the face is covered by a thin sulfide film with separate stripped diamond pyramids (run 667, duration 70 min); (e) complex twinned diamond crystals, whose faces are partly covered by sulfide films (run 698, duration 40 min); (f) diamonds formed from $Ag_2S$–C melt (run 668, duration 24 min).

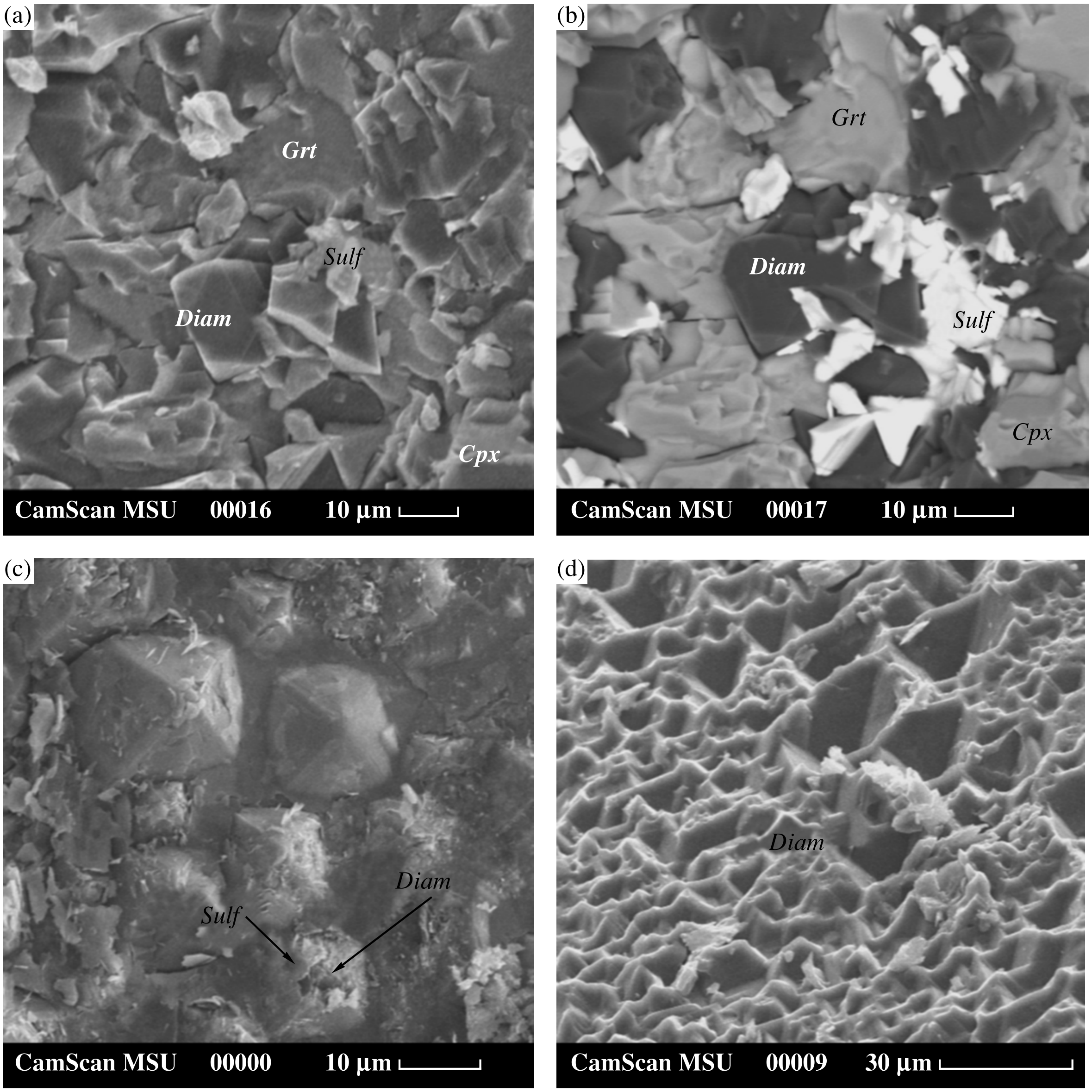

**Fig. 4.** Diamond crystallization in the melts of the eclogite–sulfide–carbon system: (a), (b) Diamonds in situ (run 698, duration 24 min), (a) secondary and (b) back-scattered electron images; the silicate phases are not dissolved at the contacts with the sulfide melts; (c) sulfide films covering a cubic face of the diamond seed with micropyramids (partly stripped) overgrown from the sulfide–carbon melts (run 658, duration 40 min); (d) cellular morphology of the diamond layer overgrowing the cubic face of metal-synthetic diamond in the sulfide–carbon melt (run 668, duration 24 min).

