



High-pressure experimental growth of diamond using C–K₂CO₃–KCl as an analogue for Cl-bearing carbonate fluid

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Abstract

High-pressure, high-temperature diamond growth experiments have been conducted in the system C–K₂CO₃–KCl at 1050–1420 °C, 7.0–7.7 GPa. KCl is of interest because of the strong effect of halogens on the phase relations of carbonate-rich systems [Geophys. Res. Lett. 30 (2003) 1022] and because of the occurrence of KCl coexisting with alkali silicate–carbonate fluids in natural-coated diamond [Geochim. Cosmochim. Acta 64 (2000) 717]. We have used system C–K₂CO₃–KCl as an analogue for these mantle fluids in diamond growth experiments. The presence of KCl reduces the potassium carbonate liquidus to ≤1000 °C at 7.7 GPa, allowing it to act as a solvent catalyst for diamond growth at temperatures below the continental geotherm. This is a reduction on the minimum diamond growth temperature reported in the alkali-carbonate–C–O–H system [Lithos 60 (2002) 145]. Diamond growth using carbonate solvent catalysts is characterised by a relatively long induction period. However, the addition of KCl also reduced the period for diamond growth in carbonate to ≪5 min; no such induction period appears to be necessary. It is suggested that KCl destabilises carbonate, allowing greater solubility and diffusion of carbon.

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1. Introduction

Crystalline (Stachel and Harris, 1997) and fluid (Navon, 1991) inclusions indicate many natural diamonds form at conditions of 5–6 GPa and 900–1400 °C in the mantle. The presence of carbonate-rich, alkali-silicate (Navon et al., 1988; Schrauder and Navon, 1994) and KCl (Burgess et al., 2002; Johnson et al., 2000; Turner et al., 1990) fluids in inclusions

in the fibrous coats of coated octahedral diamond indicates that these fluids are involved in the growth of these diamonds.

During the synthesis of diamond under high pressure–high temperature (HPHT) conditions, solvent catalysts are used to reduce the pressure–temperature conditions required for diamond nucleation and growth. Experiments in the carbonate–carbon system (Akaishi et al., 1990) demonstrated the solvent catalytic properties of carbonates. Since then, a variety of inorganic compounds have been used in experimental investigations of diamond growth and nucleation, e.g. kimberlitic melt (Arima et al., 1993);

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halides (Wang and Kanda, 1998); carbonates (Kanda et al., 1990; Litvin et al., 1997, 1998a,b, 1999a; Pal'yanov et al., 1998, 1999a,b; Sato et al., 1999; Sokol et al., 1998, 2000; Taniguchi et al., 1996); and multi-component carbonate–silicate melts (Litvin et al., 1999; Pal'yanov et al., 2002b).

Carbonates have remained the centre of attention, because of the occurrence of carbonates in inclusions in natural diamond coat (Guthrie et al., 1991; Lang and Walmsley, 1983; Walmsley and Lang, 1992). The lower boundary temperature for diamond synthesis is considered to be related to the melt temperature of the solvent catalyst. In the carbonate system, introducing an alkali component can lower the solidus temperature (Pal'yanov et al., 1999a,b, 2002a). Previous studies suggest that diamond growth in the presence of carbonate is characterised by an induction period (before which no diamond growth occurs) that can reach tens of hours (Pal'yanov et al., 2002a). The addition of C–O–H fluid to carbonate substantially decreases the minimum temperature required for diamond synthesis (from ~ 1700 °C in dolomite–carbon to ~ 1420 °C in dolomite–fluid–carbon (Sokol et al., 2001) and duration of the induction period (Pal'yanov et al., 2002a; Sokol et al., 2001) required for diamond growth.

