

Diamond Synthesis from Graphite in the Presence of Water and SiO₂: Implications for Diamond Formation in Quartzites from Kazakhstan

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Abstract

Recent studies of microdiamonds from orogenic belts related to continental collisions induced experimentalists to explore new crystallization media possible for diamond synthesis. This has led to considerable progress in diamond-synthesis experiments under high pressures and high temperatures. Diamond was found to grow in a wide variety of systems, which drastically differ from the metal-solvent-catalyst media that have been known since the 1950s in industrial diamond syntheses. The newer systems include a variety of melts consisting of silicate, carbonate, sulfur-carbon, as well as carbon-oxygen-hydrogen (C-O-H) supercritical fluid systems in the presence of different oxides. Our experimental program has focused on systems compositionally approximating natural sites of ultrahigh-pressure metamorphic rocks, where abundant microdiamonds occur. Yet to be explored are SiO₂-rich systems that constitute an important diamond-bearing lithology in the world-famous Kokchetav ultrahigh-pressure metamorphic (UHPM) terrane. The purpose of this study is to determine what effect the presence of SiO₂ has on the synthesis of diamond from C-O-H supercritical fluid. Experiments performed in a Walker-style multianvil apparatus at $T = 1450\text{--}1500^\circ\text{C}$ and $P = 8\text{--}8.5$ GPa on the Si-C-O-H system at different levels of oxygen fugacity (f_{O_2}) have led us to the conclusion that diamond crystallization requires more reduced media than its counterpart synthesized in Mg-C-O-H and Ca-Mg-C-O-H systems at similar pressures, temperatures, and times.

Introduction

DIAMOND IS ONE of several known polymorphs of carbon whose hardness, high dispersion of light, chemical inertness, and high thermal conductivity make it useful for scientific and industrial applications and jewelry. Although most natural diamonds of gem and industrial qualities originate from kimberlites and other ultramafic magmas, unusual small diamonds (1–300 microns in size) have been discovered within some orogenic belts of Kazakhstan, China, Norway, Germany, and Greece (Dobrzhinskaya et al., 1995; Massonne, 1999; Mposkos and Kostopoulos, 2001; Perraki et al., 2006; Rozen et al., 1972; Sobolev and Shatsky, 1990; van Roermund et al., 2002; Xu et al., 1992; Yang et al., 2003). All of them were formed as a result of Paleozoic and Mesozoic continental collisions and subduction of continental lithologies, followed by

exhumation from a minimum depth of ~150 km. Because these microdiamonds are hosted by metasedimentary rocks of continental affinity, formations of diamond in which according to mainstream geological theories diamond is unexpected, they are currently the focus of studies to understand subduction-zone processes and rock exhumation.

Microdiamonds from the Kokchetav massif, Kazakhstan, are hosted in felsic gneisses, quartzites, and/or marbles. Detailed studies have shown that these diamonds contain abundant nanometric crystalline and fluid inclusions, the compositional diversity of which correlates with the bulk chemistry of the host minerals and/or the host rocks (Dobrzhinskaya et al., 2003a, 2003b, 2005, 2006). For example, felsic rocks and quartzite contain diamonds rich in SiO₂ inclusions, whereas diamonds from marbles mostly contain carbonates. Such correlations, along with fluid inclusions in most Kokchetav diamonds, led some researchers to the conclusion that diamonds were crystallized from a

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C-O-H supercritical fluid (De Corte et al., 1998, 2002; Ogasawara, 2000; Pal'yanov et al., 2000; Ogasawara, 2005; Dobrzhinetskaya et al., 2003a, 2003b, 2005, 2006; Hwang et al., 2003), whereas others concluded that the medium of diamond crystallization also might be alkaline-carbonate or silicate-carbonate melt (e.g., Pal'yanov et al., 2001; Korsakov et al., 2004). The critical role of fluids in subduction zones is an important subject because fluids promote mass transfer and energy release in both thermal and mechanical forms, which may change and facilitate chemical reactions, mineral phase transformations, as well as control buoyancy forces. Experimental data suggest that fluids at high pressures and high temperatures may dissolve a large amount of solid components (e.g., Kennedy et al., 1962) and conversely, melts dissolve large amounts of volatiles, leading to a poor distinction between fluid and melt phases (e.g., Boettcher and Wyllie, 1969; Bureau and Keppler, 1999).

