

Synthesis of skeletal diamonds: Implications for microdiamond formation in orogenic belts

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ABSTRACT

Diamond was synthesized at high temperature and pressure in a Walker-style multianvil apparatus from various supercritical C-O-H-rich fluid compositional systems. Depending on the type and amount of impurities added to the system, diamonds of varying morphology and bearing solid oxide inclusions were found within the run product. These characteristics bear a striking resemblance to metamorphic microdiamonds recovered from the Kokchetav massif, Kazakhstan; these natural diamonds share morphological traits with our synthesized diamonds, and both the natural and synthesized diamonds contain similar solid oxide inclusions. Our data favor formation of Kokchetav diamonds via crystallization from a supercritical C-O-H fluid, rather than from carbonate or carbonatite melt, as others have suggested.

Keywords: diamond, hydroxyl, supercritical C-O-H fluid, high pressure, high temperature.

INTRODUCTION

The discovery of microdiamonds within metamorphic rocks of continental affinity (Sobolev and Shatsky, 1990; Xu et al., 1992; Dobrzhinetskaya et al., 1995) suggests that part of the continental crust was subducted to a minimum depth of 100–120 km during continental collision and then returned to the surface by tectonic processes that are still poorly understood. Until recently, subduction of continental materials to such depths had been thought impossible. However, the list of such diamond-bearing regions has grown (Massonne, 1999; Van Roermund et al., 2002; Bostick et al., 2003; Yang et al., 2003), suggesting that deep subduction of crustal material during collision of continental plates is probably common; this has significant implications for the process of plate tectonics and for the mixing of mantle and crustal materials at great depth.

The most remarkable features that distinguish microdiamonds of orogenic belt formations from those in kimberlite pipes are the irregular skeletal-like forms of crystals (Fig. 1A). Two hypotheses of diamond origin have been formulated: growth from C-O-H-bearing fluid (e.g., De Corte et al., 1998; Ogasawara, 2001; Dobrzhinetskaya et al., 2001, 2003a, 2003b; Stöckhert et al., 2001) versus growth from a melt (e.g., Massonne, 2001; Shatsky et al., 2001; Hwang et al., 2001).

Initial experimentation on the graphite-to-diamond transformation at high pressures (P) and temperatures (T) was successful only in the presence of metal-solvent catalysts (Bundy, 1961). Subsequently, however, octahedral and rare cube-octahedral diamonds were synthesized from a supercritical C-O-H fluid at varying oxygen fugacity (f_{O_2}) and from volatile-rich alkaline-carbonate melt at $P = 5$ – 10 GPa and $T = \sim 1250$ – 2200 °C in a variety of compositional systems (e.g., Taniguchi et al., 1996; Hong et al., 1999; Akaishi and Yamaoka, 2000; Pal'yanov et al., 2002). Nevertheless, no imperfect, skeletal-like, diamond crystals similar to natural diamonds from orogenic belts were produced in the mentioned experiments. Conversely, experiments conducted by Kanda et al. (1984) at $P = 6$ GPa and $T = 1500$ °C by the metal-solvent catalysts method with $Mg(OH)_2$ as a source of hydroxyl resulted in octahedral diamonds at <1 vol% of $Mg(OH)_2$ and hollow-hopper and skeletal-like crystals at ~ 2 vol% of $Mg(OH)_2$.