Diamond synthesis experiments using KCl–C at 6 GPa, 1620 °C (Wang and Kanda, 1998), and KCl–H₂O–C at 7–8 GPa, 1200–1700 °C (Litvin, 2003) have also been successful. Halogens are of interest because of the profound effect they have on the phase relations of carbonate-rich systems (Williams and Knittle, 2003); and because of the occurrence of KCl in inclusions in coated diamond (Israeli et al., 2001) along with alkali silicate–carbonate fluids (Navon et al., 1988; Schrauder and Navon, 1994). Chlorine has been shown to be an important component of mantle fluids, by comparisons of experimentally derived Cl partition coefficients for apatite with the Cl-content of mantle-derived apatite (Brenan, 1993). High-pressure experiments (1.5–2.0 GPa) indicate that Cl forms complexes with alkalis (K, Na, Ba, Rb), altering their partition coefficients $D^{\text{fluid/melt}}$ and causing them to fractionate into the fluid phase (Ayers and Eggler, 1995). There is a correlation between the concentration of Cl and K in micro-inclusions in natural-coated diamond.

We have used the system C–K₂CO₃–KCl as an analogue for Cl-rich mantle fluids in diamond growth experiments. The purpose of this study is to extend the range of fluids used to experimentally model diamond growth in the carbonate–fluid system. This article describes the preliminary results.

2. Experimental set-up

2.1. Starting materials

Starting materials were high purity graphite powder (UCP1-100: by Ultra Carbon Group, impurity concentration <5 ppm). For the solvent catalyst, potassium carbonate (K₂CO₃: BDH limited AnalaR, 99.9%) was used with KCl (Fisons Analytical Reagents, 99.8%). Graphite (50 mol%), K₂CO₃ (35 mol%) and KCl (15 mol%) were weighed and mixed by lightly grinding together in an agate mortar. K₂CO₃ is strongly hygroscopic; in order to minimise this effect, the powdered starting materials were dried at 120 °C for 24 h before loading the capsule, and again between loading and crimping, and between crimping and welding of the capsule.

One synthetic cubo-octahedral seed (0.9–1.1 mm) and one natural octahedral seed (0.6–0.9 mm) (Aikhal, Russia) were embedded in the powdered mix and positioned 1/3 and 2/3 along the length of the capsule so that both were the same distance from the hotspot (~ 5 mm). Both natural and synthetic diamond seeds were used because their differing morphologies provide different potential nucleation surfaces. This was also done so that results could be compared both to the natural system (natural diamond coats grow on octahedral seeds) and published experimental work (mostly using synthetic cubo-octahedral seeds). The size, shape and surface texture of seed crystals were examined by both by optical microscopy and Scanning Electron Microscopy (SEM) prior to experiments: the natural octahedra had smooth surfaces and sharp edges (Fig. 2a); the synthetic seeds also had sharp edges, but the cubic (100) faces were characterised by a dendritic surface texture (Fig. 2b), which may have aided nucleation and growth on these faces. The seeds were then cleaned using isopropanol, acetone and then distilled water.

2.2. High-pressure experiments

Multi-Anvil Press (MAP) experiments were carried out using a Walker module (modified double-stage HP apparatus similar to 6–8 type HP devices). The WC cubic inner anvils were 26- with 8-mm truncated edge length. The pressure-transmitting medium was an MgO–Cr₂O₃ octahedron with an edge length of 14- and 5-mm diameter hole, combined with pyrophyllite fin gaskets. The cylindrical graphite furnace with 7.9-mm length and 3.4-mm inner diameter sits within a ZrO thermal insulator. A platinum sample capsule of length 3 mm and inner diameter 1.7 mm was positioned so that its centre was at the hottest region in the furnace. The sample assembly is shown in Fig. 1.

One-hour duration experiments were carried out at 7.0–7.7 GPa and 1050–1420 °C, the heating rate was 52 °C min⁻¹. Pressure calibration curves were constructed for the phase transitions of bismuth (2.55 and 7.7 GPa) at room temperature. No high-temperature pressure calibration has been conducted. Temperatures were estimated from the calibration between applied electrical power and temperature using a W_{97%}Re_{3%}–W_{75%}Re_{25%} thermocouple. The accuracy of the pressure and temperature determinations was ± 0.5 GPa and ± 100 °C, respectively. The temperature distribution within the capsule was not measured, however, thermal gradients were minimised by the use of a highly conductive capsule, and by the

