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ARTICLE

Why are diamonds preserved in UHP metamorphic complexes? Experimental evidence for the effect of pressure on diamond graphitization

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ABSTRACT

The preservation of metastable diamond in ultrahigh-pressure metamorphic (UHPM) complexes challenges our understanding of the processes taking place during exhumation of these subduction zone complexes. The presence of diamonds in UHPM rocks implies that diamonds remained metastable during exhumation, and within thermodynamic stability of graphite for an extended period. This work studies the influence of pressure on the surface graphitization rate of diamond monocrystals in carbonate systems to understand the preservation of microdiamond during exhumation of UHP subduction complexes. Experiments were performed with 2–3 mm synthetic diamond monocrystals at 2–4 GPa in $CaCO_3$ (1550°C) and K_2CO_3 (1450°C) melts using a high-pressure multi-anvil apparatus. The highest rate of surface graphitization took place at 2 GPa; diamond crystals were almost completely enveloped by a graphite coating. At 4 GPa, only octahedron-shaped pits formed on flat {111} diamond crystal faces. Our results demonstrate that the surface graphitization rate of diamonds in the presence of carbonate melts at 1450–1550°C increases with decreasing pressure. Decreased pressure alone can graphitize diamond regardless of exhumation rate. Metastable diamond inclusions survive exhumation with little or no graphitization because of excess pressure up to 2 GPa acting on them, and because inclusions are protected from interaction with C-O-H fluid.

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Introduction

Ultrahigh-pressure complexes and the Kokchetav Massif

Several ultrahigh-pressure metamorphic (hereafter UHPM) complexes from collisional belts worldwide are characterized by the presence of coesite- and diamond-bearing rocks. The best-known of these continental UHP subduction complexes are the Kokchetav Massif in Kazakhstan (e.g. Nadezhdina and Posukhova 1990; Sobolev and Shatsky 1990); the Dabie-Sulu and Qaidam in China (Xu *et al*. 1992; Okay (1993); Yang *et al*. 2003); the Western Gneiss Complex of Norway (Dobrzhinetskaya *et al*. 1993, 1995; Van Roermund *et al*. 2002); the Dora Maira Massif, Italian Alps (Gebauer *et al*. 1997); the Maksyutov Complex in the south Urals, Russia (Leech and Ernst 1998; Bostick *et al*. 2003); the Saxonian Erzgebirge in Germany (Massone 1999; Hwang *et al*. 2001; Stöckhert *et al*. 2001); and the Sulawesi Complex in Indonesia (Parkinson and Katayama 1999). These UHPM complexes are of great interest to a wide array of geologists because they provide records of continental collisional and the metamorphic processes taking place in the deep crust and upper mantle. In particular, the preservation of microdiamond in these UHPM complexes has led to discussion of diamond genesis in crustal terranes and on the processes controlling diamond preservation under metastable conditions during exhumation from UHP conditions.

The Kokchetav Massif is well-studied and -referenced among the diamond-bearing UHPM complexes (e.g. Schertl and Sobolev 2013 and the references therein). The first detailed mineralogical study of Kokchetav Massif rocks discovered microdiamond inclusions in garnet and zircon that suggested subduction to ultrahigh-pressure (UHP, ≥4 GPa) and high-temperature (HT, 900–1000°C) conditions (Sobolev and Shatsky 1990; Claoué-Long *et al*. 1991). Those early UHP/HT estimates have been confirmed in numerous subsequent publications (e.g. Zhang *et al*. 1997; Maruyama and Parkinson 2000; Ogasawara *et al*. 2000, 2002; Okamoto *et al*. 2000; Hermann *et al*. 2001; Katayama *et al*. 2001; Zhu and

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Ogasawara 2002; Hacker *et al*. 2003; Massonne 2003, 2011; Dobretsov *et al*. 2006; Dobrzhinetskaya *et al*. 2006; Korsakov and Hermann 2006; Ragozin *et al*. 2009). This estimate of UHP for the Kokchetav Massif indicates these continental crustal rocks were subducted into the mantle to depths of at least 120–200 km (e.g. Sobolev and Shatsky 1990; Katayama *et al*. 2002; Ogasawara *et al*. 2002; Dobrzhinetskaya *et al*. 2006), and were later exhumed to the Earth's surface bringing microdiamond evidence for this deep subduction.

Exhumation of UHP rocks and preservation of UHP index minerals

The preservation of UHP index minerals in UHP/HT assemblages is typically explained by normal faulting- (or a wedge-type extrusion) and buoyancy-driven rapid exhumation to the surface (Ernst *et al*. 1997; Ernst 2006). For example, calculated rates for exhumation of diamondiferous rocks from the Dabie-Sulu have ranged from 6–8 mm/a to 15–30 mm/a for the Kokchetav rocks, and 20–24 mm/a for pyrope quartzite/whiteschist from the Dora Maira massif (e.g. Gebauer *et al*. 1997; Rubatto and Hermann 2001; Hacker *et al*. 2003; Ernst 2006); these faster exhumation rates of tens of mm/a are on par with plate tectonic rates of subduction (Rubatto and Hermann 2001; Hacker *et al*. 2003; Baldwin *et al*. 2004b; Parrish *et al*. 2006; Rubatto *et al*. 2011). Exhumation rates are estimated to be higher for the initial stages of exhumation: Rubatto and Hermann (2001) calculated 3.4 cm/a for the first stage of exhumation of Alpine UHP calc-silicate rocks from diamond stability conditions (estimated from pyrope quartzite/whiteschist) where density contrasts between the subducted crust and mantle are greater. A slower (but still fast) exhumation rate of 1.6 cm/a was calculated for the second stage of exhumation where erosion and extensional normal faulting play a larger role in bringing UHP rocks to the surface (Rubatto and Hermann 2001). In the case of the Kokchetav massif, exhumation from diamond stability conditions to granulite-facies conditions (1 GPa, 800°C) took place over <6 Ma, with an additional 2 Ma for the retrograde amphibolite-facies metamorphism (see Hermann *et al*. 2006). The idea that rapid exhumation plays a critical role in the preservation of UHP index minerals has become prominent and has been applied to many other UHPM complexes (e.g. Hacker *et al*. 2003; Dobretsov *et al*. 2006; Ragozin *et al*. 2009). Thus, microcrystals of diamond formed within the P-T stability field of diamond and then remained metastable, at high temperature (800–1000°C) and increasingly lower P in the graphite stability field, for at least 6 Ma. How can microcrystals of diamond (≤100–200 μm) be preserved under these high-temperature retrograde conditions?

