Diamond nucleation and growth by reduction of carbonate melts under high-pressure and high-temperature conditions

Makoto Arima
Yusuke Kozai
Geological Institute, Yokohama National University 79-7, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
Minoru Akaishi
Advanced Materials Laboratory, National Institute for Materials Science 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan

ABSTRACT

We report for the first time experimental evidence for the nucleation and growth of diamonds from carbonatitic melts by reduction in reactions with silicon metal or silicon carbide. Experiments were carried out in the $CaMg(CO_3)_2$-Si and $CaMg(CO_3)_2$-SiC systems at 7.7 GPa and temperatures of 1500–1800 °C. No graphite was added to the run powder as a carbon source; the carbonate-bearing melts supply the carbon for diamond formation. Diamond grows spontaneously from the carbonatitic melt by reducing reactions: $CaMg(CO_3)_2 + 2Si = CaMgSi_2O_6 + 2C$ in the $CaMg(CO_3)_2$-Si system, and $CaMg(CO_3)_2 + 2SiC = CaMgSi_2O_6 + 4C$ in the $CaMg(CO_3)_2$-SiC system. Our results provide strong experimental support for the view that some natural diamonds crystallized from carbonatitic melts by metasomatic reducing reactions with mantle solid phases.

Keywords: diamond formation, moissanite, metasomatic reducing reaction, carbonatitic melts.

INTRODUCTION

It has been suggested that some diamonds in Earth's mantle crystallized from carbonatitic melts by reducing reactions and/or formed from volatile (C-H-O) rich fluids (Haggerty, 1986; Luth, 1993; Blundy et al., 1991; Navon, 1999). Studies of inclusions in natural diamonds suggest a genetic link between diamond formation and volatile- and alkali-rich mantle melts or fluids, broadly similar to carbonatite to kimberlite compositions (Navon et al., 1988; Schrauder and Navon, 1994; Bulanova et al., 1998; Izraeli et al., 2001). Diamond can be synthesized from graphite in the presence of nonmetallic solvent catalysts such as carbonate melts (Akaishi et al., 1990; Taniguchi et al., 1996; Sato et al., 1999; Pal'yanov et al., 1999), kimberlitic silicate melts (Arima et al., 1993), C-O-H fluids (Akaishi et al., 2000; Akaishi and Yamaoka, 2000), and CO_2 fluids (Yamaoka et al., 2002) under high-pressure and high-temperature conditions in the thermodynamically stable region of diamond, suggesting a possible role of these compounds in diamond formation in Earth's mantle. However, because graphite was a part of the starting assemblage in all these experiments, these do not provide a clear demonstration for direct crystallization of diamond from cabonatitic melts or fluid. Here we report experimental results of nucleation and growth of diamond from carbonatitic melts by reducing reactions in graphite-free systems.

METHODS

Series of experiments were carried out in the $CaMg(CO_3)_2$-Si and $CaMg(CO_3)_2$-SiC systems at 7.7 GPa and temperatures of 1500–1800 °C for 60–1440 min (Table 1) using a modified belt-type high-pressure apparatus with a 32-mm-diameter bore (Yamaoka et al., 1992). Methods of pressure calibration and temperature measurement were described previously (Akaishi et al., 1990). No direct control or estimation of oxygen fugacity was made in this study. The starting materials with various Si/C ratios (3.0–15.6) were carefully prepared from highly pure synthetic calcite

