

DIAMOND SYNTHESIS IN SULFIDE MEDIUM AT 6-8 GPa: APPLICATION TO NATURAL DATA

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INTRODUCTION

Sulfide minerals are quite abundant in the diamond assemblage and they are met as inclusions in diamond crystals – pyrrhotite (Po), pentlandite (Pn), monosulfide solid solution (Mss) – and mantle xenoliths of peridotitic (Pn, Po) and eclogitic (Po, pyrite (Py), Cu-sulfides) types. The diversity in sulfide composition of mantle rocks results from their long evolution and such processes as mantle metasomatism, that leads to the enrichment of initial sulfides in Cu, K, Cl. Because of this, initial sulfide mantle mineralization is perfectly presented only by inclusions in diamonds (Fig. 1).

It was noticed that sulfides are contained in almost a half of the inclusion-bearing diamonds studied (Efimova et al., 1983). Findings of sulfides in the centers of diamond monocrystal nucleation (Bulanova et al., 1979) led to the suggestion that the sulfide melt served as a favorable site for

the diamond nucleation and growth and that the diamond crystallized in the mantle from slightly oversaturated carbon solution in the sulfide-silicate melt (fluid). Findings of diamond partly covered by Fe-Ni-sulfide layers or the pyrrhotite-pentlandite-chalcocopyrite assemblage is a further proof of this version. It should be noted that the diamond in iron meteorites is related to droplike sulfide grains (troilite, and others), which commonly include graphite as well.

Chalcocopyrite, pentlandite, pyrrhotite, monosulfide solid solutions (close in composition to $\text{CuFe}_{10.1}\text{Ni}_{2.5}\text{S}_{14.2}$), pyrite, violarite (Ni_2FeS_4), heazlewoodite, bornite (Cu_5FeS_4), and djerfisherite, which is a mineral with a double anion group ($\text{K}_6(\text{Cu,Fe,Ni})_{23}\text{S}_{26}\text{Cl}$), were detected in association with diamond and mantle-derived peridotites and eclogites (including diamond-bearing varieties).