Experimental parameters analogous to natural UHPM conditions

In this work, we experiment with 2–3 mm octahedral diamond monocrystals in carbonate systems at 2–4 GPa and 1450–1550°C, expanding on the preliminary experimental work presented in Sonin *et al*. (2013). These experimental materials and conditions are representative of subduction of carbon-bearing phases in natural UHPM systems: Diamonds have been found in the matrix of UHP dolomitic marbles and as inclusions within container minerals (like garnet and zircon) in UHP complexes containing marbles (Schertl and Okay 1994; Ye and Hirajima 1996; Kato *et al*. 1997; Zhang *et al*. 1997; Ogasawara *et al*. 2002). Inclusions in alluvial diamonds from the Juina kimberlite in Brazil indicate that carbonates have been transported into the ultra-deep mantle – potentially into the lower mantle – by subduction processes (Brenker *et al*. 2007; Maeda *et al*. 2017, and the references therein). Fluid inclusion studies also demonstrate that UHP diamonds from the Kokchetav and Erzgebirge massifs precipitated in the presence of supercritical C-O-H fluids with Cl, S, P, and K found in all studied fluid inclusions, along with Fe, Si, and Al in felsic rocks, and Ca and Mg in carbonate rocks (Dobrzhinetskaya 2012). Kokchetav rocks preserve evidence for UHP carbonate and silicate melts (Korsakov and Hermann 2006): polycrystalline magnesian calcite and polyphase carbonate-silicate inclusions in garnet and clinopyroxene have textural features indicating the inclusions were melt, and Korsakov and Hermann (2006) suggest that diamond may crystallize directly from such melts. Cuboidal and octahedral microdiamond (and diamond + carbonate) crystals in fluid and solid inclusions in garnet were reported in oceanic metasedimentary rocks from the UHP Italian western Alps indicating the results of our experiments are potentially applicable to continental and oceanic complexes (Frezzotti *et al*. 2011).

Diamonds from UHP complex rocks have been reported to range from 1 to 100 μm (Dobrzhinetskaya 2012), but diamond crystals as large as 1 cm (typically 2–5 mm) are inferred from cubic graphite pseudomorphs in HP-UHP mica schists from the Maksyutov Complex in the south Ural Mountains (Leech and Ernst 1998). Similarly, large graphite pseudomorphs after diamond cubes and octahedra – typically 2–8 mm in diameter, but up to 12–20 mm – are reported from the Beni Bousera (northern Morocco) and the Ronda

(southern Spain) peridotite massifs (e.g. Pearson *et al*. 1989; Davies *et al*. 1991, 1993; Pearson and Nixon 1996).

Our experiments were conducted at relatively high temperature (1450–1550°C) – somewhat higher than UHPM conditions that typically do not exceed 800–1200°C (Hacker 2006; Dobrzhinetskaya 2012) – and corresponding to the thermodynamic stability of graphite. Octahedral diamond typically crystallizes at either lower relative temperatures and/or higher pressures than cubic diamond (Robinson *et al*. 1978; Sobolev and Shatsky 1990; Deines *et al*. 1993). The synthetic diamond octahedra used in this study correspond to natural UHP systems, and experimental temperatures approach the highest temperatures during UHP metamorphism. Our experiments bear directly on the graphite-diamond transition and the graphitization of diamond, and they address the question of why microdiamonds are preserved during exhumation from UHPM conditions in continental subduction zones. This work investigates the influence of pressure on the rate and extent of surface graphitization on diamond monocrystals (2–3 mm) in UHP carbonate systems.

Previous work on diamond graphitization

Re-equilibration of diamond carbon in the graphite field can occur by (1) oxidation or dissolution of diamond, (2) surface graphitization, or (3) polymorphic replacement by graphite (e.g. Evans and Sauter 1961; Sykes and Thomas 1961; Howes 1962; Evans and James 1964; Patel and Agarwal 1966). Several studies have investigated the influence of environmental conditions on the kinetics of diamond graphitization (Evans and Sauter 1961; Phaal 1965; Sonin *et al*. 2000, 2013; Qian *et al*. 2004).

Surface graphitization vs. pseudomorphic replacement of diamond

Both surface graphitization of diamond and pseudomorphic replacement of diamond by graphite can take place at the P-T conditions in which graphite is stable. In a vacuum at low oxygen partial pressure, the temperature boundary between these two processes is 1600–1700°C (Seal 1958; Evans and James 1964). This is why surface graphitization is often called 'low-temperature' graphitization. The chemical–physical principles that govern diamond graphitization were developed as early as the second half of the twentieth century (Evans and Sauter 1961; Phaal 1965), but there has not been much recent work on the surface graphitization of diamond.

According to Evans and Sauter (1961), surface graphitization of diamond is the result of the deposition of non-diamond carbon on the diamond surface as the result of surface chemical reactions in the presence of gas reagents – the catalysts (O_2, H_2O, CO_2) – though any component of the medium interacting with the diamond may function as the catalyst. Surface graphitization first happens along the crystal edges, on diamond faces, and develops along growth steps, etch pits, and fractures. The nucleation of graphite inside the diamond is favoured by impurities and structural defects, and is responsible for the spontaneous ('high-temperature') graphitization of diamond that leads to its pseudomorphic replacement by graphite.

According to Phaal (1965), the process of diamond oxidation at the thermodynamic stability conditions for graphite consists of the following stages: (1) direct oxidation to CO and CO_2 (at a rate, R_1); (2) formation of a layer of amorphous carbon on diamond (rate R_2); and (3) direct oxidation of the amorphous carbon layer (rate R_3). Stage R_2 essentially represents the surface graphitization of diamond. If $R_2 \square R_3$, then a thick layer of non-diamond carbon forms around the diamond crystal. These conditions occur at relatively low values of the partial pressure of the possible gaseous catalysts (O_2, H_2O, CO_2). In nature, surface graphitization most likely develops in a closed system under carbon saturation conditions. In the C-O system, these conditions correspond to the CCO buffer (Sonin *et al*. 2000). A dynamic equilibrium is established, in which continuous oxidation of diamond is accompanied by precipitation on its surface of a non-diamond form of carbon, which transforms into graphite at high temperature.

Graphite-diamond stability in UHPM rocks

The co-existence of graphite and diamond is common in diamond-bearing rocks in UHPM complexes. The appearance of graphite in these rocks has been explained by direct growth from a carbon-bearing fluid or melt medium (e.g. Korsakov *et al*. 2010; Dobrzhinetskaya 2012); and thus, graphite can form as and/or persists as a metastable phase in UHP rocks at P-T conditions for the thermodynamic stability of diamond during subduction into the upper mantle (Mikhailenko *et al*. 2016); graphite occurs as separate segregations, and as layers coating diamond crystals. There are several reports of graphitization of diamond in rocks from UHP complexes (Martovitsky *et al*. 1987; Nadezhdina and Posukhova 1990; Zhang *et al*. 1997; Leech and Ernst 1998; Massonne *et al*. 1998; Ogasawara *et al*. 2000; Zhu and Ogasawara 2002; Xu *et al*. 2003). Martovitsky *et al*. (1987) and Shatsky *et al*. (1998) found that when the graphite cover is removed from cubic diamond crystals, an ornament of tetragonal

pits, faceted with octahedral flat planes, remains on the diamond surfaces. Several other studies showed that the presence of coatings and layers of graphite is typical for diamonds with smoothed, indistinctly developed apexes and edges, and irregular sculptures on the crystal surfaces (e.g. Martovitsky *et al*. 1987; Nadezhdina and Posukhova 1990; Shatsky *et al*. 1998; De Corte *et al*. 1999; Lavrova *et al*. 1999).

