Diamond formation through carbonate-silicate interaction

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ABSTRACT

Crystallization of diamond and graphite from the carbon component of magnesite, upon its decarbonation in reactions with coesite and enstatite at pressures of 6–7 GPa and temperatures of 1350–1800 °C has been accomplished experimentally. In a series of experiments, diamond was obtained in association with enstatite, coesite, and magnesite, as well as with forsterite, enstatite, and magnesite. Octahedral diamond crystals with sizes up to 450 µm were studied by FTIR spectroscopy and were found to contain nitrogen and hydrogen, which are known as the most abundant impurities in natural type Ia diamonds. We found that growth of diamond on the cubic faces of seed crystals proceeds with formation of a cellular surface structure, which is similar to natural fibrous diamonds. The isotopic composition of synthesized diamonds ($\delta^{13}C = -1.27‰$) was determined to be close to that of the initial magnesite ($\delta^{13}C = -0.2‰$).

INTRODUCTION

The source of the carbon from which diamond forms has been the subject of active debate for several years (Sobolev and Sobolev 1980; Galimov 1991; Boyd et al. 1994; Navon 1999; Cartigny et al. 2001a, 2001b). We know that the mineralogy and petrography of the upper mantle is to a considerable extent defined by the interactions between carbonates, silicates, and C-O-H fluids (Brey et al. 1983; Eggler et al. 1979; Koziol and Newton 1998; Luth 1999; Wyllie and Ryabchikov 2000). Furthermore, in a number of reports (Navon et al. 1988; Galimov 1991; Luth 1993; Cartigny et al. 2001a; Wang and Gasparik 2001) it has been suggested that natural diamonds may form from the carbon of carbonate minerals. However, the synthesis of diamond as a result of reactions between carbonates and silicates has not been accomplished experimentally. Among the hosts for carbon in the mantle, carbonate phases are of particular importance. These phases are stable under mantle *P-T* conditions (Eggler et al. 1979; Brey et al. 1983; Katsura and Ito 1990) within a relatively wide range of redox values (Luth 1999). Inclusions of carbonates in diamond (Bulanova and Pavlova 1987; Schrauder and Navon 1994; Wang et al. 1996; De Corte et al. 1998) and the discovery of diamonds in carbonate-rich ultrahigh-pressure metamorphic rocks (Sobolev and Shatsky 1990) containing magnesite (Shatsky et al. 1995) indicate participation of the carbonate phases in the diamond formation processes. Moreover, experimental data show that carbonate-fluid melts are capable of providing transport of carbon and diamond nucleation under the *P-T* conditions of natural diamond formation (Pal'yanov et al. 1999a). Lately, the relation between diamond-formation processes and mantle metasomatism, with carbonate-fluid melts as active agents (Green and Wallace 1988), has been extensively stud-

ied (Schrauder and Navon 1994; Taylor et al. 1998; Wyllie and Ryabchikov 2000; Wang and Gasparik 2001). Yet, can carbonates be the source of carbon in diamonds? Thermodynamical calculations (Luth 1993; Ogasawara et al. 1997) and some models of the mantle and metamorphic diamond formation (Navon 1999; Cartigny et al. 2001a, 2001b; Wang and Gasparik 2001) assume such a possibility. However, in previous experiments on diamond synthesis in the carbonate-carbon systems, graphite was always used as the source of carbon (Akaishi et al. 1990; Taniguchi et al. 1996; Litvin 1998; Pal'yanov et al. 1998). Furthermore, isotopic measurements showed that the diamonds were formed from the carbon of the graphite, rather than from carbonate phases (Taniguchi et al. 1996). Recently it has been reported that decomposition of rhodochrosite ($MnCO_3$), at 6–8 GPa and temperatures greater than 2000 °C, results in formation of graphite which is replaced by diamond upon increasing the pressure to 12 GPa and above (Liu et al. 2001). In fact these *P-T* parameters correspond to the direct graphite-to-diamond transition.