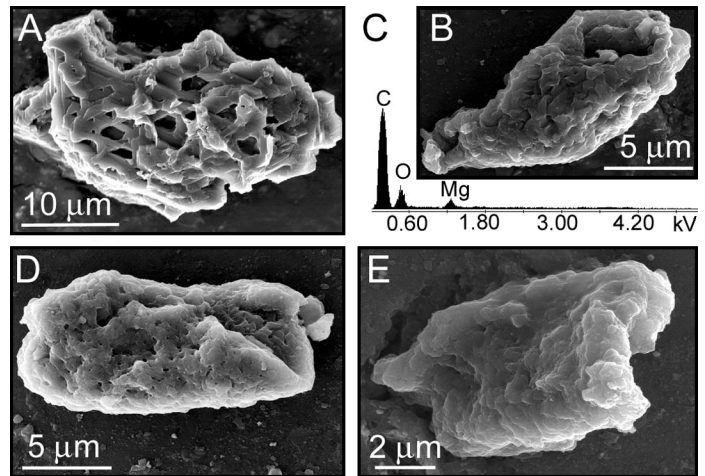


Figure 1. Secondary-electron scanning electron microscope images showing morphologies of (A) natural and (B, D, and E) synthetic diamonds. C: Energy-dispersive X-ray spectrum for diamond in B. Natural diamonds are separates from felsic gneiss of Kokchetav massif, Kazakhstan. Synthetic diamonds are crystallized from graphite + $Mg(OH)_2$ systems and exhibit irregular skeletal morphology similar to that of diamonds from natural rocks. Diamond structure was confirmed by Raman spectroscopy (all synthesized diamonds are characterized by sharp Raman peak at 1332 ± 3 cm^{-1} similar to that shown in Fig. 3B).

Here we report the first experimental production of skeletal-like diamonds from graphite in a supercritical hydrous fluid in three different compositional systems near the upper limit of oxygen fugacity compatible with diamond stabilization (e.g., Dienes, 1980; Egglar and Baker, 1982). Our experiments produced diamond from a supercritical C-O-H fluid in the presence of (1) Mg^{2+} and Si^{4+} cations derived from the dehydration reactions of brucite and talc and (2) Ca^{2+} (aragonite) due to breakdown of dolomite. These experiments show that the imperfect, skeletal-like forms of the diamonds are determined by the type of impurities added to the C-O-H system.

EXPERIMENTAL PROCEDURE

Experiments were performed in a Walker-style multianvil apparatus (Walker, 1991) by using a sample assembly and calibration technique described in Dobrzhinetskaya et al. (2000). Temperature was measured with W3%Re-W25%Re thermocouples and maintained constant to within ± 5 °C; uncertainties of pressure calibration combined with small variations in the oil pressure correspond nominally to a total uncertainty in pressure of <0.3 GPa. Temperature was not corrected for the effect of pressure on the thermocouple electromotive force (emf). Ni foil was added to some charges to buffer f_{O_2} at Ni-NiO, which approximately corresponds to a $-\log f_{O_2}$ of 6 and 4.5 for runs at 1200 °C and 1500 °C, respectively, and is near the upper limit of f_{O_2} for diamond stability (Egglar and Baker, 1982). Some experiments were performed without placing Ni foil into the assembly; in such experiments, f_{O_2} was estimated from the ratio of hydrogen to oxygen ($[H]/[O]$) included in the starting materials (e.g., Akaishi et al., 2001).

We have conducted three series of experiments at $P = 7.5$ – 8.5

GPa, $T = 1200\text{--}1500\text{ }^{\circ}\text{C}$, and duration $t = 1\text{--}138\text{ h}$ to explore diamond crystallization from graphite (99.9% pure carbon, American Carbon Inc.) and natural coal (Ward's) alone or in the presence of dolomite or calcite and with brucite $\text{Mg}(\text{OH})_2$, talc $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$, and oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) as sources of hydroxyl. Powders (5–10 μm size) were separately mixed with hydroxyl-containing compounds and placed in a Pt container as two sandwiched layers to observe differences in diamond nucleation from amorphous (coal) and crystalline carbon (graphite). Although Pt is considered among the metal-solvent catalysts, it does not act as a catalyst below its melting point (e.g., Bundy, 1961). No diamond seeds were added to any of our experiments to avoid their influence on the kinetics of diamond crystallization.