During experimental dissolution or oxidation of diamonds, etching sculptures with regular shapes develop on diamond surfaces. The form and orientation of these dissolution sculptures is determined by the symmetry of the faces on which they appear: triangular or hexagonal sculptures on octahedral faces and square sculptures on cubic faces. But irregular etching sculptures with complex contours – similar to sculptures reported for diamonds from UHPM rocks – is a definitive sign of surface graphitization of diamonds (Sonin *et al*. 1997a, 2006). Comparison of these irregular etchings with natural diamonds indicates that this surface graphitization took place at high temperature (>1000°C) and relatively low values of fO_2 (Sonin *et al*. 2000). Based on experimental evidence, the formation of graphite on diamond crystals during surface graphitization uses carbon from the diamond itself; exotic carbon supplied by external fluids or melts is not necessary.

Mikhailenko *et al*. (2016) argued that the rate of surface graphitization is so low, it should not factor into geological processes. But Sonin *et al*. (2000) showed that the rate of surface graphitization of diamond is high at 1000°C and 0.1 MPa, even at an oxygen partial pressure corresponding to the CCO buffer. The calculations carried out on the basis of these experimental data show that only about 3 years are required for the complete disappearance of a 0.7 mm diamond crystal (i.e. through surface graphitization) under these conditions (Sonin *et al*. 2000). Thus, 100 μm diamonds similar to those found in UHPM rocks should graphitize more rapidly.

Surface graphitization is not typical for kimberlite-borne diamonds due largely to the rapid eruption rates of kimberlite magmas and their high fluid content (Fedortchouk *et al*. 2007 and the references therein). In kimberlite systems, the dissolution (oxidation) of diamonds leads to the formation of sub-rounded and rounded crystals. Nevertheless, rapid surface graphitization was observed on diamond after laboratory experiments in kimberlitic melt at high pressures (1 and 2.5 GPa at 1300–1500°C; Fedortchouk *et al*. 2007; Arima and Kozai 2008), but the effect of temperature is not constrained. Surface graphitization is also observed after etching of diamonds at high P-T conditions in experiments using carbonate media ($CaCO_3$, Fedortchouk *et al*. 2007; $CaMg(CO_3)_2$, Kozai and Arima 2005) and $Mg(OH)_2$ (Dobrzhinetskaya *et al*. 2013). Surface graphitization of diamond in laboratory experiments is sometimes due to the limited reaction volume of samples; the system is saturated with dissolved carbon and the direct oxidation of diamond ends. Although experimental temperatures are somewhat higher than the temperature of UHPM rocks during exhumation, the time required for graphite to first appear on the diamond crystals was just 20–120 min (Fedortchouk *et al*. 2007; Arima and Kozai 2008), which is six orders of magnitude less than the time to exhume UHP complex rocks to relatively low temperatures.

Qian *et al*. (2004) report on the rate of diamond graphitization at high pressure (the kind of environment used in the experiments was not specified). Using nanosize diamond (5 nm) and microdiamond crystals (30–40 μm), Qian *et al*. (2004) found a decrease in surface graphitization with increasing pressure to 2 GPa at 1200°C. The relatively large diamond monocrystals (2–3 mm) used in these experiments are similar to large cuboid graphite aggregates interpreted to be pseudomorphic after diamond reported from mica schists from the HP-UHP Maksyutov Complex in the south Ural Mountains of Russia (Leech and Ernst 1998) and cuboid and octahedral graphite aggregates from the Beni Bousera (northern Morocco) and the Ronda (southern Spain) peridotite massifs (e.g. Pearson *et al*. 1989; Davies *et al*. 1993). Graphite aggregates are typically <5 mm for the Maksyutov Complex but reach up to 10–13 mm, and aggregates from the peridotite massifs are commonly 2–8 mm in diameter, but can be up to 12–20 mm (Pearson *et al*. 1989; Davies *et al*. 1991, 1993; Pearson and Nixon 1996). Kinetics should be more sluggish for these large monocrystals; the higher activation energies required for the monocrystals approach the bonding energy for the C-C bonds in diamond (Qian *et al*. 2004). It is therefore important to study the 'low temperature' surface graphitization of diamond at high pressures in media similar to natural environments.

Experimental materials and methods

We chose diamonds with habits comparable to natural microdiamonds from UHPM complexes in which diamonds often display a combination of octahedral and cubic faces (e.g. Martovitsky *et al*. 1987; Nadezhdina and Posukhova 1990; Xu *et al*. 1992; Leech and Ernst 1998; Shatsky *et al*. 1998; De Corte *et al*. 1999). We used synthetic diamond monocrystals to model the surface graphitization process because they have a well-defined octahedral habit without any surface

sculptures. Additionally, the state of nitrogen aggregation in diamonds from UHPM terranes is low, corresponding to Ib- and IaA-type diamond that is also typical for the synthetic yellow diamond monocrystals selected for our experiments (see Dobrzhinetskaya 2012 and the references therein). Because we needed to evaluate the weight loss in diamonds after graphitization, we chose 2–3 mm diamond monocrystals – larger than the most common microdiamonds from the UHPM complexes (typically 10–80 μm, and up to 100–300 μm [median of 30–50 μm]; Dobrzhinetskaya 2012); this choice of relatively large diamond crystals is consistent with earlier studies using cubo-octohedral synthetic diamond. Nanodiamond has a higher rate of graphitization than microdiamond because of the lower activation energy from the larger number of surface defects present in smaller crystals, in agreement with both theoretical and experimental data (Qian *et al*. 2004). Graphite pseudomorphs after diamond from the South Urals are commonly 2–8 mm in diameter (Leech and Ernst 1998), indicating diamonds in UHPM complexes can be as large or larger than the diamonds we used here.

The experiments were carried out using a multi-anvil split-sphere-type high-pressure apparatus (BARS) in high-pressure cells, made of refractory oxides ZrO_2, CaO, and MgO with a cylinder graphite heater 11 mm in diameter (Figure 1). The high-pressure cells have a 20 × 20 × 23 mm parallelepiped shape. The transmission of the current to the heater was performed via molybdenum rods and disks. The capsules containing the samples were isolated from the heater with a 1 mm-thick MgO plug, and were isolated at the top and at the bottom by 2 mm-high MgO disks.