TABLE 1. EXPERIMENTAL RESULTS

Run Number	Temp (°C)	Time (minutes)	Starting composition	Newly crystallized diamond*	Weight gain of seed (wt%)
$CaMg(CO_3)_2$-Si system					
Without seed					
MK-10	1800	60	$0.61CaMg(CO_3)_2 + 0.39Si$	Yes (40 μm)	-
MK-17	1600	240	$0.61CaMg(CO_3)_2 + 0.39Si$	Yes (50 μm)	-
With seed					
MK-7	1800	60	$0.89CaMg(CO_3)_2 + 0.11Si$	No	0.0
MK-12	1800	60	$0.79CaMg(CO_3)_2 + 0.21Si$	Yes (30 μm)	0.1
MK-5	1800	60	$0.79CaMg(CO_3)_2 + 0.21Si$	Yes (40 μm)	0.5
MK-8	1800	60	$0.69CaMg(CO_3)_2 + 0.31Si$	Yes (40 μm)	0.1
MK-6	1800	60	$0.61CaMg(CO_3)_2 + 0.39Si$	Yes (40 μm)	0.3
$CaMg(CO_3)_2$-SiC system					
Without seed					
MK-16	1800	60	$0.60CaMg(CO_3)_2 + 0.40SiC$	Yes (50 μm)	-
MK-15	1600	240	$0.60CaMg(CO_3)_2 + 0.40SiC$	No	-
MK-19	1600	480	$0.60CaMg(CO_3)_2 + 0.40SiC$	Yes (40 μm)	-
MK-18	1500	1440	$0.60CaMg(CO_3)_2 + 0.40SiC$	Yes (90 μm)	-
With seed					
MK-2	1800	60	$0.60CaMg(CO_3)_2 + 0.40SiC$	Yes (20 μm)	1.2
MK-1	1600	120	$0.60CaMg(CO_3)_2 + 0.40SiC$	No	0.2
MK-3	1600	250	$0.60CaMg(CO_3)_2 + 0.40SiC$	Yes (50 μm)	1.7
$CaMg(CO_3)_2$ system					
With seed					
MK-14	1800	60	$CaMg(CO_3)_2$ without Si or SiC	No	0.0
Without seed					
MK-11	1800	50	$CaMg(CO_3)_2$ without Si or SiC	No	-

*The maximum size of newly crystallized diamond is given in parentheses.
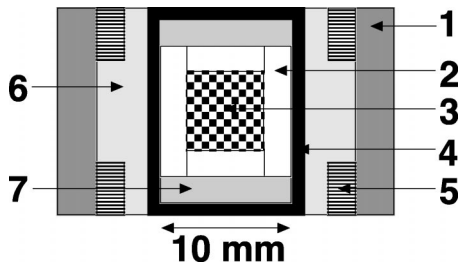
Figure 1. Sample assembly of high-pressure experiments. 1—pyrophyllite, 2—NaCl, 3—starting powder in Pt capsule, 4—graphite heater, 5—steel ring, 6—NaCl with 10 wt% ZrO_2, 7—NaCl with 20 wt% ZrO_2.

and natural magnesite from Victoria, Australia (Brey et al., 1983), with 9-grade silicon metal for the $CaMg(CO_3)_2$-Si system and with reagent-grade α-SiC (moissanite) for the $CaMg(CO_3)_2$-SiC system (Table 1).

No graphite was added to the run powder as a carbon source. The carbonate-Si or carbonate-SiC mixture was sealed into a Pt capsule made of a platinum tube 6 mm in diameter, 6 mm long, and 0.2 mm thick. The capsule was packed in a dry NaCl pressure medium and placed in the center of a graphite heater in a high-pressure sample assembly (Fig. 1). In some runs, a natural octahedral diamond with an edge length of 0.8–1.0 mm was placed in the center of the starting powder in the run capsule. The run products were examined with optical microscope, scanning electron microscope, X-ray diffraction, Raman spectroscopy, and electron microprobe.

Weighing the run capsule before and after the run checked the seal tightness during the experiment. After the run, the run capsule was soaked in hot water to remove the NaCl pressure medium. No weight change was observed in all run capsules, suggesting that the experiments behaved as a closed system for elements, including C, Ca, Mg, Si, and O. This conclusion is supported by the electron microprobe observation on the Pt run capsules, in which no element except Pt was detected. To check the carbon source for the newly crystallized diamond in the run MK-10 in the carbonate-Si system, carbon isotope analysis for $δ^{13}C$ value was made on the diamond crystals, a carbonatitic part of the run product, and the starting material. The isotopic measurements were carried out by the mass spectrometer (MAT-250) at the Shizuoka University. The $δ^{13}C$ value of the diamonds ranges from −2.0‰ to −3.9‰, suggesting that these are not in isotopic equilibrium, but the values are broadly comparable to those of the starting powder (−3.01‰) and the coexisting carbonatitic melt (−3.85‰). The data provide strong support for the conclusion that the source of carbon for the diamond was the carbonate, and that the Pt capsule was impermeable to carbon

under the pressure and temperature conditions employed in this study.