In experiments at 3.0-5.5 GPa with FeS melt and graphite as

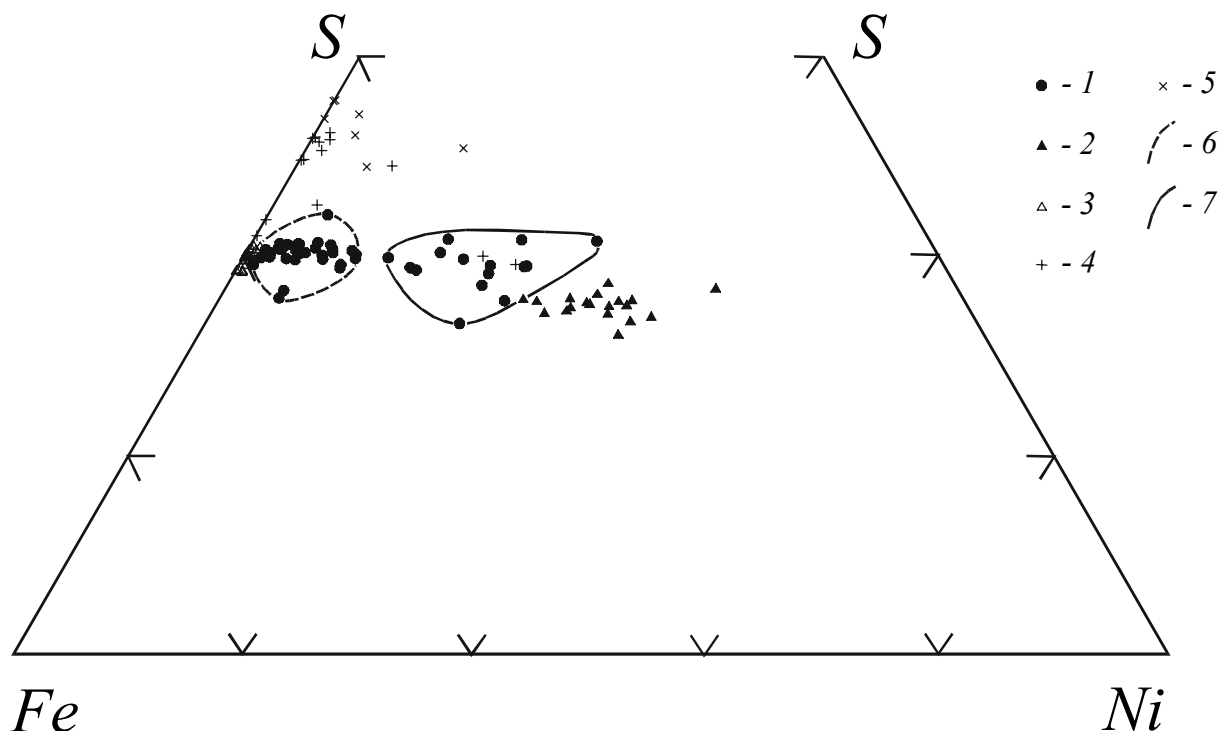


Fig. 1. Compositions of sulfides from some kimberlite pipes of Yakutia and Urals, modified after V.Garanin et al. (1988). 1 - monosulfide solid solution (Ni, Fe); 2 - pentlandite; 3 - pyrrhotite; 4 - chalcocopyrite and other Cu sulfides; 6, 7 - fields of Mss composition for eclogite (6) and peridotite (7) parageneses.

a carbon source, diamond could not be synthesized under conditions of its thermodynamic stability (Chepurov, 1988). In the more complicated metal-sulfide-carbon system (Fe-FeS-C), it crystallized only in the compositional field enriched in Fe (65-100 wt %). This was the well-known "metallurgical" metal-carbon synthesis in an iron melt containing a sulfur admixture. As was stated by A. Chepurov (1988), the diamond nucleation slows down up to the point of its complete cessation with an increase in the S content in a metallic melt. However, despite such a pessimistic conclusion, the sulfide model of diamond origin is still discussed, and its experimental verification remains a topical issue.

EXPERIMENTAL TECHNIQUES

Our work was aimed at a new experimental testing of the possibility to synthesize diamond in the sulfide-carbon system (Litvin et al., 2002). The choice of sulfide medium for the experiment took into account the key role of the Cu-Ni-Fe-S system in the mineralogy of sulfides associated with diamond and the occurrence of the Cu-Ni-Fe-monosulfide solid solution as inclusions in natural diamond (Efimova et al., 1983) and eclogite xenoliths. At the same time, we checked the simple sulfide-carbon systems with copper sulfide (covellite) and silver sulfide (argentite) in order to obtain additional evidence that namely sulfides rather than free metals, such as Fe and Ni, are responsible for diamond synthesis. Melts of these and other transitional metals, which are sometimes mistakenly considered to be catalysts, play a key role as carbon solvents in the diamond synthesis in metal-carbon systems. The suggestion of the catalyzing ability of such metals is groundless both in the case of natural diamond formation and in synthesis with the participation of sulfides.

The starting materials were prepared from powders of natural chalcopyrite with negligible Ag and Au impurities; pentlandite with about 2 wt % Co; and pyrrhotite with insignificant amounts of Cu, Ni, Co, Mn, and Zn. Chalcopyrite-pyrrhotite (1) and chalcopyrite-pentlandite (2) mixtures in a proportion of 1:1 by weight were prepared. Their compositions as follows (wt %): (1) Cu 17, Fe 35, S 48; (2) Cu 17, Fe 25, Ni 10, S 48. In addition, covellite (CuS) and argentite (Ag₂S) powders were used. Sulfide powders were mixed with especially pure graphite grains, 0.5 mm in size, in a proportion of 3:2 by weight. The equipment included a high-pressure anvil with-hole apparatus, the container made of lithographic limestone, a graphite ampule-heater (length 7.2 mm, diameter 4 mm) with 0.5 mm thick-walls, 1-mm-thick graphite corks on both ends, and a testing diamond seed (a monocrystal, 0.5-0.6 mm in size, grown from a Ni-Mn-C melt-solution). The pressure and temperature were measured with an accuracy of ± 0.1 GP; and $\pm 15^\circ\text{C}$, respectively. Phase compositions were determined by a scanning electron micro-