All experiments were quenched to $<100\text{ }^{\circ}\text{C}$ within a few seconds by shutting off power to the apparatus, then slowly depressurized at room temperature. Samples were cut into two pieces, one of which was polished by using our special technique (e.g., Dobrzhinetskaya et al., 2001). Both polished and raw run products were examined through the use of secondary electrons at 10–15 kV by scanning electron microscope (SEM, Philips XL30 FEG) equipped with an energy-dispersive X-ray spectrometer and by laser Raman spectroscopy. Some samples were carefully picked apart with a needle and etched in HF to remove the products of breakdown reactions, to better observe the morphologies of diamond.

RESULTS

Conditions of experiments are summarized in Table DR1 (see GSA Data Repository¹). We provide short descriptions for three series containing different hydroxyl-bearing components.

Series 1: Graphite + Coal + $\text{Mg}(\text{OH})_2$ System

Experiments at $1200\text{ }^{\circ}\text{C}$ were performed at 7.5–8.0 GPa for 1–122 h (runs MA126, MA128, MA130, and MA131) with 2–5 wt% of $\text{Mg}(\text{OH})_2$. Only metastably recrystallized graphite flakes were detected in run products held at $T = 1200\text{ }^{\circ}\text{C}$ for runs to 24 h, but a few spontaneously nucleated, skeletal-like, 2–3- μm -diameter diamonds were detected after 122 h. In this run, powdered graphite and coal were completely recrystallized to flakes of metastable graphite, and diamonds were nucleated at the graphite-MgO interface; a few minute diamonds ($<1\text{ }\mu\text{m}$) nucleated inside of graphite flakes.

The rate of diamond nucleation increased drastically at $1500\text{ }^{\circ}\text{C}$. Within 5 h, a few percent of 2–5 μm skeletal diamonds were found (run MA133); after 138 h, almost all graphite and coal converted to diamonds of 30–50 μm diameter (run MA134). In the coldest part of the Pt capsule, where—on the basis of our knowledge of thermal gradients in heaters of this design—the temperature is $\sim 50\text{ }^{\circ}\text{C}$ less than that measured at the thermocouple, we mostly observed flakes of newly recrystallized graphite rather than diamonds. The morphology of diamonds synthesized at $1500\text{ }^{\circ}\text{C}$ over 138 h is similar to the morphologies of diamonds retrieved from natural rocks; the synthesized diamonds consist of imperfect crystals, some of which contain large cavities (Figs. 1B, 1D, 1E). Energy-dispersive X-ray spectra (EDS) of such diamonds show an intense carbon peak and two small peaks of Mg and oxygen, probably indicating tiny MgO inclusions derived from starting brucite (Fig. 2C). Similar EDS observations previously made in Kokchetav and Erzgebirge diamonds were subsequently revealed by transmission electron microscopy (TEM) to indicate the presence of solid, nanometer-scale inclusions of oxides (Dobrzhinetskaya et al., 2001, 2003a, 2003b). No differences were observed in any of the char-

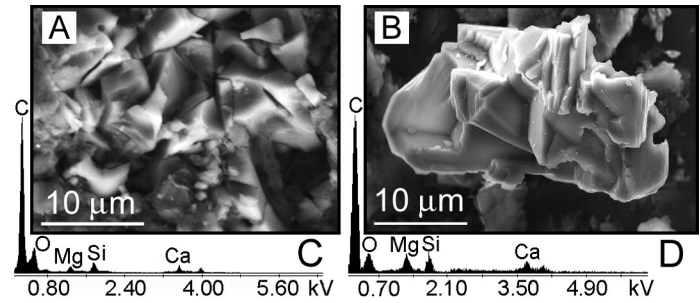


Figure 2. Secondary-electron scanning electron microscope images showing morphology of synthesized diamond crystallized from (A) dolomite + talc + graphite medium and (B) calcite + talc + graphite medium. Energy-dispersive X-ray spectra for (C) diamond in A and (D) diamond in B demonstrate presence of Si, Mg, and O impurities. Higher peak of Mg recognized in diamond of system containing dolomite.

acteristics we examined between those diamonds in our samples that started with coal and those that started with graphite.