RESULTS

The addition of higher amounts of reduction agents (Si or SiC) to the carbonate mixture, as well as higher run temperature and longer run duration, greatly enhanced the formation of diamond (Table 1). No seed growth or nucleation was observed in the run with the minimum Si (run MK-7), but all runs with higher amounts of Si contain newly crystallized diamonds. In the $CaMg(CO_3)_2$-SiC systems, all runs at 1600 and 1800 °C contain newly crystallized diamonds, except for two short time runs at 1600 °C: 240 min for run MK-15 and 120 min for run MK-1. In run MK-1, we observed growth on the seed, but no new nucleation. Longer run duration (1440 min) in the $CaMg(CO_3)_2$-SiC system led to spontaneous nucleation of diamond, even at 1500 °C (run MK-18).

To test the effect of the Pt capsule, dummy experiments were carried out in which carbonate powder was encapsulated in a Pt capsule without the reduction agents (Table 1). After the experiment (run MK-14 with seed diamond at 1800 °C and 7.7 GPa for 60 min and run MK-11 without seed at 1800 °C and 7.7 GPa for 50 min), no diamond nucleation or seed growth was detected in run MK-14 and there was no diamond nucleation in run MK-11. The results confirm that Pt metal does not act as a solvent catalyst in the experiments.

No silicon metal or SiC was identified in any of the run products. The carbonatitic part of the run products consists of a fine-grained crystal aggregate. The aggregate is dominantly composed of clinopyroxene, Ca-carbonate, and Ca-Mg-carbonate. The clinopyroxene is nonstoichiometric and has unusual compositions. Dendritic or acicular morphology of these phases indicates that these crystallized from the carbonatitic melt during fast, nonequilibrium quenching at high pressures. This conclusion is supported by the fact that the liquidus temperature of ~1450 °C at 7.7 GPa experimentally estimated for the dolomitic carbonatite compositions (Dalton and Presnall, 1998) is considerably lower than the temperature conditions of this study (1500–1800 °C at 7.7 GPa).

In the runs with seed diamond, the seed diamonds are covered by a thin film of graphite crystals (<1 μm thick) that is easily removed from the diamond surface. In the runs without seed diamond, we noted a rare amount of graphite in the form of round to hexagonal flaky crystals (<2 μm in diameter) set in a carbonatitic matrix. Relatively higher amounts of flaky graphite occur in the runs with shorter run duration in which no diamond nucleation
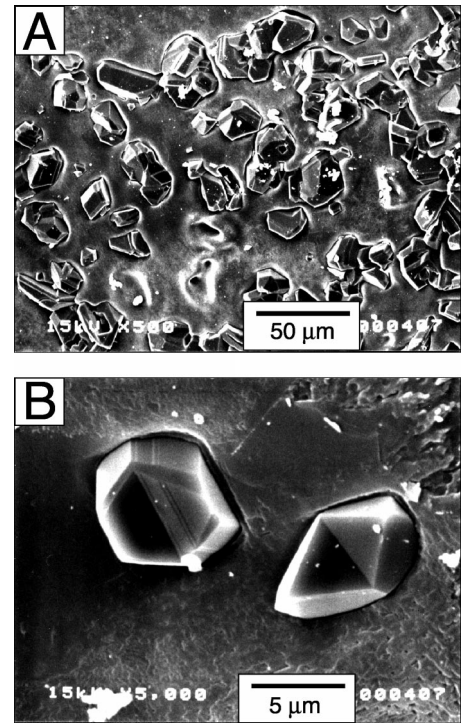

Figure 2. Scanning electron microscope photographs of diamond (run MK-17). A: Newly crystallized octahedral diamonds in matrix of quench phases. B: Octahedral diamonds with spinel twin.

and growth were detected (runs MK-1 and MK-15).