Both concepts (fluid and melt) of diamond origin have been tested and successfully confirmed by experimental synthesis of diamonds at high pressures (HP) and high temperatures (HT) (e.g., Akaishi and Yamaoka, 2000; Arima et al., 1993, 2002; Dobrzhinetskaya et al., 2002, 2004; Litvin and Zharikov, 2000; Pal'yanov et al., 2000, 2002; Sokol et al., 2001). Although previous HP and HT experiments indeed confirm that diamond easily crystallizes from graphite and/or amorphous carbon in Ca and Mg-rich media in the presence of H₂O even at f_{O_2} as high as -3.7 to -4 log units, it was noticed that adding SiO₂ to the C-O-H system restricted diamond crystallization (Renfro and Dobrzhinetskaya, 2003). A survey of the literature has revealed that the role of SiO₂ in diamond synthesis from a C-O-H supercritical fluid had not yet been examined experimentally. A great need for such knowledge exists because more than 75 vol% of diamond-bearing rocks in UHPM terranes worldwide are represented by SiO₂-rich felsic gneisses and quartzites. This paper presents our first experimental data on diamond synthesis from Si-C-O-H systems, both pure and doped with K, Na, and Al at various pressures, temperatures, times, and oxidation states (Table 1).

Previous Experimental Studies of Diamond Crystallization

Synthesis of diamond at high pressures and high temperatures was successfully performed in the

1950s by General Electric Co. at 5–6 GPa and $T = 1400$ – 1600°C (Bundy et al., 1955). Because of the kinetic barrier to the graphite-diamond reaction, metal-solvent catalysts were added to speed the phase transformation. Until recently, the most widely used conventional metal catalysts, such as Ni, Co, and Fe, formed the foundation of the approach used in experimental and industrial synthesis of diamonds. The range of metal catalysts has been extended dramatically: Pt, Rh, Ru, Pa, Ir, Os, Mn, Cr, Cu, Ti, and Zr all have been found to act as catalysts (e.g., Bovenkerk et al., 1959). These metals have eutectic or peritectic relationships with C and they easily react with C when they melt. A typical reaction time for such diamond formation is 5 to 20 min (e.g., Bundy et al., 1955; Bovenkerk et al., 1959). Furthermore, non-metallic solvent-catalysts such as halides, hydroxides, and sulfates, and alkaline/alkaline-earth carbonates have been successfully explored (e.g., Akaishi et al., 1990; Kanda et al., 1994; Pal'yanov et al., 2002; Taniguchi et al., 1996; Wang et al., 1999).

More recently, H₂O has been suggested as a new promoter of graphite transformation to diamond (e.g., Kanda et al., 1994). Experimental investigations following this suggestion as well as new observations collected from recently discovered UHPM diamonds opened a new direction for establishing diamond synthesis from graphite in the presence of water, which may open new prospects for the HP/HT diamond industry (e.g., Akaishi and Yamaoka, 2000; Dobrzhinetskaya et al., 2004; Hong et al., 1999; Pal'yanov et al., 2000; Yamaoka et al., 2000; Renfro and Dobrzhinetskaya, 2003; Sokol et al., 2000). We have successfully synthesized diamonds from graphite in nominally pure C-O-H fluid and in Mg-C-O-H and Ca-Mg-C-O-H systems at HP and HT conditions in a multianvil apparatus (Dobrzhinetskaya et al., 2004). We found that the Mg-bearing C-O-H supercritical fluid promotes nucleation and growth of irregular, skeletal-like diamond crystals, whereas Ca-bearing C-O-H fluid yielded cuboid forms, and the simple C-O-H system produced octahedral diamonds (Dobrzhinetskaya et al., 2004; Renfro and Dobrzhinetskaya, 2003).

Our experimental data on diamond synthesis from Mg-C-O-H, Ca-Mg-C-O-H, and C-O-H systems at $P = 7.5$ – 8.5 GPa and $T = 1200$ – 1500°C are in a good agreement with the results on diamond synthesis performed by other experimental groups from graphite and non-graphitic carbon in the presence of pure H₂O and other non-metallic C, O, and