Experiments of series 1 suggest that brucite was dehydrated according to the reaction

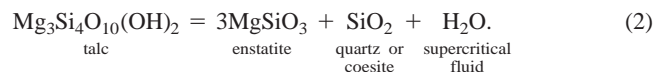


The liberated aqueous fluid dissolves carbon from both graphite and coal, as well as some Mg^{2+} from MgO; spontaneous diamond nucleation then proceeds at the interfaces of periclase and newly recrystallized metastable graphite. Although diamond nucleation from C-O-H fluid occurs faster at higher temperature ($1500\text{ }^{\circ}\text{C}$) than in runs at $1200\text{ }^{\circ}\text{C}$, it seems to be that under the chosen conditions, the abundance of brucite (and, therefore, the amount of liberated water) has little influence on the speed of diamond nucleation and growth. Experiments performed at $1200\text{ }^{\circ}\text{C}$ clearly demonstrate that there is a significant induction time (τ) before diamond nucleation occurs, which explains the minimal diamond yield of samples MA131 and MA133.

Series 2: Carbonates (Calcite and Dolomite) + Graphite + Talc

Spontaneous nucleation of diamond (crystal sizes 10–30 μm) was observed after 19 h in MA156 (Fig. 2A) and after 34 h in MA153 at 8.1 GPa and $1500\text{ }^{\circ}\text{C}$ (Fig. 2B). EDS spectra of diamond from calcite + graphite + talc display a strong carbon peak and small peaks of Ca, Mg, Si, and oxygen (Fig. 2C), whereas diamonds from dolomite + graphite + talc have similar peaks with a larger Mg peak (Fig. 2D). We expect that such diamonds contain tiny inclusions composed of Ca, Mg, Si, O, and perhaps CO_3 radical; however, special TEM-EDS studies need to be performed to determine their stoichiometry.

No melt was produced in these experiments; diamond was nucleated after liberation of water occurred during talc breakdown according to the following reaction, experimentally studied at 5 GPa and $710\text{ }^{\circ}\text{C}$ (Pawly and Wood, 1995):



Both coesite and enstatite, as well as flakes of metastable graphite, were detected in both experiments. Diamonds were observed at the interfaces between aragonite and graphite and between magnesite and aragonite or graphite. Such assemblages indicate that calcite was transformed to its high-pressure analogue, aragonite, and dolomite was decomposed during the reaction

¹GSA Data Repository item 2004144, Table DR1, experimental conditions and results, is available online at www.geosociety.org/pubs/ft2004.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

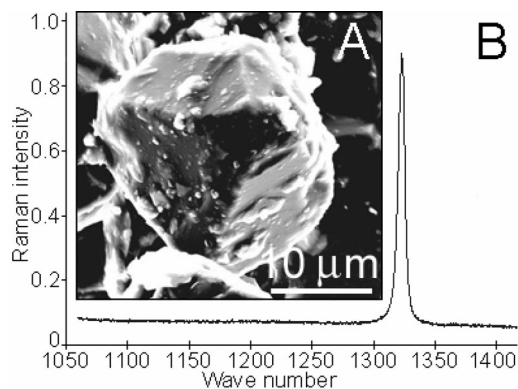


Figure 3. A: Secondary-electron scanning electron microscope image of diamond synthesized from $C_2H_2O_4 \cdot 2H_2O$. B: Raman peak at 1332 cm^{-1} for diamond in A.



In such a system, diamond coexists with magnesite and aragonite. The diamonds mostly have cuboidal (Fig. 2A) or more irregular skeletal forms (Fig. 2B) with elements of {100} faces several micrometers in size, although some crystals developed octahedral faces as well. Comparison between calcite- and dolomite-bearing run products suggests that dolomite exhibits systematically greater catalytic activity, thereby promoting diamond nucleation faster than calcite.