scope and CamScan microprobe at the Department of Petrology, Moscow State University.

RESULTS AND DISCUSSION

In high-pressure (6-8 GPa) runs, an octahedral diamond crystallized from the sulfide-carbon melt within the first 1-2 min from the onset of spontaneous nucleation. Newly formed "sulfide" diamond layers were also observed on the seed. The original position of diamonds formed in sulfide systems at 7.0-7.5 GPa is shown in Figs. 2-5. As can be deduced from textural patterns, the sulfide phases occurred as a homogeneous melt during diamond synthesis and crystallized at the final stage of the run due to the temperature fall under high pressure. Depending on the starting compositions, the sulfide phases were composed of chalcopyrite-pyrrhotite or chalcopyrite-pentlandite mixtures, covellite, or argentite. No indications of sulfide breakdown with an exsolution of free metal phases, which could form the metal-carbon melt-solution and thus serve as carbon solvents during the recrystallization of graphite and diamond, were detected by the microprobe. Structural patterns and analytical results show that the diamond was synthesized from the sulfide melt. Under experimental conditions, the graphite most likely was dissolved in a sulfide melt; as a result, a sulfide melt-solution with a high carbon content was formed. In this case, the oversaturation with carbon relative to diamond was provided both by the different solubilities of metastable graphite and stable diamond in sulfide melt and by temperature gradients in the reaction zone. The degree of oversaturation with carbon dissolved in the sulfide melt was sufficient for spontaneous diamond nucleation (according to the existing terminology, such a state of oversaturated solution is defined as a labile one).

In this work, we report the first results of diamond synthesis in sulfide-carbon systems under a high pressure. The term "synthesis" denotes the spontaneous diamond nucleation and its mass crystallization from an oversaturated carbon solution in sulfide melt. These results will undoubtedly be involved into the continuing discussion of mineralogists on possible modes of natural diamond synthesis. Meanwhile, a carbonatite model of diamond genesis was recently proved by geological and experimental data. The media that hosted the natural diamonds were captured as primary fluid inclusions. The chemical and phase compositions of the inclusions were determined with a microprobe. Under PT conditions of diamond stability, they represent carbonate-silicate (carbonatite) melts. According to the results of high-pressure experiments, such melts are effective diamond-producing media. Thus, the carbonatite model of diamond genesis imparts a specific character to the discussion. The participation of both carbonatite and sulfide melts in diamond formation is supposed.