TABLE I. Experiments and Conditions

Experiment no.	Starting materials, wt%	T, °C	P, GPa	Time, hrs	fO_2	Run product
MA-151	Grph and amorph. C: 40; SiO ₂ : 40 Muscovite: 5, H ₂ O:15	1500	8.5	27	Ni-NiO	“Raspberry-like” coesite, metastable graphite, phengite. No diamonds found.
MA-154	Grph: 42; SiO ₂ : 32 Albite: 10, Biotite: 2, H ₂ O: 14	1500	8.5	7.5	Ni-NiO	Metastable graphite, jadeite, garnet. No diamonds found.
MA-166	Grph: 47 SiO ₂ : 47 H ₂ O: 6	1450	8.5	43	Ni-NiO	Coesite, metastable graphite No diamonds found.
MA-195	Grph: 60 SiO ₂ : 30 H ₂ SiO ₃ : 10	1500	8.5	6	I-W	Sporadic diamonds (1–10 microns), SiC, coesite, metastable graphite.
MA-199	SiO ₂ : 45, Grph: 45, H ₂ SiO ₃ : 10 Seed diamonds	1500	8.0	3	Ni-NiO	Metastable graphite, coesite. No newly crystallized diamonds found.
MA-208	Grph: 60 SiO ₂ : 30 H ₂ SiO ₃ : 10	1500	8.0	13	I-W	Diamonds (5–15 μ m), metastable graphite, SiC, coesite.
MA-209	Grph: 60 SiO ₂ : 30 H ₂ SiO ₃ : 10	1500	8.0	2	I-W	Metastable graphite, SiC, coesite. No diamonds found.
MA-210	Grph: 60 SiO ₂ : 30, H ₂ SiO ₃ : 10	1500	8.0	7.5	I-W	Sporadic diamonds (1–10 μ m), metastable graphite, SiC.
MA-211	Grph: 60 SiO ₂ : 30 H ₂ SiO ₃ : 10 Seed diamonds	1500	8.0	62	I-W	Abundant newly crystallized diamond (20–40 microns), SiC. No coesite found.
MA-212	Grph: 60, SiO ₂ : 30, H ₂ SiO ₃ : 10	1500	8.0	16	I-W	Diamonds (10–20 microns), metastable graphite, SiC.
MA-221	SiO ₂ : 50, Al ₂ O ₃ : 20, Grph: 20, H ₂ SiO ₃ : 10	1500	7.0	1	Ni-NiO	Metastable graphites, kyanite, coesite, SiC. No diamonds found.
MA-222	SiO ₂ : 30, Al ₂ O ₃ : 20, Grph: 40, H ₂ SiO ₃ : 10	1500	7.0	9	I-W	Diamonds (5–10 microns), metastable graphite, kyanite, SiC, coesite.

H-containing organic and inorganic compounds mixed in different combinations (e.g., Akaishi and Yamaoka, 2000; Yamaoka et al., 2000; Kumar et al., 2001). Several interesting experiments also have been devoted to diamond morphologies and graphite-diamond kinetics in alkaline-carbonate and carbonate systems saturated in C-O-H fluid (e.g., Taniguchi et al., 1996; Sokol et al., 2000). Pal'yanov et al. (2002) concluded that diamond morphology in a fluid-alkaline-carbonate melt is not a function of P

and T as was previously thought based on the metal-solvent-catalyst experiments. They showed that the morphology of newly crystallized diamonds is controlled by the composition of the crystallization medium (presence of impurities)—e.g., cubo-octahedral diamonds crystallized from Na-carbonate melt whereas octahedral crystals formed in K-carbonate melt. Only octahedral diamonds grew in a pure C-O-H supercritical fluid media (Pal'yanov et al., 2002; Dobrzhinetskaya et al., 2004).

Experimental Procedures

Apparatus and assembly

Experiments on diamond synthesis in Si-rich media were carried out in a Walker-style multianvil apparatus (Walker, 1991) using a 6 mm truncated-edge MgO-Al₂O₃ octahedron made from powdered ceramic material of Aremco Products (584-OS) and two rolls of 0.0254 mm thick Re-foil or a graphite cylinder as a heater. The spaces between the heater and capsule containing the starting material were filled by MgO powder and semi-sintered MgO discs. D-type thermocouples (W3%Re-W25%Re) were placed beneath the capsule with the starting material. The temperature distribution within the sample was calculated using the empirical equation of O'Neill and Wood (1979) established on the base of experimental studies of Fe-Mg partitioning between garnet and olivine. Such a calibration demonstrates that the real temperature in the central part of the samples is ~50°C higher than that read by the thermocouple. Experimental temperatures shown in Table 1 were corrected in this way.

Other materials and devices placed within the internal space of the multianvil apparatus included eight 25 mm tungsten carbide (WC) cubes, each with a 6 mm octahedral truncation on one corner. They are arranged in the form of a larger cube with truncations facing inward to form an octahedral cavity, into which the MgO-Al₂O₃ octahedron containing furnace, sample, and thermocouples are placed. To minimize friction and to provide electrical insulation, sheets of fiberglass laminate (G-10) coated with a thin dry film of non-silicon Vydax Mold Release are placed between the WC cubes and the six anvils. Temperature measured with thermocouples was maintained constant to $\pm 3^\circ\text{C}$; uncertainties of pressure calibration combined with small variations in the oil pressure behind the ram corresponded nominally to a total uncertainty in pressure less than 0.1 GPa. Temperature was not corrected for the effect of pressure on the thermocouple emf. The 6 mm truncated edge length assembly was calibrated at room temperature against the phase transition of Bi metal. The calibration curve at high temperature was determined by the coesite-stishovite transition at 9.3 GPa and 1200°C, and Mg₂SiO₄ α - β transition at 14.5 GPa and 1400°C. At the end of planned run time, the experiments were quenched to T = 120–130°C within several seconds by shutting off the power to the apparatus, followed by programmed depressurization to atmospheric

pressure with RPM = -5 (0.037 kbar/sec) at room temperature.