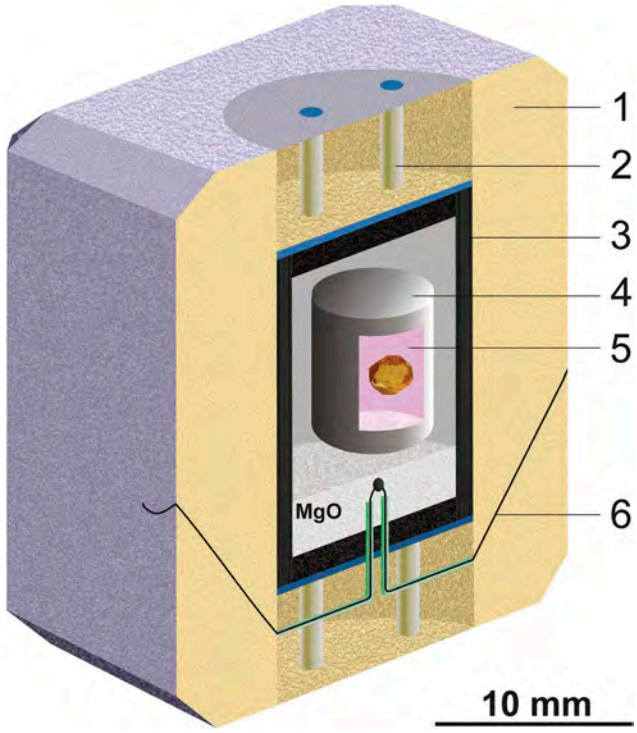

Figure 1. Vertical cross section of the high-pressure cell assembly used for experiments on graphitization of diamonds in apparatus BARS: 1 – high-pressure cell; 2 – molybdenum electrode (four electrodes in the top and four in the bottom tablets); 3 – graphite heater; 4 – Pt-capsule; 5 – sample; 6 – thermocouple. The sample consists of carbonate ($CaCO_3$ or K_2CO_3) and synthetic diamond crystal.

The methodology was the same in all of the experiments. First, pressure was increased to the desired value, then the sample was heated to the corresponding T and held at the run P-T conditions for the required time (Table 1). The samples were cooled rapidly (quenched) in 2–3 s through water-cooling of the

Table 1. Experimental conditions and results for this study.

Run no.	P (GPa)	Time (h)	$^{CaCO}3$ weight (mg)	Diamond weight – before run (mg)	Diamond weight – after run (mg)	Diamond weight loss (mg)	Diamond weight loss (%)	Graphite on diamond
$CaCO_3$ (1550°C)								
4–9	2	2	199.1	4.46	3.93	0.53	11.9	Graphite-coated
4–10	4	2	196.9	5.83	5.81	0.02	0.3	No graphite
4–12	3	2.4	192.9	4.84	2.63[a]	2.21[b]	45.7[b]	Graphite-coated
4–13	4	2	196.7	5.43	5.42	0.01	0.2	No graphite
4–16	2	2	195.2	2.52	2.11	0.41	16.3	Complete graphite coating
4–17	4	2	196.5	2.99	2.89	0.10	3.3	No graphite
K_2CO_3 (1450°C)[c]								
4–29	2	2	147.6	2.67	2.14	0.53	24.7	Complete graphite coating
4–34	4	2	101.9	4.18	4.04	0.14	3.5	No graphite
4–38	4	2.4	106.2	5.29	5.24	0.05	1.0	No graphite
4–47	3	2.4	104.6	6.09	5.31	0.72	13.6	Graphite only in cracks inside crystal

[a]Diamond crystal cracked
[b]The weight loss of the diamond crystal in run 4–12 is overestimated because the diamond cracked during the experiment.
[c]From Sonin *et al*. (2013)

internal step of the anvils. The pressure was determined from the calibration curve that describes the dependence of the pressure in the high-pressure cell from the external pressure on the multi-anvil block of the apparatus. PbSe and Bi were used as references for cell calibration in accordance with the known dependence of the electrical resistance in these substances from pressure (Decker *et al*. 1972; Chepurov *et al*. 1998). The temperature in the high-pressure cell was measured using a Pt-Rh thermocouple. Correction of thermocouple readings with increasing pressure in the cell during further heating was done according to known graphite-diamond equilibria (Day 2012). We estimate the accuracy in the determination of P and T in the experiments as being ±0.25 GPa and ±25°C, respectively; these values relate to the defined conditions in the samples, as a thermocouple was outside the Pt capsule. The details of the experimental procedures are described in Chepurov *et al*. (1998) and Chepurov *et al*. (2012).

The 2- or 24-h experiments (Table 1) were conducted under pressures of 2, 3, and 4 GPa in platinum capsules containing chemically pure reagents K_2CO_3 (1450°C) and $CaCO_3$ (1550°C). The experimental temperatures were chosen so that they exceed the melting temperatures of the carbonate phases. The pressure range of 2–4 GPa was chosen because these pressures reflect conditions for the initial stages of exhumation of diamondiferous rocks in UHPM complexes. Reagents were dried at 120°C for 2 h before sealing the Pt-capsules; capsules were sealed by electric arc welding. The diamonds used for the experiments were typical as-grown synthetic crystals, exhibiting flat-faced and sharp-edged octahedral habit with less-developed cube and tetrahedron-trioctahedron faces. Diamond monocrystals were used due to their smaller specific surface area compared to nano- or microcrystals, and diamond aggregates. The diamond crystals are characterized as being of type Ib-IaA, with a yellow colour. The diamonds were grown by the temperature gradient method in the system Fe-Ni-C at high P-T, following the method described in Chepurov *et al*. (1998). Only one crystal was used in each experiment. The diamonds were weighed before and after the experiments, and their weight (~2–6 mg before experimental runs) was controlled with a precision of ±0.02 mg. These synthetic diamonds are similar to and representative of natural diamond occurring in UHP complexes (see Discussion).

After the experiments, the diamond crystals were studied with MBS-10 and MBI-15 optical microscopes, and with a MIRA3 TESCAN scanning electron microscope in secondary electron mode. Raman spectra were collected with a Horiba Jobin Yvon LabRam HR800 spectrometer, equipped with an Olympus BX-41 confocal optic microscope. In order to obtain good spectra from small grains (≥2 μm), a 100× objective was used and the pinhole sizes were set to 50–100 μm. The samples were excited by a 50 mW CVI Melles Griot Ar-ion 514 nm laser, and the spectra were recorded by a liquid-nitrogen cooled Horiba Scientific Symphony II CCD detector.

Results

High-pressure experiments were performed on diamond monocrystals in this study to test rates of surface graphitization. The highest rate of surface graphitization was found in the 2 GPa experiments in which diamond crystals were almost completely enveloped by graphite. In experiments at 4 GPa only surface etching occurred in the form of the flat-bottomed, sometimes pyramidal- or triangular-shaped, inverted etching pits on the {111} faces.

In all of the experiments (Table 1), $CaCO_3$ and K_2CO_3 were present in a melt form; we infer this because the diamond crystals sank to the bottom of the capsules during the experiments. After the experiments, the diamond crystals retained their initial habit. Depending on the experimental pressure, they either were or were not coated with graphite.

After the experiments at 2 GPa for 2 h, the diamond crystals were largely to completely coated with a dense, opaque graphite cover (Figures 2 and 3). Raman spectra of surface graphite detected on the diamonds are shown in Figure 4. It is important to note that graphite was observed only on diamond crystals, whereas no graphite was found in the quenched $CaCO_3$ and K_2CO_3 melts or on the walls of the Pt capsules.