ing of the sulfide particle by diamond. The property of sulfide–carbon liquid to serve as a diamond-forming media can be realized in this process. Thus, the immiscibility of mantle sulfide and carbonatite (carbonate–silicate) melts is of special importance for diamond genesis. Examples of sulfide–carbonate–silicate liquid immiscibility are known in natural environments at relatively low pressures (Kogarko *et al.*, 1995). The relationships of the experimental sulfide and carbonate (carbonate–silicate) melts support their immiscibility. However, studies of model eclogite–carbonate systems under conditions of diamond stability did not show silicate–carbonate immiscibility (Safonov *et al.*, 2002); silicate and carbonate melts are characterized by complete miscibility under such conditions.

The problem of the solubility of silicate mantle minerals in carbonatite and sulfide melts becomes important for the understanding of formation of diamond and silicate minerals captured during its growth. If silicate minerals are also highly soluble in sulfide melts (similar to carbonatite), the minerals of the host rock can be recrystallized in sulfide melts to form the associations of silicate inclusions in diamonds, as it is observed in carbonate–silicate (carbonatite) melts. A physicochemical mechanism for this process is provided by the high solubilities of both dia-

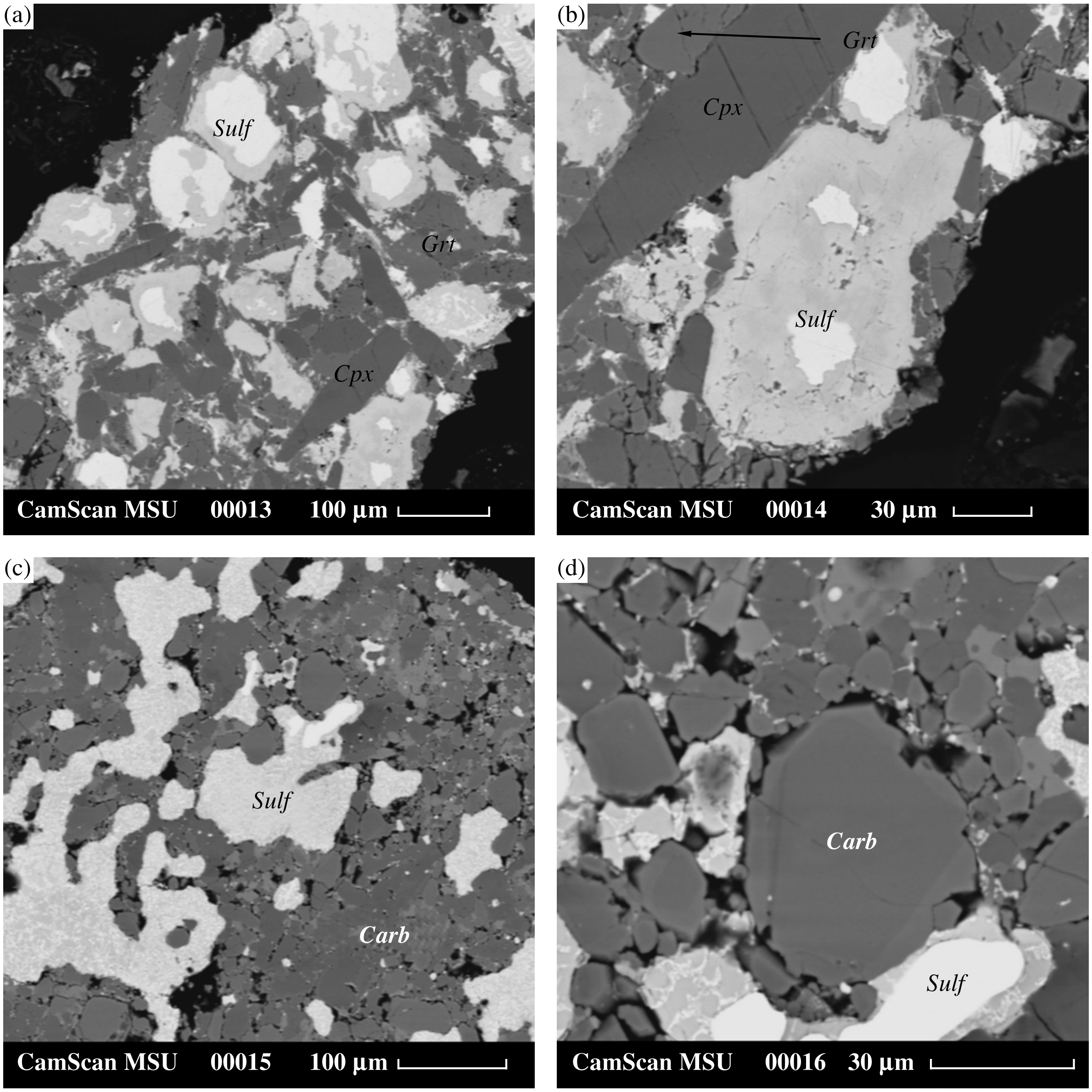