Series 3: Graphite + Oxalic Acid Dihydrate

Unlike experiments of series 1 and 2, abundant perfect octahedral and cube-octahedral diamond crystals of 30–40 μm were synthesized from this system. After 32 h at $P = 8.5\text{ GPa}$ and $T = 1500\text{ °C}$, ~20–25 vol% of diamond was found within recrystallized graphite (MA165), whereas in 120 h (MA162), almost all graphite was transformed to cube-octahedral to octahedral diamonds; the diamond structure was confirmed by Raman spectroscopy (Figs. 3A, 3B). EDS spectra revealed only one intense peak of C. According to the thermodynamic calculations, the fluid-driving agent, oxalic acid dihydrate, mixed with graphite in the proportion 70:30 at $P = 7.7\text{ GPa}$ and $T = \sim 1400\text{ °C}$, will generate (in mol%) 66H₂O:31CO₂:2CO: $(<1)CH_4$ (<1)H₂ at $\log f_{O_2} = -4.34$, meaning that spontaneous diamond nucleation occurred in a relatively oxidized C-O-H fluid. The experiments also show that the abundance of diamond and disappearance of metastable graphite depend on time. Surprisingly, diamonds in both the short-term and long-term runs have similar sizes of no more than ~40–50 μm.

DISCUSSION

All three experimental series provide evidence that diamond was crystallized from a supercritical C-O-H fluid with $[H]/[O] \leq 2$, which appeared in the system during breakdown of hydroxyl or water-bearing components. The $[H]/[O]$ fluid ratio is inferred from the composition of the hydroxyl-bearing components added as a source of water to the starting materials according to the ternary diagram of H₂O, CO₂, and CH₄ (e.g., Deines, 1980) and thermodynamic calculations on organic compounds. Liberated H₂O (fluid) dissolved C and other cations, and after a certain period of time τ , spontaneous diamond nucleation commenced. The novel result of our experiments is that we produced diamonds of imperfect, skeletal-like morphologies with cavities and channels similar to those retrieved from natural rocks of the Kokchetav massif (Dobrzhinetskaya et al., 2001). Because the fluid was mostly CO₂-H₂O in all three series, and no diamond seeds were added to the

starting material, we conclude that the morphological variation observed in diamond may be explained by differences in the composition of the impurities. These impurities include Mg in diamonds from experiments of series 1 and Ca, Mg, and Si in diamonds of series 2; impurities are absent in octahedral diamonds of series 3. Moreover, Mg-doped media yielded the most imperfect crystals, similar to those produced by Kanda et al. (1984) in the presence of 2% (MgOH)₂, whereas carbonate-rich media with impurities of Ca, Mg, and Si promoted nucleation of diamond crystals with elements of the thermodynamically more stable {100} and {111} faces. Perhaps the most striking illustration of this effect is the crystallization of distinctly different diamond morphology in run MA153 (cuboidal) as compared to that in run MA156 (skeletal), even though the two experiments differ only by the substitution of calcite for dolomite, e.g., by adding Mg impurities to the system. Perfect octahedral forms of diamond were observed only in the experiments having just the CO₂-H₂O fluid, in which no impurities were added (series 3). Other researchers (Akaishi and Yamaoka, 2000; Yamaoka et al., 2000) synthesized well-faceted diamonds at $P = \sim 5\text{--}8\text{ GPa}$ and $T = \sim 1200\text{--}2000\text{ °C}$ from starting materials containing graphite, oxalic acid dihydrate, silver oxalate, anthracene, and H₂O. The C-O-H fluid in these experiments did not contain any crystalline impurities and consequently allowed diamonds of perfect octahedral form to grow. In comparing the results of our experiments of series 1 and 2 to those of series 3 and to the others mentioned here, we demonstrate that impurities cause diamonds of imperfect morphologies to crystallize from a C-O-H fluid.