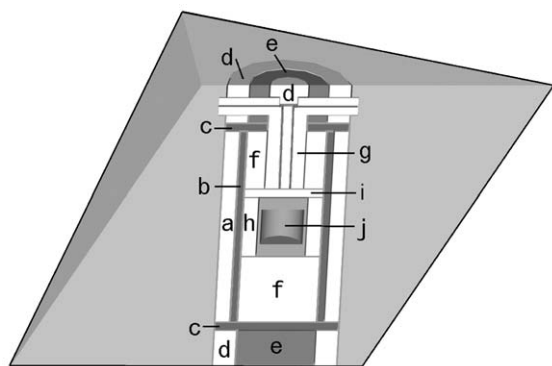


Fig. 1. Cross-section of cell assembly in the 14 mm MgO octahedra. (a) ZrO sleeve, (b) Graphite heater, (c) Graphite discs, (d) ZrO end caps, (e) Cu contact, (f) Al₂O₃ pressure medium and spacer parts, (g) Thermocouple tube, (h) MgO jacket, (i) MgO Cap, (j) Pt capsule.

positioning of the hotspot at the centre of the sample. The thermocouple was aligned axially, so measured temperatures represent the lower bound of the temperature of the sample space. Quenching was achieved by shutting of the electric power supply, while the system was still at experimental pressure.

After experiments, the capsules were sliced open using a razor. The run product was characterised by Electron Probe Micro-Analysis (EPMA), SEM observation, and with a crushed grain mount under oil using a petrological microscope. Seed diamonds were cleaned using HCl and distilled water to remove carbonate and KCl, and characterised by optical microscopy and SEM. Diamond growth was established by observing changes in the surface morphology of the seeds, and was confirmed by an increase in mass at the limit of balance precision. The K₂CO₃–KCl host was not analysed for the presence of spontaneously grown diamond. Melting of carbonate was confirmed both by quench textures in optical mount and by the sinking of diamond seeds.

3. Results

Carbonate crystals in the recovered sample are irregularly shaped with acicular and dendritic forms, while KCl forms small spherules (Fig. 2h). These textures are typical of quench crystals, indicating that the K₂CO₃–KCl mix melted in all experimental runs. Large (20 μm) graphite flakes are also present, and the seed diamond had sunk to the bottom of the capsule in all runs.

At 1050 °C, 7.0 GPa (SK-1), 1 h was sufficient for diamond growth on both the synthetic and natural seeds in the system 50C–35K₂CO₃–15KCl. Diamond growth was most prominent in the 1-h experiment at 1260 °C, 7.7 GPa (SK-4). During SK-3, the capsule ruptured during heating at 7.7 GPa, 1420 °C. However, the 5 min spent above 1050 °C (the lowest successful growth temperature) was sufficient for growth on both the natural and synthetic seed. Experimental results are presented in Table 1.

Diamond growth took place on the octahedral (111) faces of both the natural and synthetic diamond, and also on the cubic (100) face of the synthetic seed. Two growth morphologies are observed: (1) Development of numerous epitaxial octahedra {111} up to

