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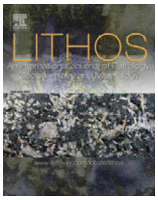

Synthesis of diamonds with mineral, fluid and melt inclusions

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ABSTRACT

Experiments on the synthesis of inclusions-bearing diamond were performed in the SiO_2–((Mg,Ca)CO_3–(Fe,Ni)S system at 6.3 GPa and 1650–1750 °C, using a multi-anvil high pressure apparatus of the "split-sphere" type. Diamond synthesis was realized in the "sandwich-type" experiments, where the carbonate–oxide mixture acted as a source of both CO_2-dominated fluid and carbonate–silicate melt, and Fe,Ni-sulfide played a role of reducing agent. As a result of redox reactions in the carbonate–oxide–sulfide system, diamond was formed in association with graphite and Mg,Fe-silicates, coexisting with CO_2-rich fluid, carbonate–silicate and sulfide melts. The synthesized diamonds are predominantly colorless or light-yellow monocrystals with octahedral habit (20–200 μm), and polycrystalline aggregates (300–400 μm). Photoluminescence spectroscopy revealed defects related to nickel impurity (S3 optical centers), which are characteristic of many diamonds in nature. The density of diamond crystallization centers over the entire reaction volume was ~3×10^2–10^3 cm^{-3}. The overwhelming majority of diamonds synthesized were inclusions-bearing. According to Raman spectroscopy data, diamond trapped a wide variety of inclusions (both mono- and polyphase), including orthopyroxene, olivine, carbonate–silicate melt, sulfide melt, CO_2-fluid, graphite, and diamond. The Raman spectral pattern of carbonate–silicate melt inclusions have bands characteristic of magnesite and orthopyroxene ($\pm SiO_2$). The spectra of sulfide melt displayed marcasite and pyrrhotite peaks. We found that compositions of sulfide, silicate and carbonate phases are in good agreement not only with diamond crystallization media in experiments, but with data on natural diamond inclusions of peridotitic and eclogitic parageneses. The proposed methodological approach of diamond synthesis can be used for experimental simulation of the formation of several types of mineral, fluid and melt inclusions, observed in natural diamonds.

1. Introduction

Mineral, fluid and melt inclusions in natural diamonds are the most reliable and valuable sources of information shedding light on the chemical and physical features of mantle environments in which diamonds grow (Bulanova, 1995; Jablon and Navon, 2016; Shirey et al., 2013; Smith et al., 2015; Sobolev, 1977; Stachel and Harris, 2009; Stachel and Luth, 2015). Being once trapped, inclusions are protected from further chemical modification and can persist after decompression shock during transport to the surface. Among the mineral inclusions in diamond, the most widespread are silicates, sulfides and oxides (Gurney, 1989; Harris, 1992; Meyer, 1987; Shirey et al., 2013; Sobolev, 1977; Sobolev et al., 1997; Stachel and Harris, 2008); findings of carbonates are relatively rare (Brenker et al., 2007; Izraeli et al., 2001; Kaminsky et al., 2009; Stachel et al., 1998; Wang et al., 1996). Fluid inclusions, lending insights into the behavior of diamond-forming fluids in the lithospheric mantle, are of exceptional interest (Izraeli et al., 2001; Klein-BenDavid et al., 2004; Navon et al., 1988; Schrauder and Navon, 1993, 1994; Skuzovatov et al., 2016-in this issue; Smith et al., 2014, 2015). Findings of fluid inclusions in monocrystalline diamonds are rather scarce, most of them are characterized by C–O–H ± N ± S compositions, such as CO_2 and H_2O (Jablon and Navon, 2016; Nimis et al., 2016; Smith et al., 2014, 2015). More common micro-inclusions trapped in fibrous diamonds contain carbonate-bearing high-density fluids (HDFs) (Izraeli et al., 2001; Klein-BenDavid et al., 2009; Navon et al., 1988; Schrauder and Navon, 1994; Shirey et al., 2013; Zedgenizov et al., 2009).