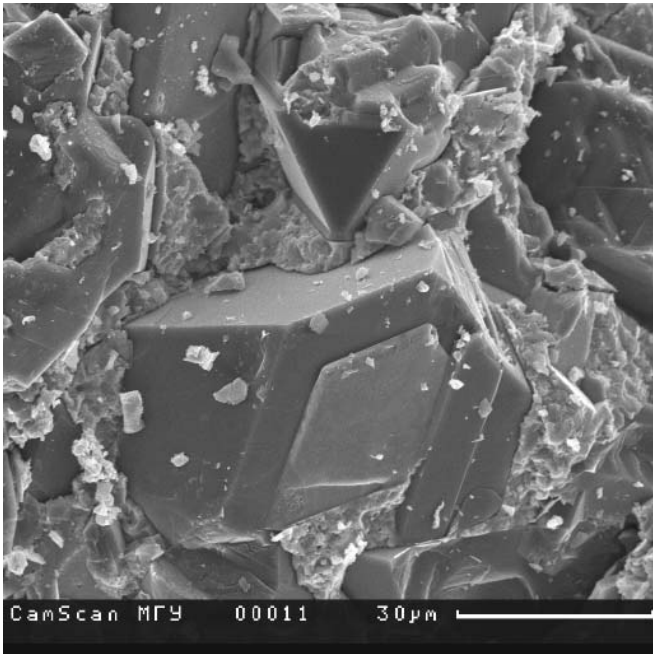


Fig. 1. Octahedral diamond crystals formed in situ as a result of spontaneous crystallization. The light gray irregular mass between diamond crystals and light particles on their faces are sulfides (Sample 693, pressure 7.2 GPa, temperature 1450°C, hold period 80 min).

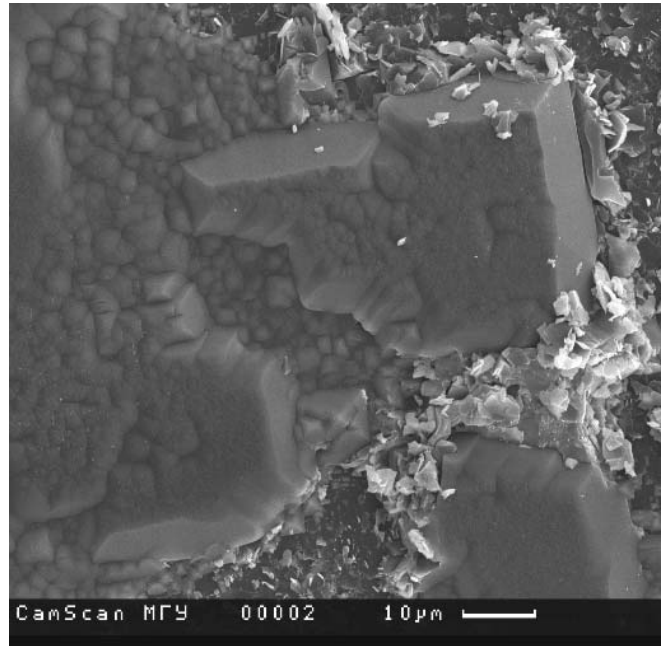


Fig. 3. The seed monocystal face (100) overgrown by the diamond crystallized from the sulfide melt. The entire seed face is covered by overgrowing crystals. Inclined smooth (111) faces and rough (100) faces (layers of closely spaced tiny octahedral pyramids) are visible on large fragments. Light gray phases are sulfides (Sample 694, pressure 7.0 GPa, temperature 1450°C, holding period 150 min).

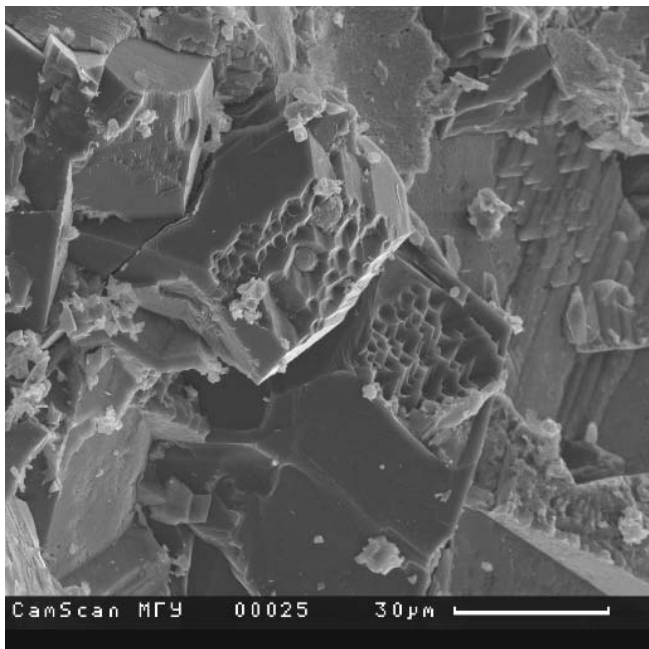


Fig. 2. Spontaneously grown octahedral diamond crystals with smooth (111) faces and rough (100) faces (closely intergrown tiny octahedral pyramids). Light gray phases are sulfides (Sample 698, pressure 7.0 GPa, temperature 1500°C, hold period 40 min).