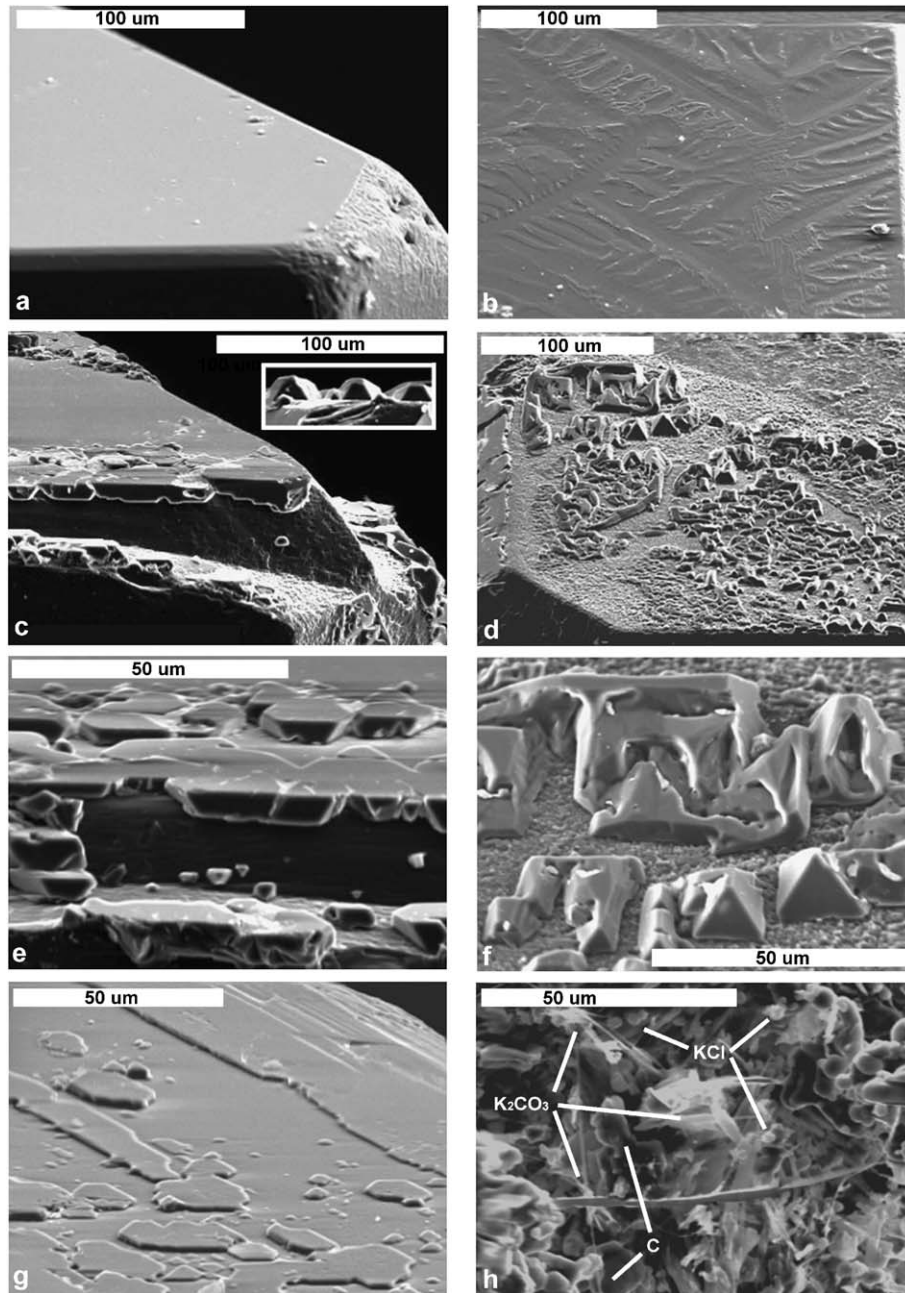


Fig. 2. Scanning Electron Micrographs of diamond growth on seeds in the system $50\text{C}-35\text{K}_2\text{CO}_3-15\text{KCl}$. (a) Smooth surface texture of pre-run natural diamond seed face; (b) dendritic texturing on surface of a pre-run synthetic diamond seed (100 μm) face; (c) new diamond growth along the edges of the octahedral face (111) of natural seed in SK-4, inset window (width 50 μm) shows octahedra developed at the apex of the natural octahedral seed; (d) high density growth of epitaxial octahedra on the cubic (100) face of the synthetic seed from SK-4; (e) epitaxial octahedra grown on an octahedral face of the natural seed in SK-4; (f) skeletal morphology of octahedra grown on the synthetic seed in SK-4; (g) layered growth and octahedra on the natural seed from SK-3, layer edges are aligned along the (111) direction; (h) graphite flakes, KCl spherules and dendrites and needles of K_2CO_3 from SK-1.

Table 1

Experimental results for diamond growth on seeds in the system 50C–35K₂CO₃–15KCl

Run no.	Run conditions				Growth layer thickness (μm)*		Tetrahedral pyramids, surface coverage			
	T (°C)	P (GPa)	t (min)	Seed	(100)	(111)	Morphology	(100)	(111)	Size (μm)
SK-1	1050	7.0	60	Syn	<2	<2	111>100	–	–	–
				Nat	–	0	111>100	–	–	–
SK-3	1420	7.7	<5	Syn	5	5	111>100	5%	<2%	5–10
				Nat	–	3	111>100	–	<2%	5–10
SK-4	1260	7.7	60	Syn	10	10	111>100	60%	45%	10–30
				Nat	–	8	111>100	–	5%	5–20

* ± 30%.