The wide range of mineral, fluid and melt inclusions observed in natural diamonds may reflect the overall heterogeneity of diamond-forming media, and is evidence of complex processes involving diamond nucleation, growth, dissolution and recrystallization. Current studies are focused mostly at revealing potential natural carbon sources, mechanisms of diamond formation and particular roles of different components in diamond-forming processes (e.g. Borzdov et al., 1999; Khokhryakov et al., 2016; Palyanov et al., 2013; Palyanov et al., 2016-in this issue; Sokol et al., 2004; Stachel and Luth, 2015; Stagno et al., 2015). By reason of the obvious connection of the compositions of the diamond mantle environment and inclusions in diamonds, there are a number of geothermobarometry studies, concerned with modeling the conditions under which the inclusions are trapped

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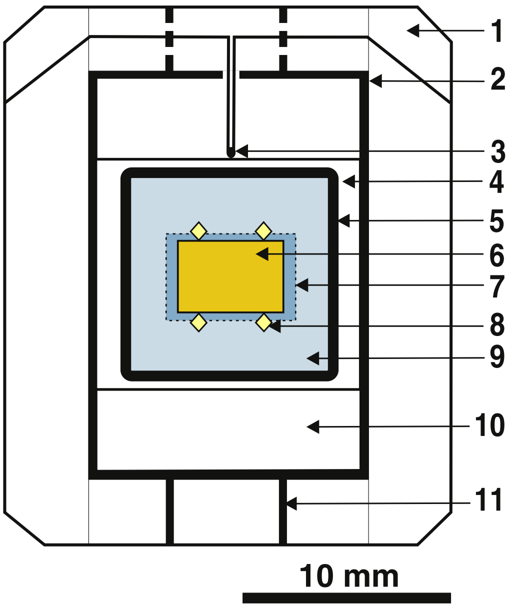

Fig. 1. The high pressure cell scheme and initial ampoule assembly: 1 — ZrO_2 container; 2 — cylindrical graphite heater; 3 — $PtRh_6/PtRh_{30}$ thermocouple; 4 — MgO sleeve; 5 — graphite capsule; 6 — sulfide ($Fe_{0.7}Ni_{0.3}S$) pellet; 7 — diamond synthesis area; 8 — diamond seed crystal; 9 — carbonate-oxide ampoule, consisting of $MgCO_3$ + $CaMg(CO_3)_2$ + SiO_2 mixture; 10 — ZrO_2; 11 — Mo leads.

(Angel et al., 2015a, 2015b; Milani et al., 2015), but experimental investigations in this direction are scarce. The first study along this line is the experimental attempt of the growth of fibrous, cloudy and polycrystalline diamonds with multi-phase fluid inclusions (Bureau et al., 2012). Various types of graphite inclusions in diamonds synthesized in chloride and carbonate systems were described in Khokhryakov and Nechaev (2015) and Khokhryakov et al. (2009). Previously, in the course of experimental investigation of diamond formation in a $MgCO_3$–SiO_2–Al_2O_3–FeS system (Palyanov et al., 2007), inclusions of coesite, silicates and C–O–H fluid in the overgrown layer of diamond seeds were obtained, but it was an accidental fact, not the basic research line. For the present study we have adopted the methodological approach of Palyanov et al. (2007), developed for diamond formation via CO_2 reduction by sulfide in the carbonate–oxide–sulfide system, to synthesize inclusions-bearing diamonds. We propose a new technique for the synthesis of monocrystalline diamonds bearing inclusions of silicates, sulfides, CO_2-rich fluid and carbonate-bearing melts.

2. Methods

2.1. High-pressure experiments

Experiments were carried out using a multi-anvil high-pressure apparatus of a "split-sphere" type (Palyanov et al., 2010). A high-pressure cell in the form of a tetragonal prism, 21.1 × 21.1 × 25.4 mm in size, was used (Fig. 1). The elongated geometry of the cell made it possible to use a graphite heater with a diameter of 12 mm and a length of 18.8 mm. Pressure was calibrated by recording the change in the resistance of Bi at 2.55 GPa and of PbSe at 4.0 and 6.8 GPa at room temperature, and by bracketing the graphite–diamond equilibrium (Kennedy and Kennedy, 1976) at high temperatures. Details on the pressure and temperature calibration have been presented elsewhere (Pal'yanov et al., 2002; Sokol et al., 2015). The temperature was measured in each experiment using a $PtRh_{30}/PtRh_6$ thermocouple.