EXPERIMENTAL METHODS

This paper describes an experimental study of diamond and graphite crystallization upon reaction of magnesite with coesite and enstatite. The experiments were conducted using a multianvil high-pressure apparatus of the split-sphere design. A high pressure cell developed for the growth of diamond single crystals was used in the study. This type cell has the shape of a tetragonal prism $19 \times 19 \times 22$ mm, and utilizes a graphite heater 9 mm in diameter and 15.8 mm in height. Pressure was calibrated at room temperature by the change in resistance of Bi at 2.55 GPa and of PbSe at 4.0 and 6.8 GPa, and at high temperatures by the graphite-diamond equilibrium. Temperature was measured in each experiment with a $PtRh_6/PtRh_{30}$ thermocouple. The thermocouple was calibrated at 7 GPa by the melting of Ni, and at 5.7 GPa by the melting of Ag, Au, and Al. We esti-

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mated the accuracy of the pressure and temperature measurements to be at the level of ±0.1 GPa and ±20 °C, respectively at 6.0 GPa and 1350–1450 °C. For experiments at 7 GPa and 1500–1800 °C the accuracy was estimated to be ±0.2 GPa and ±40 °C (Pal'yanov et al. 1998, 2002).

Naturally occurring $MgCO_3$ (Chelyabinsk Region, Russia) with an impurity content of 0.5 wt% and SiO_2 with a purity not less than 99.9% were used as starting materials. In the first series of experiments, a mixture of $MgCO_3$ (140 mg) and SiO_2 (40 mg), as well as diamond seed crystals, were put into Pt ampoules and hermetically sealed by arc welding. It should be noted that some experiments were performed without addition of diamond seed crystals. Alkaline carbonate-fluid melts have a high activity in the diamond synthesis process (Pal'yanov et al. 1999a, 1999b, 2002). In addition, data on composition of brine inclusions in cloudy diamonds from Koffiefontein (Izraeli et al. 2001) were considered. Therefore, Na_2CO_3 (8 mg) was also added to the ampoules in the second series of the experiments. Hydrogen fluid was applied in all experiments, to activate the reactions of the decarbonation. The source of the hydrogen fluid was titanium hydride $TiH_{1.9}$ placed outside the Pt ampoules (Fig. 1), so as to permit diffusion of hydrogen through the Pt. Analysis of the experimental products was performed using powder X-ray diffractometer (XRD), as well as optical and scanning electron microscopy. The isotopic analysis of carbon was performed using a Finnigan-MAT Delta mass-spectrometer. The error of the $\delta^{13}C$ measurements was not higher than ±0.1‰. Sample preparation procedures and details on the mass-spectroscopic measurements were presented previously (Reutskii et al. 1999). Infrared absorption spectra were recorded using a Bruker IFS66 FTIR spectrophotometer fitted with a Bruker model A590 microscope. A circular aperture providing a 100 μm diameter sampling area was applied. Concentrations of nitrogen impurities were derived from infrared absorption spectra using standard procedures (Zaitsev 1998).
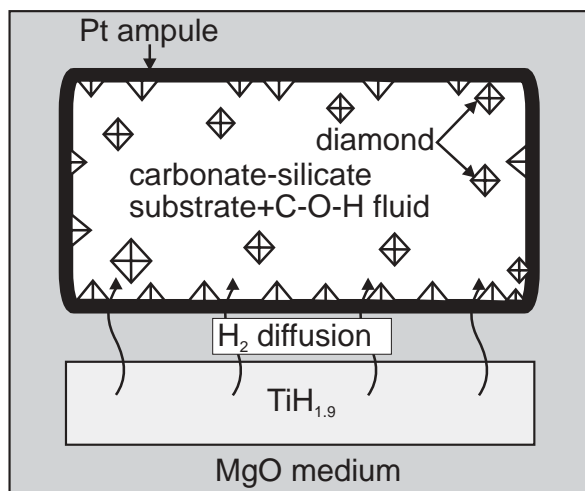
RESULTS AND DISCUSSION