Starting materials and experimental conditions

Natural graphite (University of California at Riverside Museum) and/or amorphous carbon of 99.8% purity (American Carbon Inc.) were used together with quartz, muscovite, biotite, and albite in different proportions to imitate natural diamond-bearing rocks; in some experiments, a small amount of Al₂O₃ was added. All solid ingredients were powdered to <5 micron size particles in an agate mortar with an agate pestle under ethanol, then dried for 24 hrs at 100°C in a vacuum oven. Distilled H₂O and H₂SiO₃ (chemical powder) were used as a source of fluid. The latter produces H₂O according to the reaction:



Positive control of oxygen fugacity was performed by placing Ni foil at one end of the starting material, which consumes oxygen from the interstices of the starting powder by partial reaction into NiO, and buffers $f\text{O}_2$ at a known level (-3.7 to -4 log units) at T = 1450–1500°C and P = 8.5 to 8 GPa (e.g., Sokol et. al., 2001). Experiments with the starting material surrounded by double graphite capsules were performed at lower oxygen fugacity, imitating a strongly reduced media; that was controlled by adding a layer of seeds of metallic iron placed at the end of the graphite capsule, and separated by thin graphite disk from the starting material. The reduced conditions (-8.3 to -9 log units) were confirmed by partial transformation of Fe metal to wüstite (Fe-FeO).

To exclude any presence of metal catalyst, which would accelerate diamond nucleation, we have chosen carefully the material for capsules in which we placed the starting materials. We used Pt containers despite Pt being a well-known catalyst in industrial diamond synthesis at high pressures and high temperatures, because Pt does not have any catalytic activity in the temperature/pressure/composition range chosen for our experiments. Because our run products contain volatiles, we paid special attention to the problem of volatile leakage through the welded area of the Pt capsule because the welding may thin the metal. We used double capsules with an inner Pt capsule enveloped by either an MgO or Al₂O₃ capsule of larger size. We also prepared and successfully used double graphite

self-sealed capsules, enclosed in an arc-welded Pt capsule, surrounded by a still larger MgO container (Fig. 1). After recovery of the samples from the apparatus, each of them was cut longitudinally perpendicular to the thermocouple wires and polished by our special technique (e.g., Dobrzhinetskaya et al., 2001). Both polished and raw samples were studied at 15 kV in the scanning electron microscope (SEM, Philips, XL30 FEG) equipped with an energy-dispersive X-ray spectrometer (EDAX) and by Dilor laser Raman spectroscopy with Ar^+ excitation source operated at 514.5 nm.

Experimental conditions. Experiments were performed at pressures of 8 to 8.5 GPa and temperatures of 1450–1500°C for times of 1–62 hours. Experimental conditions and a short description of run products are shown in Table 1.

Experimental Results

We conducted two different sets of experiments at high and low oxygen fugacity (Fig. 2), using Ni-NiO and Fe-FeO (IW) buffers.

Experiments with Ni-NiO buffer ($f\text{O}_2 = -3.7$ to -4 log units)

No diamond seeds were added to the starting materials. Two experiments on the Si-C-O-H system conducted with distilled water (MA-166) and with H_2SiO_3 (MA-199) produced metastable shiny flakes of graphite (Fig. 3A) and coesite. No diamond crystals were produced either in short (3 hr; MA-199), or in long-lasting (43 hr; MA-166) experiments. Run products of experiment MA-151 of 27 hrs duration (with potassium-rich muscovite added to the Si-C-O-H system) contain metastable graphite and abundant nanometric crystals of coesite, forming aggregates with a “raspberry-like” morphology (Figs. 3B–3C). Such a morphology may be explained by coesite precipitation from a Si-rich supercritical fluid. Despite a very careful search, not a single diamond was found in this run. This suggests that no carbon was dissolved in the fluid, whereas Si was dissolved in large quantity. Experiment MA-154 containing sodium component (albite) lasted 7 hrs; run products consisted of metastable graphite, jadeite, and coesite. Although it is known from many other experiments that potassium and sodium, as well as any other alkaline components added as flux, promote diamond nucleation, nevertheless, even with these components in the system, no diamonds were crystallized. Experi-

