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Graphite pseudomorphs after diamonds: An experimental study of graphite morphology and the role of H_2O in the graphitisation process

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ABSTRACT

Experiments at 1 atmosphere and 2.0–2.5 GPa over a range of temperatures of 1400–2100 °C have been carried out to investigate the diamond-to-graphite transformation in "dry" and "wet" systems. Internal and external morphologies of graphite pseudomorphs after diamonds were studied by Raman spectroscopy, reflected light microscopy and scanning electron microscopy. In a "dry" system, the results show that at 2.0–2.5 GPa, graphite pseudomorphs preserve the finest details of external morphology of original diamond crystals, whereas at 1 atmosphere only the general outline of diamond crystals can be recognised on these pseudomorphs. In all experimental runs at $P = 2.0–2.5$ GPa under various temperatures, the growth of oriented graphite crystallites was observed only on the {111} diamond faces, while randomly oriented graphite crystals were observed on the {100} and especially {110} diamond faces. In a "wet" system, we were unable to reproduce graphite pseudomorphs after diamond. However, newly formed large graphite crystals were found on the partly dissolved diamonds. The diamond crystal form has been changed from that of a sharp octahedron to octahedron having rounded edges and corners. Flat-bottomed negatively oriented trigons were formed on the octahedral {111} faces. Large graphite crystals tend to be concentrated at {100} and {110} surfaces. Rare single euhedral graphite flakes occur on the {111} faces. Visible growth spirals on {001} faces of graphite crystals appear on all crystals. The {111} faces of diamond crystal are partly covered by translucent graphite coat. The diamond-to-graphite transformation in the "wet" system occurs via coupled dissolution–precipitation processes. All morphological features (e.g., negatively oriented trigons, rounded edges) described for partly dissolved diamonds are easily recognised. None of these features have been detected so far for partly graphitised metamorphic diamond crystals. Our results suggest that in geological environments, the presence of volatiles (in particular, H_2O) definitely cannot be considered as favourable for the diamond-to-graphite transformation and, thus, show that this hypothesis seems highly unlikely.

1. Introduction

Complete graphite pseudomorphs after diamonds described from Beni-Bousera, northern Morocco, (El Atrassi et al., 2011; Pearson et al., 1989, 1995; Slodkevich, 1982) and from Ronda, southern Spain (Davies et al., 1992), include the following: (1) sharp-edged octahedra, with or without rounded fibrous graphite coats (the most abundant form); (2) rhombicuboctahedra exhibiting well-formed cube and octahedral faces; (3) contact twins or macles, with and without re-entrant angles, most of which are coated; and (4) irregular to rounded masses whose surface morphologies resemble framesite. Findings of graphite cuboids from Maksutov complex, Ural Mountains, Russia, are also interpreted as graphite pseudomorphs after diamonds (Leech & Ernst, 1998), although so far no trace of UHPM events were recognised for this complex.

In contrast to kimberlites, where black and/or graphite-coated diamonds rarely occur (Grenville-Wells, 1952), diamonds in the UHPM rocks often coexist with graphites (Dobrzhinetskaya et al., 2009; Janak et al., 2013; Katayama et al., 2000; Korsakov & Shatsky, 2004; Korsakov et al., 2010; Massonne et al., 1998; Naemura et al., 2011; Ogasawara et al., 2000; Perraki et al., 2006, 2009; Zhang et al., 1997; Zhu & Ogasawara, 2002). Metastable growth of graphite in the diamond stability field was documented for ultra-high-pressure metamorphic rocks from the Kokchetav massif (Korsakov & Shatsky, 2004; Korsakov et al., 2010). Cuboid is predominant morphology of metamorphic diamonds; however, perfect octahedral crystals occur in clinozoisite gneisses and quartz–tourmaline–muscovite metasomatic rocks (Korsakov et al., 2002, 2009; Lavrova et al., 1999; Shimizu &