In experiments at 3 GPa for 24 h, the diamond crystals were only partially coated by graphite. In the $CaCO_3$ experiment (4–12), most of the graphite formed an incomplete envelope on the diamond (Figure 3(c)). In the K_2CO_3 experiment (4–47), graphite formed as flat segregations with uneven contours on the diamond. Unfortunately, the crystal in experiment 4–12 cracked during the experiment, so only the weight of the collected parts is given in Table 1, so the weight loss of this sample (see Table 1) is high relative to the actual value for loss due to diamond dissolution. The crystal from the K_2CO_3 experiment also fractured in the experiment, and graphite appeared in the fractures (Figure 2(e)). Trigons – the triangular etching pits with a negative {111} octahedron shape – were observed on the surfaces of the diamond crystals that were free of graphite segregations (Figure 3(d)).

After experiments at 4 GPa in $CaCO_3$, the diamond crystals either were free from etching (4–10 and 4–13) or

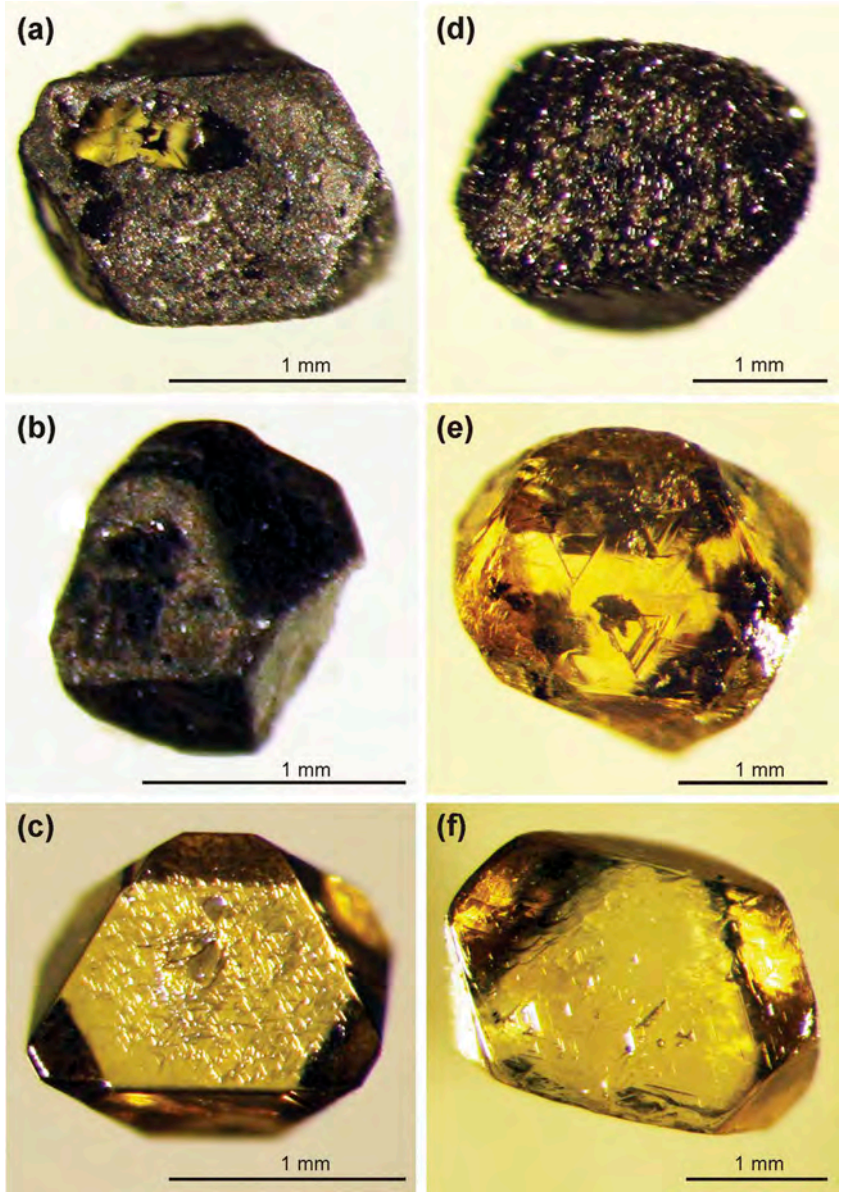

Figure 2. Diamond crystals after the experiments with $CaCO_3$ (a – 4–9, b – 4–16, c – 4–17) and K_2CO_3 (d – 4–29, e – 4–47, f – 4–34). Diamond crystals after the experiments retained their initial octahedral habit. (a–c) The graphite cover on diamond surfaces is opaque. (d–f) Negatively oriented trigons are present on the surfaces of diamond crystals that are free of graphite segregations.

exhibited only flat-bottomed trigons (4–17; Figure 2(c)). Surface graphite was not observed in any of the three crystals. After experiments at 4 GPa in K_2CO_3 (4–34, 4–38), flat-bottomed, sometimes pyramidal, triangular etching pits appeared on the octahedral diamond faces (Figure 2(f)). Columnar striations appeared in the areas close to the edges between the octahedral faces, and a sawtooth sculpturing occurred between the octahedral and the tetragonal-trioctahedral faces. No graphite was identified in the longer 24-h experiment.

There are no such graphite-free areas on the crystal from experiment 4–16 (Figure 2(b)) and only small areas of the diamond surface remained not covered by graphite on the crystal from experiment 4–9 (Figure 3(a)). Scanning electron microscope (SEM) imaging shows a fragment of the graphite cover at high magnification (Figure 3(b)). In the K_2CO_3 melt at 2 GPa, diamond was also covered with a dense carbon cover (Figure 2(d)).

Discussion

Surface graphitization of diamond has been observed at high pressures in several experimental studies (e.g. Sonin *et al*. 1997a, 1997b, 2006; Qian *et al*. 2001, 2004; Kozai and Arima 2005; Fedortchouk *et al*. 2007; Arima and Kozai 2008; Dobrzhinetskaya *et al*. 2013; this study). Kozai and Arima (2005) and Arima and Kozai (2008) used 0.7–1 mm natural octahedral diamonds from