Experiments on the synthesis of inclusions-bearing diamond were performed in the SiO_2–$(Mg,Ca)CO_3$–$(Fe,Ni)S$ system at a pressure of 6.3 GPa, in the temperature range of 1650–1750 °C. The run duration spanned the range from 2 to 24 h, thereby enabling the examination of different stages of the diamond formation and the corresponding specific features of the inclusions therein. To enable the synthesis of inclusions-bearing diamond we have adopted the methodical approach and the corresponding scheme of the reaction ampoule assembly (the so called "sandwich-type assembly"), developed by Palyanov et al. (2007). The efficiency of this approach for the diamond formation via carbonate–oxide–sulfide, carbonate–iron and carbonate–carbide interactions was demonstrated by Palyanov et al. (2007, 2013). An initial scheme of a reaction ampoule assembly is shown in Fig. 1. According to the scheme, ampoule volume was divided into peripheral (carbonate-oxide) and central (sulfide) parts. As it was previously shown by Palyanov et al. (2007), under P–T parameters of the experiments the carbonate–oxide mixture from the peripheral part of the ampoule undergoes decarbonation and partial melting processes, releasing CO_2-rich fluid and carbonate–silicate melt, both acting as a carbon source and crystallization media for diamond formation. Redox interaction of the released fluid and melt with sulfide results in diamond synthesis at the contact of the peripheral and central parts of the ampoule. To create conditions for the synthesis of inclusions-bearing diamond via carbonate–oxide–sulfide interaction, a carbonate–oxide container, made from a mixture of finely powdered and pressed $MgCO_3$, $CaMg(CO_3)_2$, and SiO_2, was placed in the graphite capsule (9.5 mm inner diameter). A pellet of the pressed sulfide (5 mm diameter) was mounted in the center of the carbonate-oxide container. Four cubo-octahedral synthetic diamond seed crystals approximately 0.5 mm in size were placed in the carbonate–oxide ampoule, as shown in Fig. 1. Graphite capsules were used because of their suitability for HPHT-experiments in sulfide-, sulfur- and iron-bearing systems (Bataleva et al., 2015, 2016a, 2016b; Dasgupta et al., 2009; Palyanov et al., 2007). Moreover, graphite capsules can act as an outer buffer, setting the upper limit of fO_2 values in the sample close to CCO buffer equilibrium during the experiments (Palyanov et al., 2007). Using capsules of relatively large volume and adopting a "sandwich-type assembly" permitted the creation of an area of direct contact of sulfide with the fluid and melt, i.e. a potential diamond formation area of ~1 cm^2 (Fig. 1, "diamond synthesis area").

2.2. Starting materials

Starting materials consisted of natural specimens of magnesite [$MgCO_3$] and dolomite [$CaMg(CO_3)_2$] (massive carbonate layers, Satka deposits, Chelyabinsk Region, Russia) with impurity contents <0.5 wt.%, and powders of chemically pure SiO_2 and $Fe_{0.7}Ni_{0.3}S$. Proportions of starting materials are shown in Table 1. The initial mixture of the carbonates had a bulk composition of $Mg_{0.9}Ca_{0.1}CO_3$. As it is shown in Table 1, two series of experiments of "carbonate-poor" and "carbonate-rich" bulk system compositions were carried out, with the (Mg + Ca)/Si molar ratio of 1 and 2, respectively.

As was mentioned above, the carbonate–oxide mixture that undergoes decarbonation and partial melting under experimental P–T

Table 1
Bulk composition of the carbonate-oxide-sulfide systems.

Series	Run N	Mass, mg				Mass concentrations, wt.%							
		$MgCO_3$	$CaMg(CO_3)_2$	SiO_2	$Fe_{0.7}Ni_{0.3}S$	Si	Ca	Mg	Fe	Ni	S	C	O
Carbonate-poor	1195, 1199	408	102	340	300	14	2	11	12	5	9	6	41
Carbonate-rich	1202, 1201	584	146	243	300	9	2	15	10	5	9	8	42