In the first series of experiments (Table 1), it was determined that with increasing temperature from 1350 to 1450 °C at 6 GPa, the amount of magnesite and coesite in the experimental products decreased, whereas enstatite increased from about 5 to 20%. The appearance of graphite in the form of flaky crystals with sizes up to 100 μm was detected at 1350 °C. In experiment CS-2 (1400 °C), the graphite crystals were larger and had a flattened habit (Fig. 2a). Diamond growth on seeds was established in this experiment, whereas at 1450 °C some newly nucleated diamond crystals, up to 30 μm in size, were found on the Pt-ampoule walls, seeds, and directly within the carbonate-silicate substrate (Fig. 2b). In experiment CS-4 (1500 °C), the pressure was increased to 7 GPa, and no decarbonation reaction occurred. But when the temperature was increased to 1600 °C (experiment CS-5), minute graphite crystals up to 50 μm were observed, indicating the initial stages of the reaction. No coesite and graphite, only magnesite, enstatite, forsterite, and diamond were determined in the experimental products at temperatures in the range 1750–1800 °C. Transparent, octahedral diamond crystals and twins (Fig. 2c) attained sizes of 200 and 400 μm, respectively, in the experiments at 1750 and 1800 °C.

In the second series of the experiments (Table 1) with the addition of Na_2CO_3, the appearance of enstatite and graphite was registered at 1350 °C (experiment CS-8), with the amount of these phases being considerably higher than in the first series of experiments. At 1400 °C (experiment CS-9), in addition to graphite, aggregates of tiny octahedral diamond crystals were detected on the Pt ampoule walls. The products of the experiment performed at 1500 °C, as determined by XRD, were forsterite, magnesite, and diamond (see Table 1, experiment CS-10). Octahedral diamond crystals were found in this experiment on the ampoule walls and seed crystals (Fig. 2d). In the experiment at 1800 °C (see Table 1, experiment CS-11), diamonds with sizes up to 450 μm formed a druse-aggregate in the "cold" zone of the ampoule; also crystals and twins were observed within the carbonate-silicate substrate.

FIGURE 1. Sample assembly for diamond crystallization under carbonate-silicate interaction.

TABLE 1. Experimental results

Number	Temperature (°C)	Pressure (GPa)	Time (h)	Run products	Diamond growth on seeds
		$MgCO_3+SiO_2$			
CS-1	1350	6.0	40	Ms+Co+En+G	No
CS-2	1400	6.0	42	Ms+Co+En+G	Yes
CS-3	1450	6.0	43	Ms+En+Co+G+D	Yes
CS-4	1500	7.0	40	Ms+Co	No
CS-5	1600	7.0	10	Ms+Co	No
CS-6	1750	7.0	22	Ms+En+Fo+D	†
CS-7	1800	7.0	18	Ms+En+Fo+D	†
		$MgCO_3+SiO_2+Na_2CO_3$			
CS-8	1350	6.0	42	Ms+Co+En+G	No
CS-9	1400	6.0	42	Ms+En+Co+G+D	Yes
CS-10*	1500	6.0	42	Ms+Fo+D	Yes
CS-11*	1800	7.0	18	Ms+Fo+D	Yes