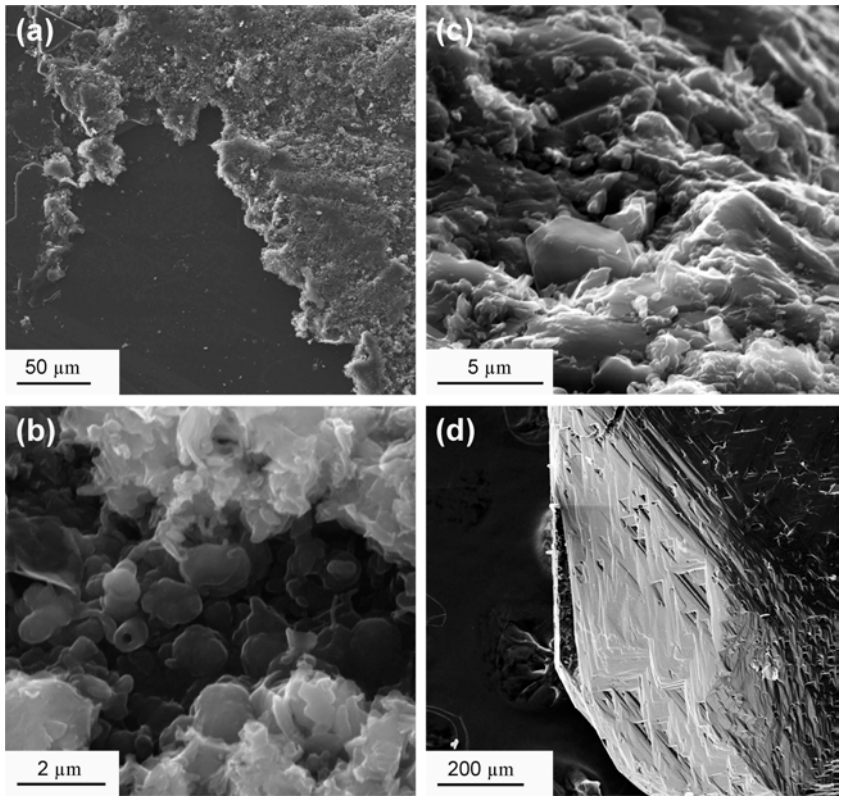

Figure 3. SEM images of diamond crystals after the experiments: (a–b) graphite forms a layer several microns thick on the diamond surface from run 4–9; (c) the graphite on the surface of the diamond from run 4–12 shows hexagonal crystallites; (d) negatively oriented trigons on the octahedral face of diamond crystal from run 4–47 (see also Figure 2(e)).

kimberlite and carbonate substrates, and found that an increase of the carbonate component in the melt leads to graphitization. Fedortchouk *et al*. (2007) studied the etching process on diamond in kimberlite and carbonate melts using 0.5–1.3 mm natural octahedral diamonds and diamond plates; they found that an absence of a free fluid leads to graphitization. Dobrzhinetskaya *et al*. (2013) observed surface graphitization on cuboctahedron synthetic diamonds in experiments in a $Mg(OH)_2$-medium, and Sonin *et al*. (1997a, 1997b, 2006) studied the surface graphitization process on both natural and synthetic octahedral diamonds (up to 50 mg) in basalt melt and a MgO-medium. These studies demonstrate that during surface graphitization, diamonds preserve their initial crystal form, but the influence of pressure variations on the process of surface graphitization was not investigated.

The effect of pressure on graphitization

Qian *et al*. (2001, 2004) report on the effects of pressure, temperature, and particle size on graphitization. Nano- to micron-scale diamond crystals were used in experiments from 2 to 8 GPa and 973° to 1673°K, but the morphology of the crystals and the nature of the medium used in the experiments are not specified in Qian *et al*. (2001, 2004). The rate of graphitization increases with temperature and decreases with pressure (Qian *et al*. 2001, 2004). Qian *et al*. (2001) also ran experiments with water included in the reaction chamber; 22% graphite was produced when water was present, and only 1% formed during the dry run. There is a clear catalytic effect of water on the diamond-to-graphite phase transition. Smaller diamond crystals (~5 nm) have lower activation energies than larger diamond crystals (30–40 μm, which approach the bonding energy of the C-C bond in diamond) because smaller crystals have a higher surface defect density (Qian *et al*. 2004). Because graphitization begins on surface defects, graphitization of nanodiamond starts earlier and at lower temperatures than microdiamond. Pressure suppresses graphitization and there is no graphitization of the 30–40 μm diamond at as low as 5 GPa, while a higher pressure of 8 GPa is required to prevent graphitization of the 5 nm diamond crystals (Qian *et al*. 2004).

Our experimental results provide new constraints on the role of pressure in diamond graphitization. In all of our experiments, the interaction of diamonds with the surrounding carbonate melt started with etching on

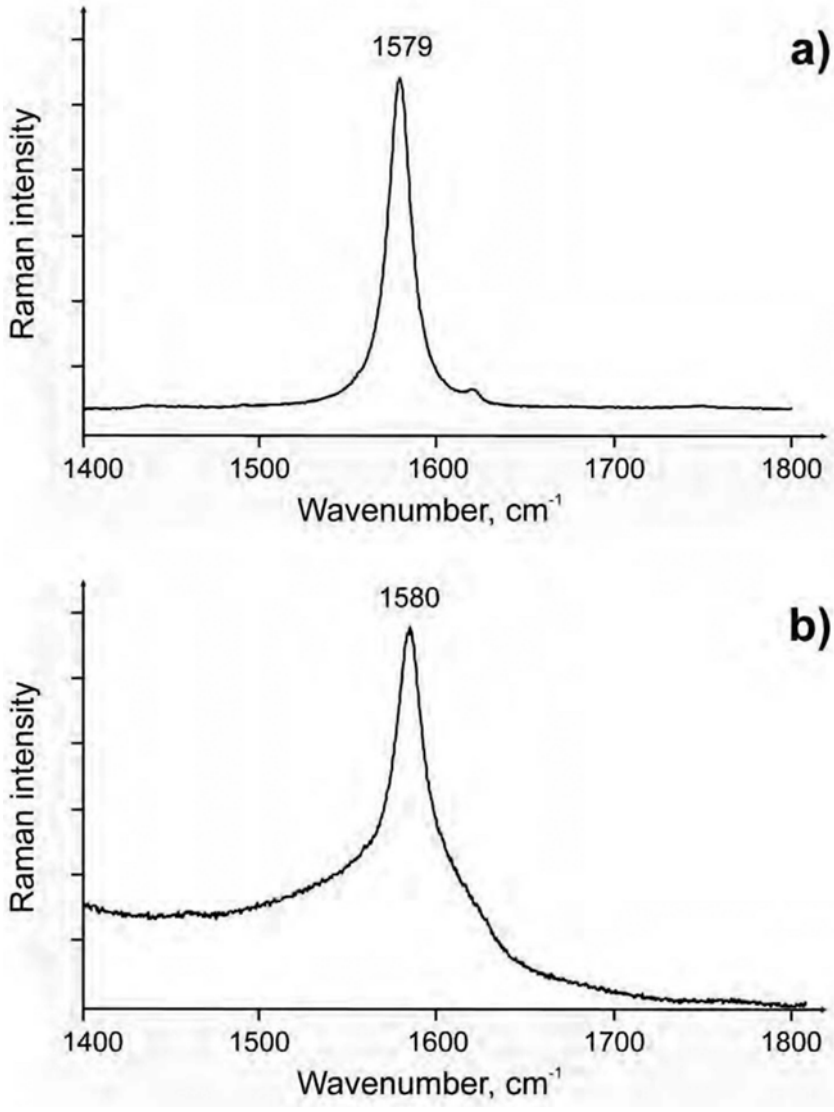

Figure 4. Raman spectrum of graphite on diamond surfaces after experiments (a) 4–16 and (b) 4–29. The broadened primary peaks for graphite at 1579 and 1580 cm^{-1} display a weak high-energy peak in (a) and a high wavenumber shoulder in (b) that indicate minor disorder in the microcrystalline graphite.

diamond recorded by the appearance of pits and sculptures on crystal surfaces. After carbon saturation of a system consisting of carbonate melt + fluid (that is, air in pores in the starting materials trapped during assembly of the capsules), the process switched to surface graphitization. The highest rate of surface graphitization is recorded at 2 GPa in the experiments. At 3 GPa, only the initial stage of surface graphitization is observed. No graphite formed in the 24-h experiment at 4 GPa. We can conclude that the rate of surface graphitization of diamonds in K_2CO_3 and $CaCO_3$ melts at high temperature (1450–1550°C) decreases considerably with increasing pressure.