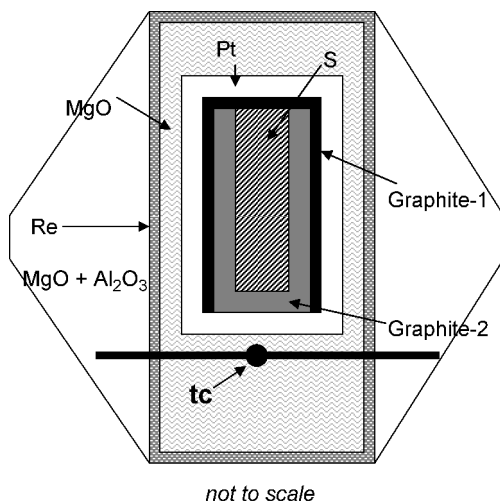


FIG. 1. 6 mm truncated-edge $\text{MgO}+\text{Al}_2\text{O}_3$ octahedron with rhenium (Re) heater (2-rolls), D-type thermocouples (tc), and an inner, mechanically sealed double graphite capsule (Graphite-1 and Graphite-2) enclosed in an arc-welded larger platinum capsule (Pt). The package of capsules is surrounded by a still larger MgO container; starting material (S) is inside the graphite capsule.

ment MA-221 containing Al_2O_3 as a flux lasted 1 hr; the run products consisted of graphite, coesite, and a few crystals of kyanite. Diamonds also were not synthesized in this run product.

Experiments with IW buffer ($f\text{O}_2 = -8.3$ to -8.7 log units)

Unlike experiments buffered with Ni-NiO, abundant diamond crystals were synthesized from the Si-C-O-H system in these low-oxygen-fugacity experiments. The rate of diamond nucleation correlates with so-called *induction* time, the time required for formation of metastable graphite prior to diamond nucleation (e.g., Akaishi and Yamaoka, 2000). For example, in experiment MA-209 (2 hrs), no diamond was crystallized, only flakes of metastable graphite, coesite, and moissanite (SiC). The first spontaneous diamond nucleation was observed in 6 hrs (MA-195); sporadic diamond crystals of 1–10 micron size nucleated along the grain boundaries of metastable graphite flakes, or between graphite and coesite. Minor elongated crystals of moissanite also were present. Examination of the run products showed that the size and amount of diamonds correlate with the duration of the experiments (t = time) at given temperature and pressure. For example, in runs MA-195, MA-210,

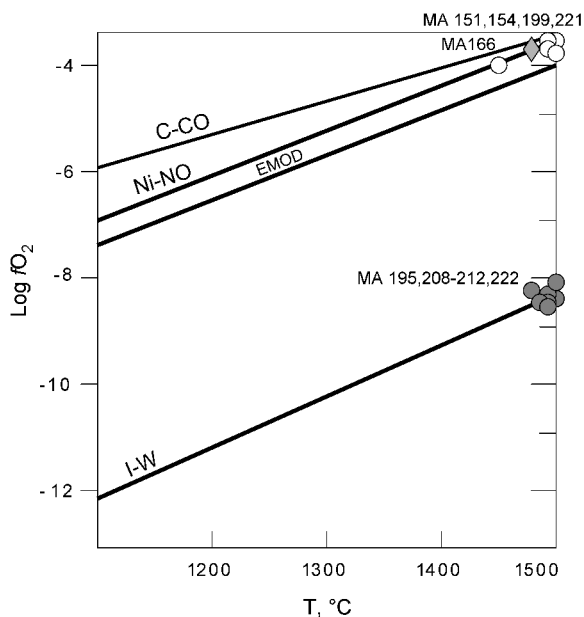


FIG. 2. Diagram of oxygen fugacity ($\log f_{O_2}$) versus temperature (T). Experiments on the Si-C-O-H system lacking diamond in the run products are plotted as open circles; grey circles present experiments with diamonds in the run products. The grey diamond symbol indicates conditions of the experiments in the Mg-C-O-H, Ca-Mg-C-O-H, and C-O-H systems where diamond was synthesized previously (Dobrzhinetskaya et al., 2004). C-CO, N-NiO, EMOD (enstatite + magnesite + olivine + diamond), and IW are known buffer curves (e.g., Eggler and Baker, 1982; Sokol et al., 2000).

and MA-208, lasting 6, 7.5, and 13 hrs, respectively, only a few sporadic diamonds, 1–15 μm in diameter, were synthesized. After 16 hours (MA-212), a larger number of 10–20 μm diamonds were generated in association with metastable graphite, coesite, and moissanite (Fig. 3E). In experiment MA-211 lasting 62 hrs, abundant 20–40 μm diamond crystals were synthesized in association with moissanite. No coesite was found in this run product.

Diamond morphology is imperfect, or skeletal-like, in runs where no diamond seeds were added (Figs. 3E–3F), whereas in the presence of artificial diamond seeds, the newly crystallized diamonds have perfect octahedral shapes (Fig. 3D).

Diamond and coesite in the run products were confirmed by Raman spectroscopy: diamonds uniformly show well-developed peaks at 1332.5–1333 cm^{-1} ; coesite is recognized by the presence of its diagnostic peak at 521 cm^{-1} . Moissanite was recognized by the presence of large (almost equal heights) of carbon and Si peaks recorded in electron energy dispersive spectra (EDS).