No significant difference in morphology was noticed between newly crystallized diamonds in both the $CaMg(CO_3)_2$-Si and $CaMg(CO_3)_2$-SiC systems. The newly crystallized diamonds, to 100 μm in diameter, have well-developed {111} faces (Fig. 2). Some isolated crystals are well-faceted octahedrons (Fig. 2A), but most crystals exhibit a spinel-type twinning (Fig. 2B). Seed diamonds show a remarkable morphological change. These have healed growth of fibrous crystals at the corners and edges (Fig. 3A) and growth hillocks with triangular shapes on the {111} faces. The hillocks have sharp triangular, truncated triangular, or rounded triangular shapes, having both positive and negative orientation to the original triangular {111} faces of the seed crystal (Fig. 3B). This growth pattern differs from that of natural diamonds in which triangular growth hillocks have the same orientation as that of the triangle of the octahedral face (Sunagawa et al., 1984; van Enckevort, 1992). In a rare case, however, growth pyramids of triangular morphology of the seed crystal clearly show growth steps similar to those observed on natural diamonds (Sunagawa, 1984).

Overall, the results indicate that the diamond is formed from the carbonatitic melt by reducing reactions of the following form:
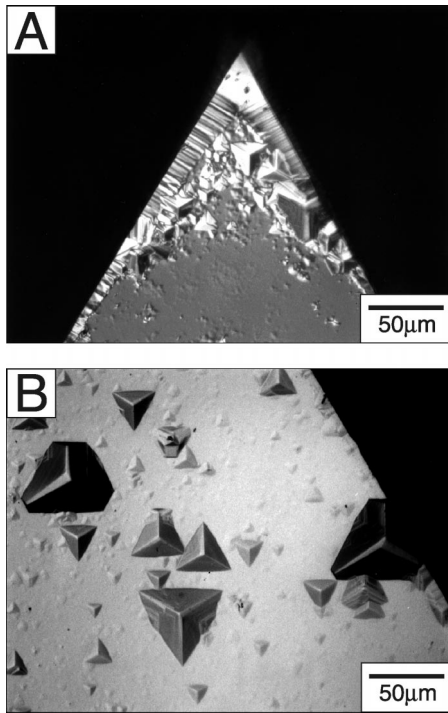
Figure 3. Differential interference micrograph of {111} face of seed diamond. A: Resorbed dull edge of seed crystal was sharpened after run by newly grown fibrous diamonds (run MK-8). B: Triangular growth hillocks having both positive and negative orientation to {111} faces of seed (run MK-5).

$CaMg(CO_3)_2 + 2Si = CaMgSi_2O_6 + 2C$ in the $CaMg(CO_3)_2$-Si system and $CaMg(CO_3)_2 + 2SiC = CaMgSi_2O_6 + 4C$ in the $CaMg(CO_3)_2$-SiC system.

DISCUSSION

Although temperatures in the experiments (1500–1800 °C) are somewhat higher than those estimated for diamond formation (950–1500 °C) (Haggerty, 1986), our results provide an important link for deciphering the genesis of diamond in Earth's mantle. This study provides strong experimental support for the view that some natural diamonds crystallized from carbonatitic melts by metasomatic reducing reaction with mantle solid phases (Navon, 1999). Although α-SiC (moissanite) and β-SiC are reported as inclusions in natural diamonds (Moore et al., 1986; Leung et al., 1990), and silicon metal was reported as an inclusion of moissanites in kimberlites (Mathez et al., 1995), these are very rare and represent extremely reducing conditions in Earth's mantle. Nevertheless, it is probable that carbonate may be reduced under less extreme conditions (Luth, 1993; Blundy et al., 1991; Bulanova et al., 1998).

Akaishi et al. (2000) studied diamond crystallization processes in the supercritical H_2O-CO_2 fluids at 7.7 GPa and 1600 °C, and observed that flaky graphite crystals, similar to those of our study, first crystallized from and coexisted with supercritical fluids, then transformed into diamond after a substantial incubation period. Akaishi et al. (2000) suggested that the incubation period is probably the induction time, which determines the diamond formation in the fluid systems. In this study, relatively larger concentrations of graphite crystals occurred in the runs with shorter duration, in which no diamond nucleation and growth were detected. The spontaneous diamond growth occurred after a substantial incubation period. The metastable graphite would be a quench phase that crystallized from excess carbon dissolved in the carbonate melt at higher temperatures. Alternatively, the graphite could be a precursor that first crystallized from the carbonatitic melt, and was the substrate on which diamond crystallized after a substantial incubation period via a mechanism similar to that suggested by Akaishi et al. (2000).