The 'pressure vessel' effect

The total lack of surface graphitization at 4 GPa in these experiments demonstrates the important role pressure plays in the preservation of diamond in UHPM complexes. The tectonic model for fast exhumation of diamond-bearing UHPM rocks (tectonic rates up to cm/a) implies fast decompression to ca. 1 GPa at an almost constant high temperature (Figure 5). Based on results of this study, decreased pressure alone causes graphitization of diamond regardless of the exhumation rate. Microdiamonds are often found as inclusions in other minerals like garnet and zircon in UHP metamorphic

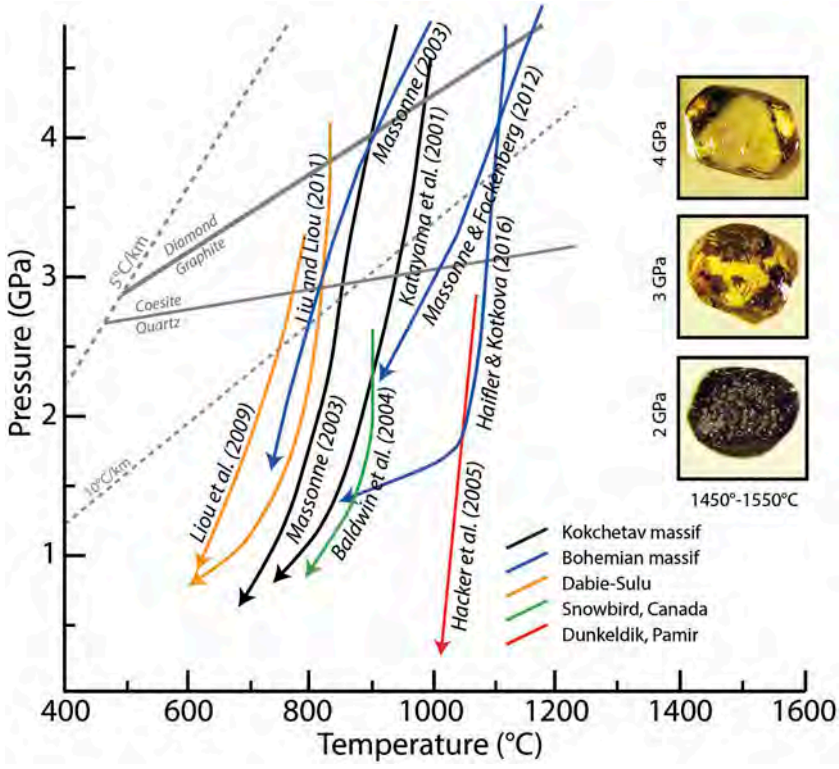

Figure 5. Representative exhumation paths for ultrahigh-pressure metamorphic (UHPM) complexes including the Kokchetav Massif, and two near-UHPM complexes, showing near-isothermal decompression at somewhat lower temperatures than our 1450–1550°C experimental conditions (modified after Haifler and Kotková 2016). Images of etched diamond and graphitized diamond crystals from our experiments aligned along an isothermal exhumation path at 1450–1550°C and 4, 3, and 2 GPa; showing an increase in surface graphitization rate at lower pressures (Runs #4–29, 4–34, 4–47; see Table 1 and Figure 2(d–f) and 3(d)). The quartz-coesite transition line is adopted from Bose and Ganguly (1995); the graphite-diamond transition line is after Day (2012).

rocks; these inclusions experience a residual pressure of up to 1–2 GPa during exhumation that results from the 'pressure vessel' effect that occurs in isolated inclusions in container minerals (Chopin 1984; Sobolev and Shatsky 1987, 1990; Sobolev *et al*. 2000; Van Roermund *et al*. 2002; Nasdala *et al*. 2003; Enami *et al*. 2007; Barron *et al*. 2008; Korsakov *et al*. 2009). A similar pressure vessel effect is achieved for larger, more kinetically stable diamonds in kimberlites in which they are exhumed as inclusions in olivine or in mantle xenoliths (e.g. Sonin *et al*. 2000 and the references therein). Metastable diamond inclusions survive exhumation in UHP complex rocks with little or no graphitization because of the excess pressure on these isolated inclusions, and because inclusions are protected from interaction with C-O-H subduction fluids.

The residual pressure on inclusions in container minerals is commonly measured by a shift in the Raman peak for the inclusion minerals. Ashley *et al*. (2014) estimated the residual pressure of quartz inclusion in garnet from blueschist-facies rocks on Sifnos, Greece, to be 0.74 GPa based on a maximum Raman peak shift of 6.57 cm^{-1}, while the garnet itself grew at 2.03 GPa (assuming growth at 530°C). Parkinson and Katayama (1999b) and Parkinson (2000) reported monocrystalline coesite inclusions with a 2–5 cm^{-1} Raman frequency shift of the coesite band that retain ultrahigh confining pressures of 1.9–2.3 GPa for UHP complexes in Kazakhstan, Indonesia, and China. Izraeli *et al*. (1999) reported an internal pressure of 0.13–0.65 GPa in olivine included in diamond, and calculated source pressures of 4.4–5.2 GPa for Siberian diamonds. Enami *et al*. (2007) assessed the quantitative correlation between the Raman frequency shift and metamorphic pressure. Pressures are calculated using the bulk moduli and thermal expansion of the two phases involved (the inclusion and the including phase). Enami *et al*. (2007) found a higher frequency shift for inclusions than for the same phase in the matrix, and the frequency shift is specific to the individual host minerals in eclogites. Quartz inclusions in garnet and minerals like kyanite have a higher Raman frequency shift than container minerals like omphacite or epidote. And the Raman frequency shift systematically increases with increasing peak metamorphic pressure. Yamamoto *et al*. (2002) estimated residual pressure of 0.96–1.04 GPa for CO_2-dominated fluid inclusions; their results were similar to

Enami *et al*. (2007) finding that inclusions show residual pressures that were specific to the individual host minerals of spinel, orthopyroxene, clinopyroxene, and olivine.