Discussion

Although Ni-NiO oxidation state conditions are slightly below the upper limit of the diamond stability field (C-CO) established for diamond nucleation from the C-O-H supercritical fluid at 5.7 GPa and 1200–1420°C (e.g., Sokol et al. 2001), no diamonds were crystallized in the Si-C-O-H system using the Ni-NiO buffer. Perhaps the most significant difference noted between the runs containing H_2SiO_3 and those that did not, despite the similar times spent at experimental conditions, is the presence of diamond in the run products of the former and its absence from the latter. This difference cannot be explained in terms of fluid amount because MA-166 contained 6% by weight H_2O and did not host diamond formation despite the relatively long duration (43 hrs) of the experiment. Furthermore, experiments on diamond synthesis in C-O-H fluid systems performed by other researchers (e.g., Kumar et al., 2001) have indicated that beyond a certain concentration, additional amounts of fluid do not enhance diamond growth, and that the amount of mixing among starting materials (before the powder is loaded into a

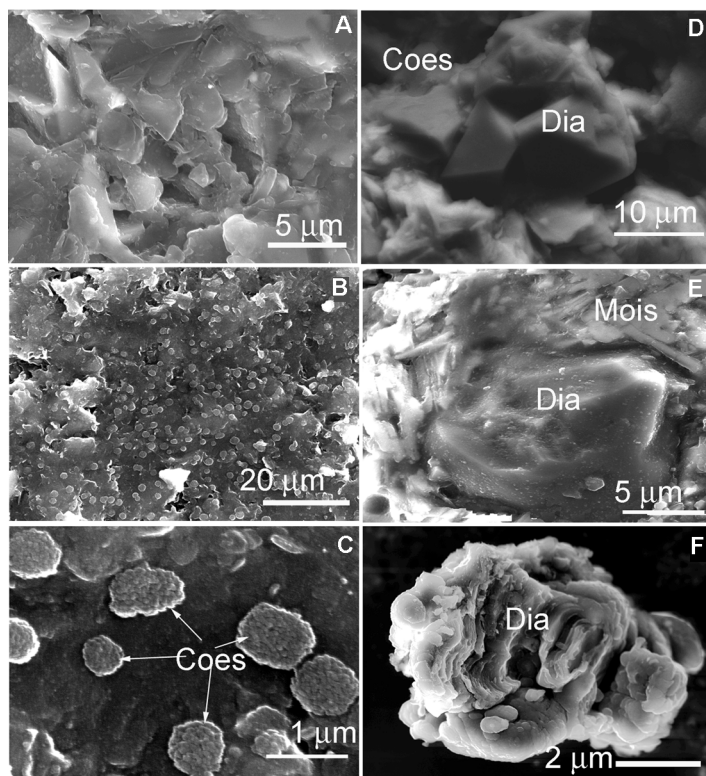


FIG. 3. SEM secondary electron images (15kV, spot size 3) of run products. A. Flakes of metastable graphite (MA-166). B. "Raspberry-like" coesite precipitates and flakes of metastable graphite (MA-151). C. Enlarged image of "raspberry-like" coesite (MA-151). D. Octahedral diamond crystals surrounded by coesite (MA-211: artificial diamond seeds were added to the starting material). E. Diamond crystal surrounded by prismatic crystals of moissanite (MA-212). F. Skeletal-like diamond (MA-210; no diamond seeds were added).

capsule) is a much more important parameter. However, the detection of moissanite in all experiments buffered to I-W might explain the differences between these two systems.

Our previous experiments on diamond synthesis in the Mg-Ca-C-O-H, Mg-C-O-H, and C-O-H systems at a temperature of 1500°C and pressure of 8.5 GPa (Dobrzhinetskaya et al., 2004) and experiments performed by others (e.g., Hong et al., 1999; Akashi and Yamaoka, 2000; Sokol et al., 2001) showed that spontaneous diamond nucleation occurs at oxygen fugacity levels as high as -3.7 to -4 log units in non-metallic C-O-H systems in the presence of Ca, Mg, K, and/or Na oxides. As a consequence, we believe that the absence of diamonds in the experiment MA-166 in the Si-C-O-H system buffered at Ni-NiO and kept at $T = 1500^\circ\text{C}$ and $P = 8$ GPa for 43 hours is not because diamond is unstable at such conditions. A better explanation is that the presence or absence of

diamonds in the run product probably is due to that fact that SiO_2 —but very little carbon—was dissolved in the fluid. Formation of raspberry-like coesite domains suggest that coesite with such a morphology was precipitated from a Si-O-H fluid. The given morphology also may rule out possible crystallization of coesite from a melt because euhedral [010] tablets of coesite were produced in experiments on high-pressure melting of granite containing ~ 3 wt% H_2O (Reiner et al., 2001).