**Fig. 5.** Relationships of sulfide melts with eclogite minerals and carbonatite melts. (a) (b) Solidified sulfide melts in the intergranular pores between silicate minerals; there is no interaction along grain boundaries (run 986, duration 10 min); (c), (d) solidified (quenched) sulfide and carbonatite melts after the complete melting of the sulfide–carbonatite system showing morphological features of complete liquid immiscibility (run 985, duration 40 min).

mond and silicate minerals in carbonatite melt. If the solubility of silicate minerals in sulfide melts is negligible (which is established by experiments), it is evident that the formation of silicate inclusions in natural sulfide-bearing diamonds occurs independently of the sulfide media. This suggests that natural diamonds, both with central and peripheral sulfide inclusions and with octahedral silicate–sulfide intergrowths (Efimova *et al.*, 1983), were also formed in carbonate–silicate parental melts enriched to some extent in immiscible sulfide melts. Further experimental studies of phase relations in silicate and sulfide melts under the conditions of diamond stability are very interesting for the problem of genesis of diamond and cogenetic inclusions. It cannot be excluded that sulfide–carbon melts also contributed to the growth of diamonds with sulfide inclusions. This can be understood if one imagines that a growing diamond is mechanically moved from carbon-oversaturated carbonate–silicate melt into sulfide melt and vice versa.

Experimental, mineralogical, and geochemical data allow us to conclude that the chemical compositions of parental diamond-forming media are controlled by a single multicomponent carbonate–silicate system during the formation of diamondiferous peridotitic and eclogitic assemblages. Nevertheless, the natural media of diamond growth may be characterized by chemical