Graphite microinclusions, located in the genetic center of Yakutian diamonds, were described by Bulanova et al. (1998). The graphite is closely associated with metallic iron, wüstite, and carbonate phases. They suggested nucleation of the Yakutian diamonds on the matrix of graphite–metallic iron-wüstite in the presence of carbonate-rich fluids or melts. Our experimental results support the genetic model proposed by Bulanova et al. (1998) for the Yakutian diamonds.

Recent high-pressure melting experiments suggest that the incipient melt of a carbonate-bearing mantle peridotite is carbonatitic in composition (Dalton and Presnall, 1998; Martinez et al., 1998). Analyses of fluid inclusions in natural diamonds indicate that carbonatitic melts or fluids were present during the formation of some natural coated diamonds (Navon et al., 1988; Schrauder and Navon, 1994; Izraeli et al., 2001). It is noteworthy that the diamond seed crystals have fibrous growth on them (Fig. 3), morphologically similar to the carbonate-bearing coated diamonds (Navon et al., 1988). The experiments reported here demonstrate that diamond grows spontaneously from such melts and that carbonate-bearing melts actually supply the carbon for diamond formation. The extremely low viscosity of carbonate-bearing melts (Dobson et al., 1996) allows them to percolate easily through mantle rocks, to transport the carbon into more reduced host mantle regions, and to crystallize diamond by reducing reactions.

REFERENCES CITED

Akaishi, M., and Yamaoka, H., 2000, Crystallization of diamond from C-O-H fluids under high-temperature and high-pressure conditions: Journal of Crystal Growth, v. 209, p. 999–1003.

Akaishi, M., Kanda, H., and Yamaoka, S., 1990, Synthesis of diamond from graphite-carbonate systems under very high temperature and pressure: Journal of Crystal Growth, v. 104, p. 578–581.

Akaishi, M., Kumar, M.D.S., Kanda, H., and Yamaoka, S., 2000, Formation process of diamond from supercritical H_2O-CO_2 fluid under high pressure and high temperature conditions: Diamond Related Materials, v. 9, p. 1945–1950.

Arima, M., Nakayama, K., Akaishi, M., Yamaoka, S., and Kanda, H., 1993, Crystallization of diamond from a silicate melt of kimberlite composition in high-pressure and high-temperature experiments: Geology, v. 21, p. 968–970.

Blundy, J.D., Brodholt, J.P., and Wood, B.J., 1991, Carbon-fluid equilibria and the oxidation state of the upper mantle: Nature, v. 349, p. 321–324.

Brey, G.P., Brice, W.R., Ellis, D.J., Green, D.H., Harris, K.L., and Ryabchikov, I.D., 1983, Pyroxene-carbonate reactions in the upper mantle: Earth and Planetary Science Letters, v. 62, p. 63–74.

Bulanova, G.O., Griffin, W.L., and Ryan, C.G., 1998, Nucleation environment of diamonds from Yakutian kimberlites: Mineralogical Magazine, v. 62, p. 409–419.

Dalton, J., and Presnall, D.C., 1998, Carbonatitic melt along the solidus of model lherzolite in the system CaO-MgO-Al_2O_3-SiO_2-CO_2 from 3 to 7 GPa: Contributions to Mineralogy and Petrology, v. 131, p. 123–135.

Dobson, D.P., Jones, A.P., Rabe, R., Sekine, T., Kurita, K., Taniguchi, T., Kondo, T., Kato, T., Shimomura, O., and Urakawa, S., 1996, In-situ measurement of viscosity and density of carbonate melts at high pressure: Earth and Planetary Science Letters, v. 143, p. 207–215.