Notes: Ms-magnesite = $MgCO_3$; Co-coesite = SiO_2; En-enstatite = $MgSiO_3$; Fo-forsterite = Mg_2SiO_4; G = graphite; D = spontaneously nucleated diamond.
* Runs where sinking of seed crystals was registered that indicates complete melting of the substrate.
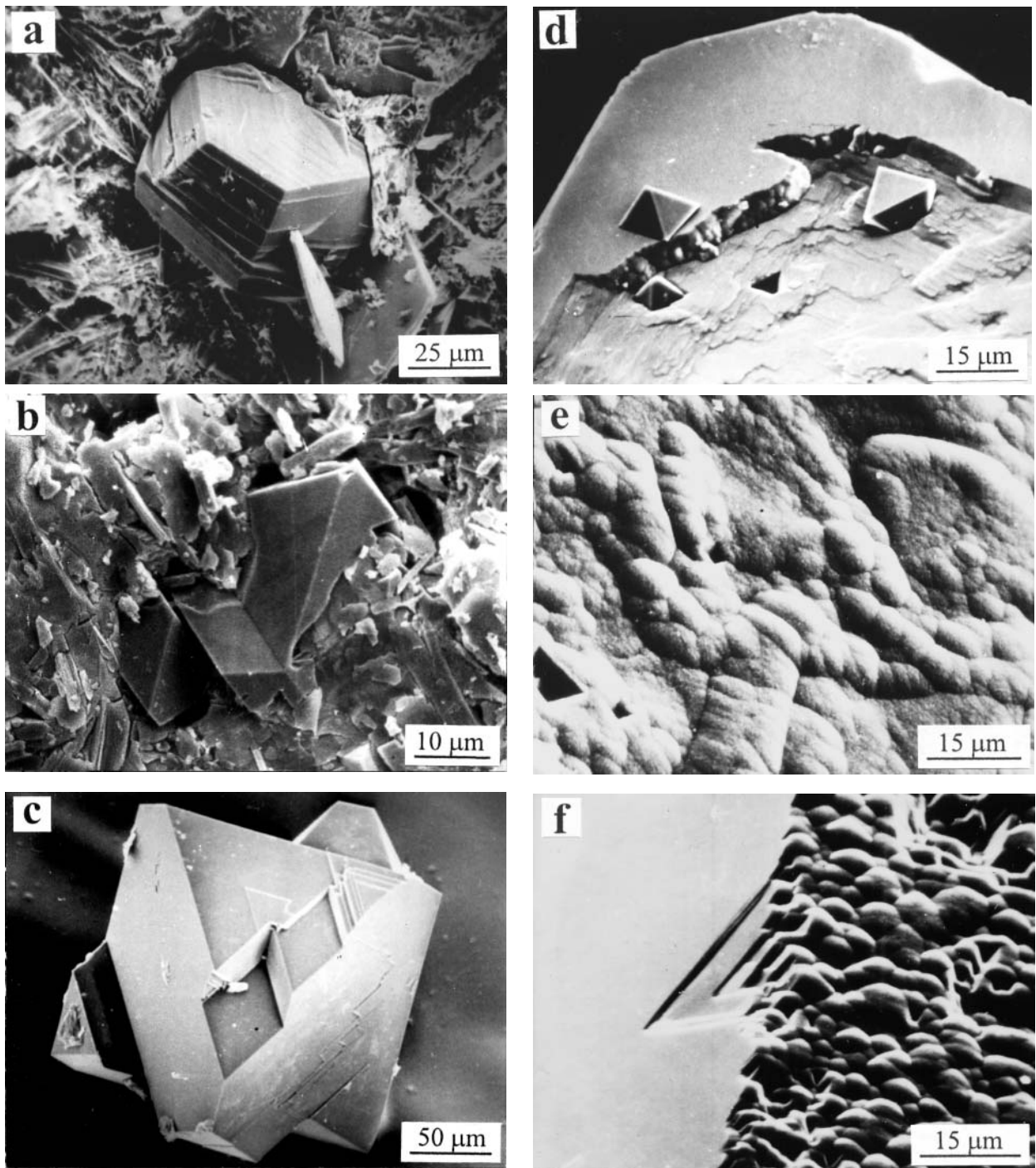† Runs without seed crystals.

FIGURE 2. Scanning electron micrographs of diamond and graphite. (**a**) A flattened crystal of graphite in the carbonate-silicate substrate (run CS-2). (**b**) Octahedral diamonds in the carbonate-silicate substrate (run CS-3). (**c**) A star twin of octahedral diamonds (run CS-6). (**d**) Spontaneous diamonds and growth layers on the {111} face of a seed crystal (run CS-10). (**e**) Cellular surface structure on the {100} face of a seed crystal (run CS-2). (**f**) Triangular growth layers on the {111} face (left) and fibrous patterns on the {100} face (right) of a seed crystal (run CS-9).
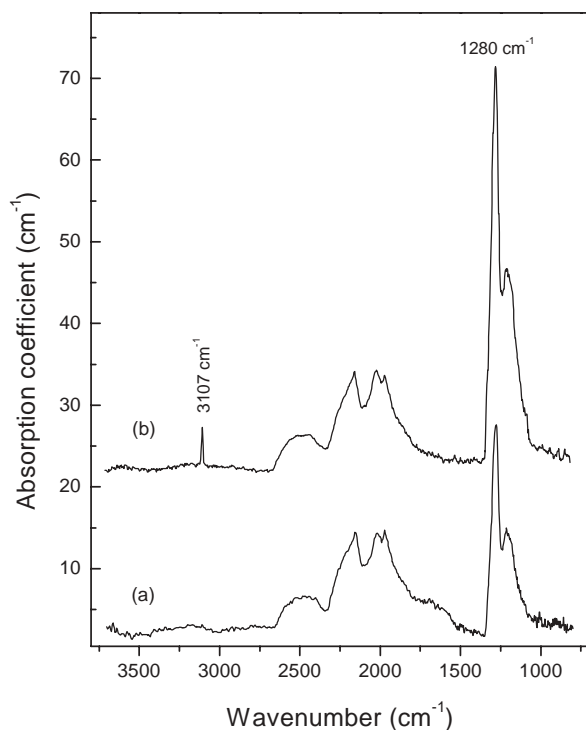
FIGURE 3. Infrared absorption spectra of diamond crystals synthesized in the runs CS-7 (**a**) and CS-11 (**b**). Spectrum **b** has been displaced vertically for clarity.