The second notable feature of crystallization in the C-O-H fluid environments reported here is the considerable induction time for diamond nucleation and appearance of metastable graphite prior to diamond nucleation. This delay time is observed to decrease with increasing temperature at constant pressure. A possible link between the tendency of C-O-H fluids to induce metastable graphite recrystallization prior to diamond nucleation and the induction time may be explained as a consequence of the energy barrier faced in converting from sp^2 to sp^3 carbon bonding. Owing to this barrier, growing crystals tend to slowly approach a critical size, at which point the kinetics of the system allows for diamond growth to proceed much more rapidly (Chernov, 1974). The presence of minute diamond (1 μm) on a flake of graphite (MA130) needs to be reproduced by additional experiments and investigated at the atomic level, because this is an important observation that may provide a better understanding of the graphite-to-diamond transformation.

Contrary to the conclusions based on experiments in metal-carbon systems that diamond morphology depends primarily on P - T conditions and rate of crystallization (cf. Sunagawa, 1993), we conclude that diamond morphology in C-O-H fluid + X systems depends on the composition of X (e.g., its chemical potential and solubility at given conditions), which is the crystallization medium. Although other workers using conditions close to ours were able to synthesize perfect octahedral and cube-octahedral forms (Yamaoka et al., 2000; Pal'yanov et al., 2002), we suspect that these dramatic differences in diamond morphologies are a consequence of differing kinetics of diamond crystallization caused by the addition of diamond seeds to the starting materials in the previous experiments.

Another dramatic difference in the experimental determination of a possible mechanism of diamond origin in orogenic belts is high temperature (~1700 °C) applied to the natural carbonate rocks from the Kokchetav massif by Shatsky et al. (2001). At these conditions, an alkaline-carbonate melt containing octahedral diamonds was produced, whereas our experiments produced no melt to assist the diamond nucleation. In terms of explaining the natural occurrences, the alkaline-carbonate melt experiments do not account for the presence of molecular water and the compositional diversity of nanometer-scale

inclusions (mostly SiO₂ and TiO₂), which are established in Kokchetav diamonds (e.g., De Corte et al., 1998; Dobrzhinetskaya et al., 2001, 2003b). The hypothesis of Shatsky et al. (2001) also offers no explanation of how carbonate and carbonatite melt could have intruded quartzites and feldspathic gneisses, where it promoted diamond nucleation, but then disappeared without any evidence of such an intrusion or intermixing with Si- and Si-Al-rich materials. In contrast, the C-O-H fluid hypothesis appears consistent with both natural and experimental observations.

Diamond synthesis experiments have been conducted over many years by a large number of high-pressure laboratories, both in academia and in industry. These studies have shown that diamond can be grown at high pressures and temperatures from molten metal-solvent catalysts, from carbonates, alkaline-carbonate melt, and from fluids dominated by CH₄, CO₂, and H₂O. Many of these studies have been in search of means to synthesize gem diamonds for jewelry and industry; whereas studies for specific geological investigation have been rare. These studies and our work show that diamond may be crystallized from essentially any carbon source, so long as the system chosen can host a fluid supersaturated in carbon, and the pressure, temperature, and oxygen fugacity conditions correspond to the diamond stability field. These conditions are consistent with those determined for diamonds and associated hydrous mineral phases (e.g., phengite, clinohumite) occurring in ultrahigh-*P* (UHP) metamorphic terranes. The supercritical fluid generated at UHP by dehydration reactions can dissolve a considerable amount of carbon along with many other components; it can be not only a source for diamond growth, but may also provide a decisive weakening effect on rheological behavior of the rocks during deep subduction, or lead to brittle failure and earthquakes (e.g., Jung et al., 2004).

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REFERENCES CITED

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

Akaishi, M., Kumar, M.D.S., Kanda, H., and Yamaoka, S., 2001, Reactions between carbon and a reduced C-O-H fluid under diamond-stable HP-HT condition: *Diamond and Related Materials*, v. 10, p. 2125–2130.