20 μm in size (Fig. 2c–f). On the natural seed, the octahedra have nucleated along the edges of the seed facets (Fig. 2c and d); on the synthetic seed, octahedra appear to be aligned and in places are so densely packed that they form a growth layer parallel to the seed surface (Fig. 2d). The apparent alignment of growth features and presence of areas of high nucleation density for octahedra {111} may be related to the original dendritic surface texture of the synthetic seed, because defects and steps at the surface of the seed face will provide high-energy nucleation sites. Many octahedra {111} on both the natural and synthetic seeds from SK-4 display skeletal forms (Fig. 2f); the development of skeletal morphologies testifies to high crystallisation rates. (2) Layered growth occurred on both seed types in all runs. Layers generally grow inwards from the edge of the seed faces (Fig. 2g); however, they also developed away from the crystal edge (again this may be related to textures on the original seed face). In both cases, the edges of the layers are aligned parallel to the edges of the seed face (Fig. 2g). In SK-3, layered growth is the dominant growth mechanism; this is surprising since peak temperatures in SK-3 were ~ 200 °C higher than in SK-4 (1420 and 1260 °C, respectively), in which skeletal growth is prevalent. This may be because SK-3 spent a greater proportion of its total run time at lower temperatures, and also because conditions in SK-3 were unstable. All the developed growth features show flat surfaces with sharp edges, these features are characteristic of solution growth.

The development of octahedra and growth layers are characteristics similar to those observed using K₂CO₃–H₂O–CO₂ at 5.7 GPa, 1150–1420 °C during experiments in excess of 20 h (Pal'yanov et al., 2002a). Skeletal growth forms have been observed

in experiments using KCl–C at 1200–1600 °C at 7–8 GPa (Litvin 2003).

4. Discussion and conclusions

The straight edges and flat surfaces of grown diamond indicate a solution process, i.e. growth was by precipitation process from fluid-rich liquid. It is likely that graphite was preserved as a metastable phase in the starting mix, until the conditions of eutectic melting of KCl–K₂CO₃ were reached. Graphite is more soluble than diamond because it is thermodynamically metastable at the experimental conditions. The dissolution of graphite leads to formation of carbon saturated melt solutions, from which carbon is precipitated as diamond. In practice, levels of carbon concentration in the sample capsule are also likely to be affected by temperature gradients.

Halides are known to reduce carbonate liquidus temperatures: at 1 bar, 15 mol% KF and KCl lower the K₂CO₃ liquidus temperature from 896, to 840 and 800 °C, respectively (Nyankovskaya, 1952, cited in Levin et al., 1956). Williams and Knittle (2003) used F to reduce the liquidus temperature of carbonate to 700 °C at 1.6 GPa, in experiments investigating the structural complexity of carbonate. These authors observe a shift of the C–O symmetric stretch (from 1050–1075 cm⁻¹ in non-fluorinated carbonate glasses to 970 cm⁻¹) in the Raman spectra, which they suggest is most likely to be due to disruption of the carbonate group by F, which allows extensive bridging between C–O bond units and cations (in this case K⁺) in the melt. It is likely that chlorine has a similar affect on the carbonate

liquidus, and is responsible for the reduction of the K_2CO_3 liquidus temperature of potassium carbonate from ~ 1300 to ≤ 1000 °C at 7.7 GPa. Therefore, the presence of liquid KCl allows K_2CO_3 to act as a solvent catalyst at conditions below the continental geotherm (Fig. 3).