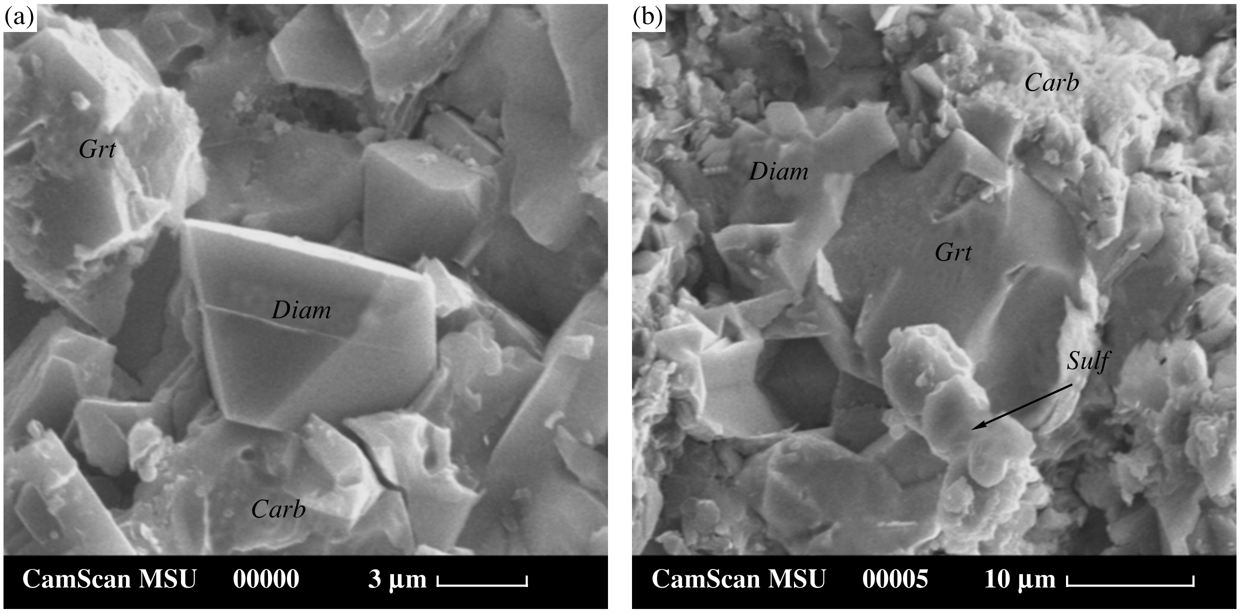

**Fig. 6.** In situ diamonds formed in the melts of the eclogite–carbonatite–sulfide–carbon system. (a), (b) The is no evidence for the melting of silicate and sulfide phases (run 657, duration 30 min).

variability. This variability includes the relative concentrations of both the major carbonate and silicate components and the minor components of the parental media. Among the minor components, sulfides play an important role in the genesis of cogenetic inclusions in diamonds and, sometimes, of diamonds themselves.

## CONCLUSION

Diamond crystallization was experimentally studied in the multicomponent system eclogite–carbonatite–sulfide–carbon at pressures of 6.0–8.5 GPa and high temperatures. The experimental materials contained silicate, carbonate, and sulfide compounds, which are often considered as the parental media of diamond formation. Diamonds were synthesized for the first time in the sulfide–carbon and eclogite–sulfide–carbon systems. The chemical composition of the sulfide media was based on chalcopyrite, pyrrhotite, and pentlandite, which often associate with diamonds and silicate mantle rocks. It was found that the parental media for diamond growth in the systems considered are carbonate, carbonate–silicate, and sulfide melts containing dissolved carbon. It was shown that the natural diamond-forming media are multicomponent carbonate–silicate melts, which contain some major (carbonates and silicates) and minor (sulfides, oxides, chlorides, phosphates, carbon dioxide, water, etc.) components and dissolved carbon in a state of labile oversaturation with respect to diamond. The concentrations of both major and minor components are variable, but the carbonate components play a key role in the genesis of diamond. The immiscibility of sulfide and carbonate–silicate melts can result in a significant accumulation of sulfide components in the parental media, and sulfide species can become major components along with carbonates and silicates. The problems of silicate mantle mineral solubility in carbonatite and sulfide melts were discussed in relation to the cogenetic formation of diamonds and silicate minerals entrapped during diamond growth. During the formation of diamondiferous peridotites and eclogites, the chemical compositions of diamond-forming media are controlled by a single multicomponent carbonate–silicate system.

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## REFERENCES

1. M. Arima, K. Nakayama, M. Akaishi, *et al.*, “Crystallization of Diamond from a Silicate Melt of Kimberlite Composition in High-Pressure and High-Temperature Experiments,” Geology **21**, 978–970 (1993).
2. Yu. M. Borzdov, A.G. Sokol, Yu. N. Pal’yanov, *et al.*, “Study of Diamond Crystallization in Alkalic Silicate, Carbonate and Carbonate–Silicate Melts,” Dokl. Akad. Nauk **366**, 530–533 (1999) [Dokl. Earth Sci. **366**, 578–581 (1999)].