In experiments CS-2, 3, 9, and 10, a specific diamond growth on the cubic faces of seed crystals was observed. The newly formed diamond layers, which were up to 15 μm thick, had a distinct cellular structure (Fig. 2e) with rounded hillocks up to 20 μm in size. At the same time, octahedral faces adjacent to the cubic ones, in general, were flat with characteristic triangular growth layers (Fig. 2f). The observed cellular surface structure of the cubic faces is similar to that of natural fibrous diamonds that were studied previously by Kamiya and Lang (1964) and Moore and Lang (1972).

Among the diamonds synthesized at temperatures of 1750–1800 °C, there were crystals with sizes and quality appropriate for examination by FTIR absorption microscopy. Typical infrared spectra recorded for these samples are shown in Figure 3. We found that these diamonds contain nitrogen impurities in the form of pairs of neighboring substitutional atoms (A-centers), with concentrations varying from about 300 to 800 atomic ppm. The hydrogen-related absorption peak at 3107 cm^{-1} was also observed in the IR spectra.

Isotopic analysis revealed that the carbon of the initial magnesite had $\delta^{13}C = -0.2$‰, whereas for the diamond formed by the decarbonation, this value was -1.27‰ (experiment CS-6). The difference $\Delta\delta^{13}C = 1.07$ is possibly due to fractionation of the carbon isotopes in the decarbonation reaction.

Thus the results obtained in the present study provide the first experimental evidence for the possibility of diamond formation from the carbon of carbonates upon their interaction with silicates. The formation of elemental carbon as graphite and diamond in the experiments reported here is most likely governed by the following reactions: $MgCO_3 + SiO_2 = MgSiO_3 + CO_2$, $MgCO_3 + MgSiO_3 = Mg_2SiO_4 + CO_2$, $CO_2 + 2H_2 = C + 2H_2O$. Based on the thermodynamical calculations made previously (Ogasawara et al. 1997; Luth 1999) we can infer that the oxygen fugacity in the decarbonation reactions varied from the CCO buffer to CCO for –2 logarithmic units. Crystallization of metastable graphite under the *P-T* conditions of thermodynamical stability for diamond has been previously observed for a number of non-metallic systems, such as fluid-containing carbonates and C-O-H fluids (Pal'yanov et al. 1999a; Akaishi and Yamaoka 2000; Yamaoka et al. 2002; Sokol et al. 2001). The reasons for this phenomenon, however, are still unclear.

Diamond formation by decarbonation is mainly governed by the temperature, pressure, and redox conditions. This inference is based on previous studies of carbonate-silicate interactions (Brey et al. 1983; Eggler et al. 1979; Katsura and Ito 1990; Luth 1993, 1999; Ogasawara et al. 1997; Koziol and Newton 1998; Wyllie and Ryabchikov 2000) and the results from this study. In addition, the presence of alkalis acts as a catalyst for the reaction of the decarbonation and formation of diamond. It should be stressed that nucleation and growth of diamond proceeded both via fluid without melting of the carbonate-silicate substrate and directly within the carbonate-silicate melt containing C-O-H fluid. Thus, carbonates and carbonate-fluid melts can be a medium capable of providing diamond nucleation and can also be a source of carbon for the formation of natural diamond. In the mantle, the reactions between carbonates and silicates releasing carbon in the form of diamond might occur as the result of subduction of carbonate-bearing rocks or mantle convection.

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