Bostick, B.C., Jones, R.E., Chen, C., Ernst, W.G., Leech, M.L., and Beane, R.J., 2003, Low-temperature microdiamond aggregates in the Maksutov Metamorphic Complex, South Ural Mountains, Russia: *American Mineralogist*, v. 88, p. 1709–1717.

Bundy, F.P.J., 1961, Direct conversion of graphite to diamond in static pressure apparatus: *Journal of Chemical Physics*, v. 41, p. 631–635.

Chernov, A.A., 1974, Stability of faceted shapes: *Journal of Crystal Growth*, v. 24–25, p. 11–31.

De Corte, K., Cartigny, P., Shatsky, V.S., Sobolev, N., and Javoy, M., 1998, Evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, northern Kazakhstan: *Geochimica et Cosmochimica Acta*, v. 62, p. 3765–3773.

Deines, P., 1980, The carbon isotopic composition of diamonds—Relationship to diamond shape, color, occurrence and vapor composition: *Geochimica et Cosmochimica Acta*, v. 44, p. 943–961.

Dobrzhinetskaya, L.F., Eide, E., Korneliussen, A., Larsen, R., Millege, J., Posukhova, T.V., Smith, D.S., Sturt, B.A., Taylor, W.R., and Tronnes, R.G., 1995, Diamond in metamorphic rocks of the Western Gneiss Region in Norway: *Geology*, v. 23, p. 597–600.

Dobrzhinetskaya, L.F., Bozhilov, K.N., and Green, H.W., II, 2000, The solubility of TiO₂ in olivine: Implications for the mantle wedge environment: *Chemical Geology*, v. 163, p. 325–338.

Dobrzhinetskaya, L.F., Green, H.W., II, Mitchell, T.E., and Dickerson, R.M., 2001, Metamorphic diamonds: Mechanism of growth and inclusion of oxides: *Geology*, v. 29, p. 263–266.

Dobrzhinetskaya, L.F., Green, H.W., II, Weshler, M., Darus, M., Wang, Y.-C., Massonne, H.-J., and Stöckhert, B., 2003a, Focused ion beam technique

and transmission electron microscope studies of metamorphic diamonds from the Saxonian Erzgebirge, Germany: *Earth and Planetary Science Letters*, v. 210, p. 399–410.

Dobrzhinetskaya, L.F., Green, H.W., II, Mitchell, T.E., Dickerson, R.M., and Bozhilov, K.N., 2003b, Crystallization environment of Kazakhstan microdiamonds: Evidence from nanometric inclusions and mineral associations: *Journal of Metamorphic Geology*, v. 21, p. 425–437.

Eggler, D.H., and Baker, D.R., 1982, Reduced volatiles in the system C-O-H: Implications to mantle melting, fluid formation, and diamond genesis, in Akimoto, S., and Manghni, M.H., eds., *High pressure research in geophysics*: Tokyo, Japan, Center for Academic Publications, p. 237–250.

Hong, S.M., Akaishi, M., and Yamaoka, S., 1999, Nucleation of diamond in the system of carbon and water under very high pressure and temperature: *Journal of Crystal Growth*, v. 200, p. 326–328.

Hwang, S.L., Shen, P., Chu, H.T., Yui, T.F., and Lin, C.C., 2001, Genesis of microdiamonds from melt and associated multiphase inclusions in garnet of ultrahigh-pressure gneiss from Erzgebirge, Germany: *Earth and Planetary Science Letters*, v. 188, p. 9–15.

Jung, H., Green, H.W., and Dobrzhinetskaya, L.F., 2004, Intermediate-depth earthquake faulting by dehydration embrittlement with negative volume change: *Nature*, v. 428, p. 545–549.

Kanda, H., Akaishi, M., and Yamaoka, S., 1984, New catalysts for diamond growth under high pressure and high temperature: *Applied Physics Letters*, v. 65, p. 784–786.