Our experiments in the iron-wüstite-buffered system showed that diamond crystallization occurred during a three-step process: (1) thermal decomposition of H_2SiO_3 at $T = 1450\text{--}1500^\circ\text{C}$ and $P = 8.5$ GPa (Eq. 1), which releases H_2O , creating the supercritical fluid; (2) dissolution of graphite and/or silica into the fluid; and (3) enrichment of the fluid in carbon, which leads to spontaneous nucleation of diamond. The diamond growth process in the Si-C-O-H system

in I-W-buffered conditions typically entails a long (between 2 and 7 hrs) induction time, during which metastable graphite precipitated to form shiny flakes but diamond did not grow. By increasing the experimental time from 7 to 62 hours, diamond nucleated and grew along the grain boundaries of coesite, metastable graphite, and SiC, although we found no coesite in the longest run (62 hrs).

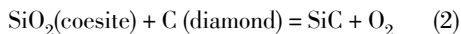
Our previous experiments in the Mg-C-O-H and Ca-Mg-C-O-H systems (Dobrzhinetskaya et al., 2004) showed that the induction time strongly decreases with increasing temperature. This observation is in agreement with experiments conducted by Akaishi et al. (2001), who also assumed that the delay time is most likely due to nucleation of diamond from dissolved carbon. The latter is supported by a variety of experimental results. One feature noted in a number of experiments is the preliminary step where graphite is recrystallized into well-formed flakes. This phenomenon preceding diamond formation has even been observed to occur when the C-O-H fluid was well within the field of diamond stability. Our experiments as well as those of others clearly show that in the presence of H₂O with or without any kind of oxides, starting graphite recrystallized from mosaic or blocky polycrystals to flaky single crystals similar to that shown in Figure 3A. A survey of the literature shows that this change started at temperatures as low as 1200°C, and became significant at 1500°C and 5–9 GPa (e.g., Yamaoka et al., 2000; Akaishi et al., 2001; Dobrzhinetskaya et al., 2004; this study). Experiments with no H₂O added to starting graphite conducted at the same P, T, and time conditions show no recrystallization of the graphite (Yamaoka et al., 2000). A possible link between metastable graphite crystallization prior to diamond nucleation is due to an energy barrier in converting from the low-symmetry *sp*² carbon bonding (graphite) to the high-symmetry *sp*³ carbon bonding of diamond. Because of the energy barrier, growing crystals tend to slowly approach a critical size, at which point the kinetics of the system allows for diamond nucleation and growth to proceed much more rapidly. In other words, this appears to be an example of the Ostwald Step Rule in which undeformed graphite replaces imperfect graphite, followed by nucleation of the stable phase, diamond.

One more remarkable feature of diamond crystallization under reducing conditions is that the size of the newly synthesized diamonds also clearly increases with increase of experimental annealing time. Perfect octahedral diamonds were synthesized

when seeds of artificial diamond were added, whereas skeletal-like and imperfect crystals crystallized without any seeds. Both observations are in good agreement with our previous observations and those of many other previous researchers (e.g., Dobrzhinetskaya et al., 2004; Sokol et al., 2001; Pal'yanov et al., 2002).

In general, our experiments suggest that, in the SiO₂-graphite-water system, only recrystallized graphite and coesite are produced during both short and long-lasting experiments at Ni-NiO buffering. Comparison of these results with our experiments performed on SiO₂-free systems (Dobrzhinetskaya et al., 2004), as well as those of many others (e.g., Hong et al., 1999; Sato et al., 1999; Akaishi and Yamaoka, 2000) show that at a similar level of *f*O₂ and even slightly higher (C-CO buffer), diamond nucleation becomes conspicuous.

Contrarily, in the same SiO₂-graphite-water system at reduced conditions controlled by the I-W buffer, diamond nucleation and growth occurs accompanied by crystallization of moissanite and coesite. The three minerals diamond, coesite, and moissanite coexist if the reaction



has not run to completion, establishing a new oxygen buffer. However, with longer reaction times, all SiO₂ reacts with carbon, producing abundant moissanite crystals (with no coesite left) associated with diamonds, as we have observed in the 62-hour experiment.

Although our intention had been to control oxygen fugacity by the I-W buffer, the presence of moissanite suggests that the real oxygen fugacity was below the I-W buffer. At ambient pressure, the *f*O₂ stability field of moissanite is about –14 to –15 log units, about six log units below the I-W buffer (Mathez et al., 1995). Although experimental data on the *f*O₂ moissanite stability field at high pressures do not exist, Mathez et al. (1995), using thermochemical data, calculated the stability field of moissanite in an Fe-free model peridotite composition for mantle pressures. Their calculations show that in that system at P = 9 GPa and T = 1527°C, the reaction in Eq. 2 occurred at –12 log units of *f*O₂, whereas the *f*O₂ of the I-W buffer corresponds to –7 log units. However, no experiments or calculations are available yet on the *f*O₂ dependence of moissanite stability in a SiO₂-rich system.