The best container vessel is diamond itself: Navon *et al*. (2017) recently demonstrated residual pressure for solid nitrogen inclusions in diamond crystals as high as 10.9 GPa. Raman spectroscopy confirmed the super deep origin of the Juina diamonds based on sub-micrometer inclusions of crystalline molecular nitrogen, the cubic δ-N_2 phase, at 10.9 ± 0.2 GPa, the highest pressure ever measured in a mineral inclusion (Navon *et al*. 2017). The high pressure calculated from the Raman spectra is supported by atomic force microscopy results (Navon *et al*. 2017), and the mineralogy of diamond inclusions corresponds to experimental predictions for a transition zone or lower mantle origin (Harte 2010; Walter *et al*. 2011; Harte and Richardson 2012; Kaminsky 2012)

Preserved UHP diamond protected from interaction with fluid

Based on the results of this study, diamond stability increases considerably with increasing pressure and decreasing temperature (cf. Sonin *et al*. 2000). The process of surface graphitization of diamond also strongly depends on the availability and composition of a fluid phase, which acts as a catalyst in the graphitization process (Evans and Sauter 1961; Phaal 1965; Dobrzhinetskaya 2012). Diamonds from the UHP Kokchetav and Erzgebirge massifs precipitated in the presence of supercritical C-O-H fluids based on their fluid inclusion analysis (Dobrzhinetskaya 2012). Kimberlite systems have a high fluid content and the dissolution of diamonds in kimberlites leads to the formation of sub-rounded and rounded crystals (Fedortchouk *et al*. 2007). And a near absence of diamond dissolution occurs when diamond is contained within a solid silicate matrix compared to diamond in melt (Sonin *et al*. 1997b; Zhimulev *et al*. 2004). Further study of the effect of C-O-H fluids or silicate and carbonate melts on diamond graphitization is necessary because surface graphitization of diamond is inevitable at P-T conditions for the thermodynamic stability of graphite, and certainly at the relatively high temperatures (up to 1000–1200°C) that UHP rocks experience during metamorphism and exhumation that can last for periods up to millions of years.

We have demonstrated that at 2–3 GPa and temperatures of ~1500°C, surface graphitization of diamond can comprise up to 25 wt.% (Table 1). Peak metamorphic temperatures for UHPM rocks (e.g. the Kokchetav massif) that range from ~900–1200°C, corresponding to exhumation through pressures of 2–3 GPa, are lower than in our experiments (Figure 5); these lower temperature conditions will result in a lesser degree of surface graphitization of diamond compared to our experiments. In an open system, a percolating C-O-H subduction fluid could precipitate graphite on diamond, but the absence of dissolution structures (striation, etching pits) on the diamond surfaces and the presence of cubic and octahedral diamond found in UHPM complexes (see Dobrzhinetskaya 2012) suggests that the preserved diamonds were well-protected from interactions with external fluids (see Stöckhert *et al*. 2001). Those diamonds that were trapped in pressure vessels like zircon or garnet were not only protected from the chemical influence of an external fluid, but as we infer, also experienced high residual pressure within their container minerals, enhancing their preservation from surface graphitization. This has allowed these diamonds to preserve their initial morphologies or to be only partially influenced by surface graphitization (Shatsky *et al*. 1998; Ogasawara *et al*. 2000; Ishida *et al*. 2003; Korsakov *et al*. 2010; Schertl and Sobolev 2013). We conclude that the main controlling factor for the preservation of microdiamond in UHPM complex rocks is their inclusion within 'pressure vessels' (i.e. in minerals such as zircon and garnet) meaning that diamond inclusions experience a relative increase in pressure of 1–2 GPa, and those microdiamond inclusions were also protected from any circulating fluids that would have driven graphitization.

Exhumation as fast as subduction

Extrapolating our experimental data and applying this and the results of the previous work to UHPM complexes suggest that the most favourable conditions for diamond preservation during exhumation of UHP rocks are a combination of 1) maintaining high-pressure conditions likely with the aid of a 'pressure vessel' effect on diamond inclusions in container minerals; and 2) dry conditions in the rock or mineral containing diamond. Microdiamonds in UHPM complexes crystallize at 6–9 GPa and 800–1200°C corresponding to minimum subduction depths of 120–150 km, and up to ~190–280 km (Hacker 2006; Dobrzhinetskaya 2012). Stöckhert and Gerya (2005) used numerical modelling to show UHP rocks returning to 1.0 GPa in 1–5 Ma; this gives exhumation rates at least as fast as subduction on the scale of 10 s of km/Ma (e.g. Rubatto and Hermann 2001; Hacker *et al*. 2003; Baldwin *et al*. 2004; Ernst 2006; Hacker 2006; Parrish *et al*. 2006; Rubatto *et al*. 2011; Dobrzhinetskaya 2012).

Exhumation rates for representative diamond-bearing UHP complexes range from as low as 6–8 mm/a (Dabie-Sulu) to as much as 30+ mm/a (Kokchetav and the Italian Alps) to rise to the mid-crust, corresponding to plate tectonic rates (Ernst and Peacock 1996; Peacock 1996; Ernst and Peacock 1996; Hacker *et al*. 1998, 2000; Gebauer *et al*. 2001; Hermann *et al*. 2001; Rubatto and Hermann 2001; Hacker *et al*. 2003; Baldwin *et al*. 2004; Ernst 2006; Rubatto *et al*. 2011). Using the results of numerical modelling by Stöckhert and Gerya (2005), exhumation of UHP complex rocks from the diamond stability field at upper mantle depths to ~1.0 GPa takes place in 1–5 Ma; if we assume exhumation from a minimum of 120 km and a maximum of 280 km (see Dobrzhinetskaya 2012), we estimate exhumation rates of 24–56 mm/a (a 'fast' tectonic rate) up to as much as 120–280 mm/a. The much faster exhumation rates would require an additional force to enhance exhumation – *buoyancy* of the UHP complex as a whole is typically employed to assist tectonic forces (Ernst *et al*. 1997; Ernst 2006). The mafic/eclogitic component of the subducted continental crust comprises <10% of the subduction complex, at least in the tectonic slice that is exhumed and not subducted (Ernst *et al*. 1997; Ernst 2006).

Conclusions and future work

Our experimental results demonstrate that the rate of surface graphitization of diamonds in the presence of carbonate melts increases with decreasing pressure, and graphitization is completely suppressed at 4 GPa. The results of this and other experiments suggest that when diamonds are subjected to lower P-T conditions in the graphite stability field, surface graphitization of diamond is a rapid process – 20–120 min in this study – six orders of magnitude less than the time required to exhume UHP rocks. It is not the exhumation *rate* that controls whether diamond is preserved in UHP rocks but the increased pressure acting on the diamond inclusion (the 'pressure vessel' effect). The container mineral also shields diamond from interaction with a fluid or melt phase, kinetic drivers of graphitization.

It is necessary to establish criteria for differentiating between graphite that is crystallized from a fluid or melt, and graphite that formed during surface graphitization, to identify which of the macro- and micromorphological characteristics of diamonds result from each process. To gain further insight into diamond preservation in UHPM subduction complexes, more experimental work needs to be done to understand diamond growth and graphitization in silicate melts and C-O-H fluids; and analysis of fluid inclusions in diamond and other index minerals is necessary to understand the composition of the subduction fluids, mantle metasomatism, and how melts/fluids interact with subducted continental crust at UHPs.

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Disclosure statement

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