Haggerty, S.E., 1986, Diamond genesis in a multiply-constrained model: Nature, v. 320, p. 34–37.

Izraeli, E.S., Harris, J.W., and Navon, O., 2001, Brine inclusions in diamonds: A new upper mantle fluid: Earth and Planetary Science Letters, v. 187, p. 323–332.

Leung, I.S., Guo, W., Friedman, I., and Gleason, J., 1990, Natural occurrence of silicon carbide in diamondiferous kimberlite from Fuxian: Nature, v. 346, p. 352–354.

Luth, R.W., 1993, Diamonds, eclogites, and the oxidation state of the Earth's mantle: Science, v. 261, p. 66–68.

Martinez, I., Peréz, E.M.C., Matas, J., Gillet, P., and Vidal, G., 1998, Experimental investigation of silicate-carbonate system at high pressure and high temperature: Journal of Geophysical Research, v. 103, p. 5143–5163.

Mathez, E.A., Fogel, R.A., Hutcheon, I.D., and Marshintsev, V.K., 1995, Carbon isotopic composition and origin of SiC from kimberlites of Yakutia, Russia: Geochimica et Cosmochimica Acta, v. 59, p. 781–791.

Moore, R.O., Otter, M.L., Richardson, R.S., Harris, J.W., and Gurney, J.J., 1986, The occurrence

of moissanite and ferro-periclase as inclusions in diamond: Geological Society of Australia Abstracts, v. 16, p. 409–411.

Navon, O., 1999, Diamond formation in the Earth's mantle, *in* Gurney, J.J., et al., eds., Proceedings of the 7th International Kimberlite Conference: Cape Town, South Africa, Red Roof Design, p. 584–604.

Navon, O., Hutcheon, I.D., Rossman, G.R., and Wasserburg, G.J., 1988, Mantle-derived fluids in diamond micro-inclusions: Nature, v. 335, p. 784–789.

Pal'yanov, Y.N., Sokol, A.G., Borzdov, Y.M., Khokhryakov, A.F., and Sobolev, N.V., 1999, Diamond formation from mantle carbonate fluids: Nature, v. 400, p. 417–418.

Sato, K., Akaishi, M., and Yamaoka, S., 1999, Spontaneous nucleation of diamond in the system $MgCO_3$-$CaCO_3$-C at 7.7 GPa: Diamond Related Materials, v. 8, p. 1900–1905.

Schrauder, M., and Navon, O., 1994, Hydrous and carbonatitic mantle fluids in fibrous diamonds from Jwaneng, Botswana: Geochimica et Cosmochimica Acta, v. 58, p. 761–771.

Sunagawa, I., 1984, Morphology of natural and synthetic diamond crystals, *in* Sunagawa, I., ed., Material science of the Earth's interior: Tokyo, Terra Scientific, p. 303–330.

Sunagawa, I., Tsukamoto, K., and Yasuda, T., 1984, Surface microtopographic and X-ray topographic study of octahedral crystals of natural diamond from Siberia, *in* Sunagawa, I., ed., Material science of the Earth's interior: Tokyo, Terra Scientific, p. 331–349.

Taniguchi, T., Dobson, D., Jones, A.P., Rabe, R., and Milledge, H.J., 1996, Synthesis of cubic diamond in the graphite-magnesium carbonate and graphite-$K_2Mg(CO_3)_2$ systems at high pressure of 9–10 GPa region: Journal of Material Research, v. 11, p. 2622–2632.

van Enckevort, W.J.P., 1992, Phase shifting interferometry of growth patterns on the octahedral faces of natural diamonds: Journal of Crystal Growth, v. 119, p. 177–194.

Yamaoka, S., Akaishi, M., Kanda, H., Osawa, T., Taniguchi, T., Sei, H., and Fukunaga, O., 1992, Development of belt type high pressure apparatus for material synthesis at ~8 GPa: High Pressure Institute of Japan Journal, v. 30, p. 15–24.

Yamaoka, S., Kumar, M.D.S., Kanda, H., and Akaishi, M., 2002, Crystallization of diamond from CO_2 fluid at high pressure and high temperature: Journal of Crystal Growth, v. 234, p. 5–6.