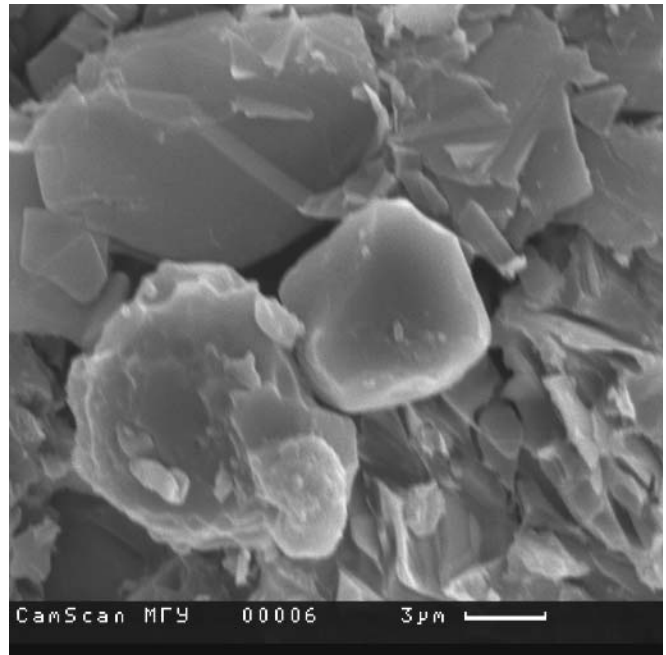


Fig. 4. Diamond crystals spontaneously crystallized from the argentite melt; sulfide phases are also seen (Sample 696, pressure 7.5 GPa, temperature 1450°C, holding period 30 min).

Thus, the experimental results support the efficiency of both carbonatite and sulfide media for diamond formation. As is indicated by primary inclusions in diamond, both media exist in nature. However, the scope of carbonatite- and sulfide-related diamond formation remains ambiguous. The majority of natural diamonds presumably crystallized from mantle carbonatite melts with a high content of dissolved silicates. A modified version of such a model assumes diamond formation in carbonatite melts that contain immiscible sulfide liquid as inclusions. The pure sulfide version was proved by experiments described in this work and thus cannot be ruled out in the discussion on physicochemical mechanisms of natural diamond formation. This version may likely be applied to diamonds in meteorites. As concerns the terrestrial conditions, a new mineralogical problem arises: In what specific medium (carbonatite or sulfide) does natural diamond crystallize? It is evident that we should elaborate a system of typomorphic features showing the relationship between medium and specific diamond samples. It may be inferred that in some cases the diamond crystal could sequentially grow from carbonatite and sulfide melts.

CONCLUSIONS

Results of our experimental study may briefly be summarized as follows:

(1) For the first time, diamond has been synthesized in the sulfide-carbon system at a pressure of 6-8 GPa. Sulfide-carbon melts (solutions) used in the synthesis were obtained during the melting of mixtures of graphite with chalcopyrite, pyrrhotite and pentlandite that are most frequently associated with diamonds and mantle silicate rocks.

(2) The ability of sulfide melts to crystallize diamond was also demonstrated for simple sulfides like covellite (CuS) and argentite (Ag₂S) devoid of such transitional metals as Fe and Ni, which are often regarded as catalysts for diamond synthesis.

(3) Experimental data demonstrated the feasibility of diamond crystallization from natural sulfide media. The sulfide model should be taken into account as a possible version of diamond formation along with a carbonatite model. The study of typomorphic features of natural diamonds is required for the identification of chemical environment of their growth medium.

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