A reduction of the minimum diamond growth temperature is 1050 °C at 7.7 GPa is a reduction of the minimum growth temperature reported in the alkali-carbonate-C-O-H system (Pal'yanov et al., 2002a). A minimal temperature of 1050 °C cannot be considered a minimum temperature, i.e. diamond growth occurred in all experimental runs so we cannot rule out the possibility of growth at even lower temperatures. Furthermore, the experiments in this study were conducted in a narrow pressure range and are limited to durations of 1 h or less, the minimum growth temperature will be reduced at lower pressures. Minimum synthesis temperatures are likely to be controlled by phase relations in the system K_2CO_3 -KCl, which are poorly constrained.

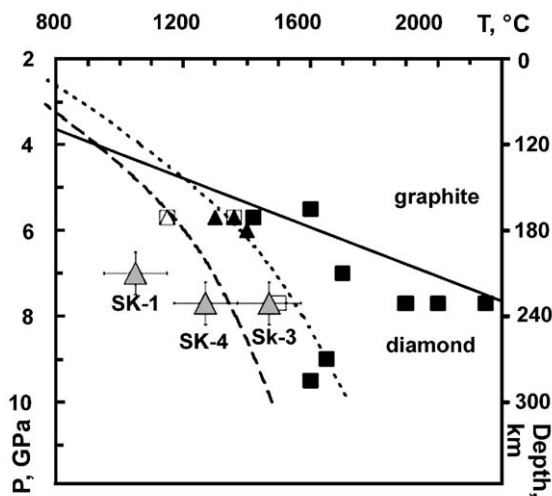


Fig. 3. PT conditions of successful diamond growth experiments (grey triangles). Error bars are 100 °C, 0.5 GPa. Also shown, continental geotherms 35 mW/m² (– –) and 40 mW/m² (- · - ·), and published conditions of diamond synthesis in carbonate on seeds (triangles) and spontaneous (squares). Solid symbols show synthesis in carbonate only (Akaishi et al., 1990; Pal'yanov et al., 1998, 1999a, 2002a; Sato et al., 1999; Sokol et al., 1998, 2000, 2001; Taniguchi et al., 1996); Open symbols show synthesis using carbonate-fluid (CO₂, H₂O, H₂O-CO₂) (Pal'yanov et al., 2002a; Pal'yanov et al., 1999b; Sokol et al., 2001; Yamaoka et al., 2002) systems.

Previous diamond growth experiments in carbonate-carbon systems below 1500 °C (Pal'yanov et al., 1999a,b, 2002a,b; Sokol et al., 2000, 2001) suggest that diamond growth is characterised by a relatively long induction period before diamond nucleation (<30 h at 5.7 GPa and 1420 °C using K_2CO_3 ; Pal'yanov et al., 2002a). C-O-H fluids reduce, but do not eliminate, this induction period (<20 h at 5.7 GPa, 1420 °C in the K_2CO_3 -H₂C₂O₄·2H₂O-C system; Pal'yanov et al., 2002a). However, diamond growth in carbonate has been achieved in 20 min at conditions above 1500 °C (Taniguchi et al., 1996). The concept of an induction period is completely at odds with our experimental data; In the K_2CO_3 -KCl system, significant growth occurred in 5 min as the temperature was increased from 1050 to 1460 °C in SK-3, indicating a very short induction period. In the 1-h runs, growth rates are sufficiently high as to allow the formation of a skeletal growth of diamond octahedra and layers. Perhaps the high reactivity of KCl in carbonate means that carbonate decomposition is a rapid process and so diamond growth in the carbonate-carbon-alkali chloride system is less limited by kinetic factors than in the carbonate-carbon systems.

There are several possible reasons for this accelerated growth rate: (1) KCl reduces the carbonate melting by destabilising the carbonate unit, as suggested by Williams and Knittle (2003) for CaF. This is supported by the melting of K_2CO_3 melted in all experiments. (2) the presence of KCl may increase the solubility of graphite in carbonate, which is then re-crystallised as diamond. (3) KCl may increase the diffusion rate of carbon, thus improving the supply to the diamond growth face. High growth rates, and therefore high carbon diffusion (supply) rates are a necessary feature of mantle regions in which fibrous diamond is grown. (4) There may be compositional effects at the carbonate-diamond interface, caused by a change in the anion ligands at the surface. Further work is needed to identify which mechanism(s) is responsible for the accelerated diamond growth rates in the system C- K_2CO_3 -KCl.

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