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Ogasawara, 2013). Therefore, the presence of graphite cuboids in UHPM rocks is predominantly interpreted as partial graphitisation of diamonds in terms of solid-state reaction or dissolution–precipitation processes (Dobrzhinetskaya et al., 2009; Janak et al., 2013; Massonne et al., 1998; Ogasawara et al., 2000; Zhang et al., 1997; Zhu & Ogasawara, 2002). However, it is very difficult to find P–T conditions at which the diamond dissolution and graphite precipitation reactions take place simultaneously (Putnis & Putnis, 2007). In all previous experimental studies (Arima & Kozai, 2008; Chou & Anderson, 2009; Fedortchouk & Canil, 2009; Fedortchouk et al., 2011; Khokhryakov & Pal'yanov, 2007; Kozai & Arima, 2005), only dissolution of diamond was investigated in detail, but none of those publications reported the precipitation of graphite. The presence of very thin film of graphite was reported by Kozai and Arima (2005), but no dissolution features were documented in those runs. Unlike the case of experiments, diamond graphitisation in natural samples is often attributed to the effect of an "omnipotent" fluid, which would drastically change the situation and promote diamond conversion to graphite within a relatively short time, even under unsuitable P–T conditions (Bostick et al., 2003; Dobrzhinetskaya et al., 2009; Leech & Ernst, 1998). This study aims (i) to present the peculiar features of graphite pseudomorphs after diamond, which allow to distinguish such pseudomorphs from graphite coating around diamond that formed due to metastable growth, and (ii) to test the possible catalytic effect of H_2O on the diamond-to-graphite transformation. Additionally, in this paper, we substantiate that graphite pseudomorphs after diamond is hard to produce even in the presence of a significant amount of fluid.

2. Experiment

In this study, we used synthetic diamond crystals of cubo-octahedron form with {111}, {100} and {110} faces. They were synthesised in the Fe–Ni–C system at $P = 5.5$–6 GPa and $T = 1350$–1450 °C, for details to refer Chepurov et al. (1997). All the crystals were perfectly faceted, with sharp edges and smooth faces, containing inclusions of sizes less than 5 μm. Natural diamonds selected from Udachnaya and Diavik mines had octahedron, cuboid or irregular morphologies. The size of diamond crystals was 0.5–2.5 mm.

Table 1
Experimental results. Gr_f—thin translucent film of graphite, Gr—graphite aggregate, ND and SD—natural and synthetic diamond crystal, respectively.

Run n0	Time	*P*, GPa	*T*, °C	Diamond	Phases
"Dry" experiments					
LP1	10 min	10–4	1500	2 SD	MgO + Grf
LP2	20 min	10–4	1800	2 SD	MgO + Gr
LP3	1 h	10–4	2000	2 SD	MgO + Gr
LP4	1 h	10–4	1500	2 SD	MgO + Grf
LP5	12 h	10–4	1500	2 SD	MgO + Grf
LP6	12 h	10–4	1800	2 SD	MgO + Gr
5-29-07	20 min	2.0	1800	2 SD	MgO + Gr
5-32-07	23 min	2.0	1800	2 SD	MgO + Gr
5-35-07	5 min	2.0	2050	2 SD	MgO + Gr
5-40-07	20 min	2.0	2050	2 SD	MgO + Gr
5-48-07	30 min	2.0	2050	2 ND	MgO + Gr
5-4-08	5 min	2.0	2050	2 ND +2 SD	MgO + Gr
5-10-08	2 h	2.5	1250	2 ND +2 SD	MgO + Grf
5-13-08	24 h	2.5	1250	2 ND +2 SD	MgO + Gr
4-8-08	5 min	2.0	2150	2 SD	MgO + Gr
"Wet" experiments					
5-22-08	1 h	2.5	1550	2 SD	Ca(OH)2 + Gr
5-29-08	15 min	2.5	1620	2 SD	Ca(OH)2 + Gr
4-4-08	1 h	2.5	1600	2 SD	Ca(OH)2 + Gr
4-5-08	1 h	2.5	1550	3 SD	Ca(OH)2 + Gr
4-9-08	1 h	2.5	1560	2 SD	Ca(OH)2 + Gr
4-1-14	2 h	2.0	1470	2 ND+ 1 SD	Ca(OH)2 + Gr