3. G. P. Bulanova, *Natural Diamonds: Genetic Aspects* (Nauka, Novosibirsk, 1993) [in Russian].
4. G. P. Bulanova, "The Formation of Diamond," J. Geochem. Explor. **53**, 1–23 (1995).
5. G. P. Bulanova, A. V. Varshavskii, N. V. Leskova, and L. V. Nikishova, "Central Inclusions as an Indicator of Nucleation Conditions of Natural Diamond," in *Physical Properties and Mineralogy of Natural Diamonds* (Izd. YaF SO AN SSSR, 1979), pp. 29–45 [in Russian].
6. G. P. Bulanova, Z. V. Spetsius, and N. V. Leskova, *Sulfides in Diamonds and Mantle Xenoliths from Yakutian Kimberlite Pipes* (Nauka, Novosibirsk, 1990) [in Russian].
7. G. P. Bulanova, W. L. Griffin, and C. G. Ryan, "Nucleation Environment of Diamonds from Yakutian Kimberlites," Miner. Mag. **62**, 409–419 (1998).
8. V. G. Butvina, Yu. A. Litvin, and Z. V. Spetsius, "Diamond Synthesis in Sulfide Melts in the Eclogite–Sulfide–Carbonate System at 6–8 GPa," Exp. Geosci. **10** (1), 7–9 (2002).
9. A. I. Chepurov, "On the Role of Sulfide Melts in the Process of Natural Diamond Formation," Geol. Geofiz., No. 8, 119–124 (1988).
10. G. A. Desborough and G. K. Czamanske, "Sulfides in Eclogite Nodules from a Kimberlite Pipe, South Africa: With Comments on Violarite Stoichiometry," Am. Mineral. **58**, 195–202 (1973).
11. E. S. Efimova, N. V. Sobolev, and L. N. Pospelova, "Sulfide Inclusions in Diamonds and Peculiarities of Their Paragenesis," Zap. Vses. Mineral. O–va **112**, Issue 3, 300–310 (1983).
12. E. S. Izraeli, J. H. Harris, and O. Navon, "Brine Inclusions in Diamonds: A New Upper Mantle Fluid," Earth Planet. Sci. Lett. **187**, 323–332 (2001).
13. C. S. Kennedy and G. C. Kennedy, "The Equilibrium Boundary between Graphite and Diamond," J. Geophys. Res. **81**, 2467–2470 (1976).
14. L. N. Kogarko, C. M. B. Henderson, and H. Pacheco, "Primary Ca-Rich Carbonatite Magma and Carbonate–Silicate–Sulphide Liquid Immiscibility in the Upper Mantle," Contrib. Mineral. Petrol. **121**, 267–274 (1995).
15. Yu. A. Litvin, "On the Mechanism of Diamond Formation in Metal–Carbon Systems," Izv. Akad. Nauk SSSR, Neorg. Mater. **4** (2), 175–181 (1968).
16. Yu. A. Litvin, *Physicochemical Study of Melting of Deep-Seated Terrestrial Materials* (Nauka, Moscow, 1991) [in Russian].
17. Yu. A. Litvin, "Alkali–Chloride Components in the Processes of Diamond Growth under Mantle Conditions and in High-Pressure Experiment," Dokl. Akad. Nauk **389**, (2003) [Dokl. Earth Sci. **389A**, 388–391 (2003)].
18. Yu. A. Litvin and V. A. Zharikov, "Primary Fluid–Carbonatite Inclusions in Diamond Modeled in Terms of the $K_2O$–$Na_2O$–CaO–MgO–FeO–$CO_2$ System as a Medium for Diamond Formation in Experiments at 7–9 GPa," Dokl. Akad. Nauk **367**, 397–401 (1999) [Dokl. Earth Sci. **367A**, 801–806 (1999)].
19. Yu. A. Litvin 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. Akad. Nauk **372**, 808–811 (2000) [Dokl. Earth Sci. **373**, 867–871 (2000)].