The design of our experimental program did not allow us to establish the upper level of oxidizing

conditions at which diamond might crystallize in Si-C-O-H media. At this point, we know only that this system buffered to -3.7 to -4 log units does not allow diamond crystallization at our chosen HP and HT conditions in less than 43 hrs. The understanding of diamond crystallization from a Si-C-O-H medium at an oxidation level between -4 and -8.3 log units awaits additional experimental work.

Implications for Natural Rocks

Both academic studies and industrial exploration and prospecting of the Kokchetav deposit have shown that diamond distribution in the rocks is inhomogeneous: some marbles are free of diamonds, some contain up to 2700 carats/ton, whereas the average content of diamonds in felsic gneisses and quartzites is ~ 20 – 30 carats/ton. The rarity or absence of diamonds in some lithologies is often explained as due to a complete replacement of diamond by graphite during recrystallization of rock-forming minerals at low temperatures and low pressures during exhumation, or due to a very low concentration of CO_2 ($X_{\text{CO}_2} < 0.01$), or both (Ogasawara et al., 2000; Ogasawara, 2005). Given that many factors may influence the diamond concentrations in rocks, our experiments suggest one more factor, differences in oxygen fugacity in SiO_2 -rich and SiO_2 -poor bulk-rock chemistry, that might control the abundance or absence of diamonds.

Geologists from the Kokchetav Geological Survey (Kazakhstan) have reported finding moissanite together with diamonds within the heavy mineral fraction obtained during exploration of the Kumdykol diamond deposit (Ekimova et al., 1992). Unfortunately the presence of moissanite together with diamond in the Kokchetav rocks has never been taken seriously due to a psychological barrier on the part of many scientists, who have believed that there is enough artificial SiC scattered around the globe to "provide a dozen dust-size particles on every square meter of [it's] surface" (Milton and Vitaliano, 1985). However, after extensive research by Leung et al. (1990, 1996) and others (e.g., Mathez et al., 1995; Di Pierro et al., 2003), there is no doubt that moissanite may occur in terrestrial rocks, and it is an important mineral recording reducing conditions in the Earth's mantle. Therefore, moissanite found in heavy mineral separates from the Kokchetav diamond-bearing rocks is unlikely to be an artifact of contamination. Such mineral assemblages (diamond + moissanite) were

produced in our experiments in a Si-C-O-H chemical medium with $f\text{O}_2 = -8.3$ to -8.7 log units, and probably would also coexist at 5 – 6 log units lower. In the Kokchetav massif, both diamond-bearing and diamond-free Ca- and Mg-rich carbonate rocks occur. Our results suggest an alternative interpretation to that of Ogasawara et al. (2000). Instead of explaining the absence of diamonds by a very low concentration of CO_2 ($X_{\text{CO}_2} < 0.01$), we suggest that varying $f\text{O}_2$ must also be considered as an important factor influencing diamond formation. This interpretation is also consistent with the observation of pyrite (FeS_2) and other sulfides in rocks with large diamond concentrations (Ekimova et al., 1992), also indicating the possible controlling effects of redox reactions. Further petrographic studies of the diamond-bearing rocks should address these questions through the special search for independent mineralogical records related to the evaluation of the attending $f\text{O}_2$. This argument also suggests that the rarity of diamonds in SiO_2 -rich rocks may be attributed to a high level of oxygen fugacity.

Conclusions

In this study, diamond crystallized in the system Si-C-O-H only at low $f\text{O}_2$ levels (below -3.7 to -4 log units), whereas previously we and others showed that Ca- and Mg-rich C-O-H media favor diamond nucleation and growth under such conditions. The new experiments suggest that SiO_2 may serve as an inhibitor to carbon dissolution and thus, to diamond preferential growth under more reducing conditions, but not at the upper limit of the oxygen fugacity where diamond is still stable in Ca- and Mg-rich media without SiO_2 . Our results are in agreement with a previous determination that SiO_2 solubility in hydrous fluid drops drastically if water activity is reduced by adding either CO_2 or CH_4 (Walter and Orville, 1983). The result provides a new constraint on diamond crystallization in SiO_2 -rich and in SiO_2 -poor media, and therefore may have implications for interpretation of natural diamond-bearing metamorphic rocks. To further study the behavior of Si-C-O-H systems, thermodynamic modeling of fluid-bearing phases needs to be undertaken, with special attention paid to the value of the oxygen fugacity.

Acknowledgments

We thank Frank Forgit for technical assistance with our experiments. Profs. H. Kanda and H. Kagi,

and Dr. J. Zhang are appreciated for fruitful discussions and for the constructive suggestions to improve the manuscript. The project was supported by grants EAR-0107118 and EAR-02296666 from the National Science Foundation.

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