Massonne, H.-J., 1999, A new occurrence of microdiamonds in quartzofeldspathic rocks of the Saxonian Erzgebirge, Germany, and their metamorphic evolution, in *Proceedings, 7th International Kimberlite Conference, 1999*: Cape Town, South Africa, Red Roof Design, p. 533–539.

Massonne, H.-J., 2001, Origin of microdiamond-bearing quartzofeldspathic rocks (Sadenbachites) from the Erzgebirge, Germany: A progress report, in *Proceedings, UHPM Workshop 2001*: Tokyo, Japan, Waseda University, p. 11–15.

Ogasawara, Y., 2001, Fluid control on metamorphic evolution of deeply subducted carbonates: The case of Kokchetav UHP rocks: *Virginia Polytechnic Institute and State University, Goldschmidt Conference, 11th*, Hot Springs, Virginia, USA, Abstract 3609.

Pal'yanov, Y.N., Sokol, A.G., Borzdov, Y.M., and Khokhryakov, A.F., 2002, Fluid-bearing alkaline carbonate melts as the medium for the formation of diamonds in the Earth's mantle: An experimental study: *Lithos*, v. 60, p. 145–159.

Pawly, A.R., and Wood, B.J., 1995, The high pressure stability of talc and 10 Å phase: Potential storage sites for H₂O in subduction zones: *American Mineralogist*, v. 80, p. 998–1003.

Shatsky, V.S., Pal'yanov, Y.N., Sokol, A.G., Tomilenko, A.A., and Sobolev, N.V., 2001, Diamond formation in UHP metamorphic rocks: Natural and experimental evidence, in *Proceedings, UHPM Workshop 2001*: Tokyo, Japan, Waseda University, p. 6–10.

Sobolev, N.V., and Shatsky, V.S., 1990, Diamond inclusions in garnets from metamorphic rocks: A new environment of diamond formation: *Nature*, v. 343, p. 742–746.

Stöckhert, B., Duyster, J., Trepman, C., and Massonne, H.J., 2001, Microdiamond daughter crystals precipitated from supercritical COH plus silicate fluids included in garnet, Erzgebirge, Germany: *Geology*, v. 29, p. 391–394.

Sunagawa, I., 1993, In-situ investigation on growth and dissolution of crystals in aqueous-solution: *Aquatic Sciences*, v. 55, p. 347–357.

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-K₂Mg(CO₃) systems at high pressure of 9–10 GPa region: *Journal of Materials Research*, v. 11, p. 2622.

Van Roermund, H.L.M., Carswell, D.A., Drury, M.R., and Heijboer, T.C., 2002, Microdiamonds in megacrystic garnet websterite pod from Bardane on the island of Fjortoft, western Norway: Evidence for diamond formation in mantle rocks during deep continental subduction: *Geology*, v. 30, p. 959–962.

Walker, D., 1991, Lubrication, gasketing, and precision in multianvil experiments: *American Mineralogist*, v. 76, p. 1092–1100.

Xu, S.T., Okay, A.I., Ji, S.Y., Senog, A.M.C., Wen, S., Liu, Y.C., and Jiang, L.L., 1992, Diamond from the Dabie-Shan metamorphic rocks and its implication for tectonic setting: *Science*, v. 256, p. 80–82.

Yamaoka, S., Kumar, S.M.D., Akaishi, M., and Kanda, H., 2000, Reaction between carbon and water under diamond-stable high pressure and high temperature conditions: *Diamond and Related Materials*, v. 9, p. 1480–1486.

Yang, J., Xu, Z., Dobrzhinetskaya, L.F., Green, H.W., II, Pei, X., Shi, R., Wu, C., Wooden, J.L., Zhang, J., Wan, Y., and Li, H., 2003, Discovery of metamorphic diamonds in central China: An indication of a ≥4000-km-long zone of deep subduction resulting from multiple continental collisions: *Terra Nova*, v. 15, p. 370–379.

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