20. Yu. A. Litvin, L. T. Chudinovskikh, and V. A. Zharikov, "Diamond and Graphite Crystallization in Mantle Alkalic Carbonate Melts in Experiments at 7–11 GPa," Dokl. Akad. Nauk **355**, 668–670 (1997) [Dokl. Earth Sci. **355A**, 908–911 (1997)].
21. Yu. A. Litvin, K. A. Aldushin, and V. A. Zharikov, "Diamond Synthesis at 8.5–9.5 GPa in the $K_2Ca(CO_3)_2$–$Na_2Ca(CO_3)_2$ System Corresponding to the Fluid–Carbonatite Inclusions in Diamonds from Kimberlites," Dokl. Akad. Nauk **367**, 529–532 (1999) [Dokl. Earth Sci. **367A**, 813–816 (1999)].
22. Yu. A. Litvin, A. P. Jones, A. D. Beard, *et al.*, "Crystallization of Diamond and Syngenetic Minerals in the Melts of Diamondiferous Carbonatites of the Chagatai Massif, Uzbekistan: Experiment at 7 GPa," Dokl. Akad. Nauk **381**, 528–531 (2001) [Dokl. Earth Sci. **381A** (9), 1066–1069 (2001)].
23. Yu. A. Litvin, V. G. Butvina, A. V. Bobrov, and V. A. Zharikov, "First Synthesis of Diamond in Sulfide–Carbon Systems: Role of Sulfides in Diamond Genesis," Dokl. Akad. Nauk **382**, 106–109 (2002) [Dokl. Earth Sci. **382**, 40–43 (2002)].
24. O. Navon, "Diamond Formation in the Earth's Mantle," in *Proceedings of the VIII International Kimberlite Conference, Cape Town, South Africa, 1999* (Red Roof Design, Cape Town, 1999), pp. 584–604.
25. Yu. N. Pal'yanov, V. S. Shatsky, A. G. Sokol, *et al.*, "Crystallization of Metamorphic Diamonds: An Experimental Modeling," Dokl. Acad. Nauk **380** (5), 671–375 (2001) [Dokl. Earth Sci. **381** (8), 935–938 (2001)].
26. Yu. N. Pal'yanov, A. G. Sokol, Yu. M. Borzdov, *et al.*, "Diamond Formation through Carbonate–Silicate Interaction," Am. Mineral. **87**, 1009–1013 (2002).
27. O. G. Safonov, Yu. A. Matveev, Yu. A. Litvin, and L. L. Perchuk, "Experimental Study of Some Joins in the System $CaMgSi_2O_6$–$(Ca, Mg)_3Al_2Si_3O_{12}$–$KAlSi_2O_6$–$K_2(Ca, Mg)(CO_3)_2$ at 5–7 GPa in Relation to the Genesis of Garnet–Clinopyroxene–Carbonate Rocks of the Kokchetav Complex, Northern Kazakhstan," Petrologiya **10**, 589–610 (2002) [Petrology **10**, 519–539 (2002)].
28. M. Schrauder and O. Navon, "Hydrous and Carbonatitic Mantle Fluids in Fibrous Diamonds from Jwaneng, Botswana," Geochim. Cosmochim. Acta. **58**, 761–771 (1994).
29. N. V. Sobolev, *The Deep-Seated Inclusions in Kimberlites and the Problem of the Composition of the Upper Mantle* (Nauka, Novosibirsk, 1974; American Geophysical Union, Washington, 1977).
30. N. V. Sobolev and V. A. Vakhrushev, "Sulfides in Pyrope Peridotites from Yakutian Kimberlites," Zap. Vses. Mineral. O–va **96**, Issue 4, 450–453 (1967).
31. A. G. Sokol, Yu. N. Pal'yanov, Yu. M. Borzdov, *et al.*, "Diamond Crystallization in $K_2CO_3$ Melt," Dokl. Akad. Nauk **361**, 388–391 (1998) [Dokl. Earth Sci. **361A**, 821–824 (1998)].
32. Z. V. Spetsius, "Two Generations of Diamonds in the Eclogite Xenoliths," in *Proceedings of the VIII International Kimberlite Conference, Cape Town, South Africa, 1999* (Red Roof Design, Cape Town, 1999), pp. 823–828.
33. R. H. Wentorf, "Solutions of Carbon at High Pressure," Ber. Bunsengesells. **70**, 975–982 (1966).