High-pressure experiments on diamond graphitisation were carried out using a "split-sphere" (BARS) type multi-anvil apparatus at P–T range 2.0–2.5 GPa and $T = 1400$–2000 °C (Table 1). A high-pressure cell in the form of a tetragonal prism 20 × 20 × 23 mm^3 in size, with cut edges and apexes, containing a graphite heater with 11 mm in diameter was used. The temperature was measured using a PtRh6/PtRh30 thermocouple. Details on the pressure and temperature calibration are given by Chepurov et al. (1997, 2012, 2013). HT experiments (1800–2100 °C) on diamond graphitisation in "dry" systems were performed without Pt capsules, whereas for 1400–1600 °C, Pt capsules were used. Several crystals were placed into MgO powder with 1–2 μm grain size that subsequently was pressed into solid tablets. These tablets were placed inside graphite heater. Similar MgO tablets were used in diamond graphitisation experiments with CO–CO_2 atmosphere and in ambient pressure experiments to prevent breakdown of graphite pseudomorphs. For volatile-bearing systems ("wet"), Pt capsules with 6 mm in diameter and with wall width of 0.5 mm thick were utilised. Several diamond crystals were placed inside $Ca(OH)_2$ and pressed into solid tablets (Table 1). Reagents MgO and $Ca(OH)_2$ with a purity of 99.9% were used as starting materials. After treatment, graphite/diamond crystals were extracted from MgO and $Ca(OH)_2$ by heating in acid (to prevent the destruction of the pseudomorphs) and then were studied by Raman spectroscopy and scanning electron microscopy (SEM) methods.

The graphitised diamond crystals were mounted into epoxy (Petropoxy 154). They were cut with high-speed diamond saw with thin diamond blade (thickness 0.2 mm and diameter 130 mm). Then crystals were polished with special diamond lap (diamond size 20 μm). Further details of diamond polishing can be found elsewhere (De Corte et al., 2000; Korsakov & Shatsky, 2004; Korsakov et al., 2010). Final polishing was performed using soft lap and 1 μm diamond paste. Grain size of artificial diamond particles from diamond-bearing materials at all stages of sample preparation was always less than that of original diamond crystals and diamonds relics (up to 300 μm in size) found in cores of graphitised diamond, and thus, the latter ones cannot be regarded as a result of contamination of experimental products by preparation material.

Raman spectra were obtained using a Horiba LabRam HR800 system. Excitation wavelength 532 nm was used with a power of 10 mW. Scattered light was dispersed using a holographic grating with 1800 grooves per millimetre. Spectral resolution was about 3.0 cm^{-1}. An Olympus BH-2 microscope with a 100× objective allowed collecting scattered light from spots as small as 1 μm in diameter. Raman spectra were recorded from 100 to 4000 cm^{-1}. Similarly to Naemura et al. (2011), band position, band height, band area and band width (i.e., full width at half maximum, FWHM) were determined after baseline correction and curve fitting with the Voigt function by applying data analysis software Fityk 0.8.9.

The study of diamond faces and graphite layers with back-scattered electron imaging (BSE) was performed on a scanning electron microscope (SEM) JEOL SM-6100 using 20 kV accelerating voltage, probe current over a range of 10^{-12}–10^{-6} A, and maximum magnification up to 20000.

Reflected optical microscopy (ROM) provides important information about the internal morphology of graphite pseudomorphs after diamond. An Olympus BH-2 microscope with 10, 20, 50 and 100× objectives was used.

3. Results

All experiments with temperature below 1500 °C and different duration (up to 12 hours) reveal that only a thin translucent layer of graphite, defined by Raman spectroscopy, appears on diamond crystals in the first 10 minutes and no changes in thickness or morphology of graphite coatings were detected at long-term experiments (Table 1).