Graphite inclusions in diamond, K-bearing clinopyroxene, garnet and kyanite and graphite coatings around microdiamonds from the ultrahigh-pressure Kokchetav Massif, northern Kazakhstan were investigated by means of scanning electron microscopy, laser Raman spectroscopy and X-ray diffraction. Important observations include the increasing size of the graphite crystals from the diamond–graphite interface to the external part of the graphite coatings, the high volume fraction of graphite in the graphite coatings, the presence of composite crystals of successively formed diamond core–graphite mantle zone–diamond rim–external graphite coating, the spherulitic texture of the graphite coatings, the formation of both ordered and disordered graphite and the absence of any fluid associated with the graphite inclusions in diamond and other ultrahigh-pressure metamorphic (UHPM) minerals. These features combined with the presence of oriented graphite flakes in K-bearing clinopyroxene and in diamond-bearing garnet and kyanite and the presence of intergranular diamonds without graphite coatings in the quartzo-feldspathic matrix require reconsideration of the generally accepted diamond graphitization model for interpreting the formation of graphite in UHPM rocks. Metastable growth of graphite within the diamond stability field is suggested and the following crystallization scheme for the C-polymorph is proposed: graphite was the first C-polymorph formed in the diamond stability field, followed by diamond; the graphite coatings around diamond formed during the final stage of UHPM conditions.

KEY WORDS: diamond; graphite; metastable growth; UHP metamorphism; Raman spectroscopy; Kokchetav Massif

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INTRODUCTION

The diamond–graphite equilibrium has been thoroughly investigated in both natural and experimental systems (Kennedy & Kennedy, 1976; Akaishi et al., 1990; Bundy et al., 1996; Sokol et al., 2001b). This equilibrium reaction has been used for the subdivision of the Earth’s mantle into the graphite and diamond facies (Dobretsov et al., 1970). Diamond in crustal-derived metamorphic rocks from the Kokchetav Massif (northern Kazakhstan) was initially interpreted to be of metastable origin (Letnikov, 1983; Nadejdina & Posukhova, 1990; Dohrzhinetkaya et al., 1994). Nonetheless, the abundance of ultrahigh-pressure metamorphic (UHPM) relics in diamond-bearing rocks from the Kokchetav Massif (Sobolev & Shatsky, 1990; Shatsky et al., 1995), and from the Erzgebirge, Germany (Massonne, 1999; Nasdala & Massonne, 2000) and the Rhodope Metamorphic Province, Greece (Mposkos & Kostopoulos, 2001; Perraki et al., 2006) supports a metamorphic origin of the diamond stability field as a result of co-crystallization of diamond and graphite within its ultrahigh-pressure (UHP) stability field.

Graphite in UHPM rocks has been attributed to the partial replacement of diamond within the graphite stability field (Zhang et al., 1997; Massonne et al., 1998; Ogasawara et al., 2000; Zhu & Ogasawara, 2002). In contrast, metastable crystallization of graphite within the diamond stability field has been reported in experiments carried out in metal-free systems (Akaishi et al., 1990; Yamaoka et al., 2002a, b; Sokol et al., 2004, and references therein). Khokhryakov et al. (2009) showed experimentally that graphite inclusions in diamond crystals could form not only within the graphite stability field prior to or after diamond crystallization, but also within the diamond stability field as a result of co-crystallization of diamond and graphite. Zang et al. (2009) demonstrated that at diamond-stable conditions, in metal solvent assisted experiments, the transformation from diamond to graphite could occur despite thermodynamic predictions to the contrary.

Pearson et al. (1994) were the first to study the possible metastable crystallization of graphite within the diamond stability field. They found that P–T estimates for some graphite-bearing xenoliths fell in the diamond stability field, although they were lower than those obtained from diamond-bearing xenoliths. Pal’yanov et al. (2007) observed the appearance of metastable graphite in the thermodynamic stability field of diamond in a carbonate–chloride–silicate–water–carbon system, and proposed the possible co-crystallization of diamond and metastable graphite in the Kokchetav rocks as a result of a change in fluid composition.

The transformation of organic material originally present in sedimentary rocks to graphite has been well established for regionally metamorphosed rocks (e.g. Pasteris & Wopenka, 1991; Beyssac et al., 2002, and references therein). It is well known that the degree of crystallinity of carbonaceous material increases with the grade of metamorphism (e.g. Pasteris & Wopenka, 1991; Beyssac et al., 2002, and references therein). However, both highly and poorly ordered graphite has recently been identified as inclusions in garnet from diamondiferous metapelitic rocks from the Rhodope Massif of Greece (Perraki et al., 2006). In addition, graphite with poor crystallinity has been grown in the diamond stability field during HP–HT experiments (Yamaoka et al., 2002b). Poorly ordered graphite has also been reported in experiments involving partial graphitization (at P = 2·0 GPa and T = 1400 K) of nanometric diamonds by Qian et al. (2004), although only well-ordered graphite was identified in their experiments with submicroscopic diamonds (30–40 μm). These studies indicate that factors other than temperature can affect the graphite crystallinity, especially in high- or ultrahigh-pressure metamorphic rocks.

In the above context graphitization is considered to be the solid-state transformation of thermodynamically unstable non-graphite carbon into graphite by means of heat treatment (IUPAC Compendium of Chemical Terminology, 2nd edition, 1997). Here we use the term to indicate the transformation of metastable diamond into graphite by heat treatment.

In this study, we performed a combined in situ scanning electron microscope (SEM), micro-Raman and X-ray study of graphite inclusions in diamonds and graphite coatings around diamonds from the UHPM rocks of the Kokchetav Massif, northern Kazakhstan, to investigate the diamond–graphite relationship and to determine the internal structure of the graphite inclusions and obtain information about the pressure conditions under which the inclusions were trapped.

PETROGRAPHY

Diamonds were selected from calc-silicate rocks (impure marbles and garnet–clinopyroxene (K-bearing diopside) rocks) and gneisses (garnet–biotite, garnet–clinopyroxene–biotite, garnet–kyanite–biotite, garnet–clininozoisite–biotite gneisses) from the Barchi-Kol area and the Kumdy-Kol microdiamond deposit (Kokchetav Massif, northern Kazakhstan). All the rock types have been previously described elsewhere (Shatsky et al., 1995, 1998; De Corte et al., 1998, 2000; Korsakov et al., 2002, 2006). More than 17 samples from different lithologies and sample localities in the Kokchetav massif (Table 1) were selected for this study.

The samples of calc-silicate rocks are light-coloured and coarse-grained, commonly with compositional layering. The mineral assemblages of the impure calcite marbles and garnet–clinopyroxene rocks is the same garnet, K-bearing clinopyroxene and calcite, with or without biotite, K-feldspar and quartz. However, the modal compositions of these rock types are different. In the impure
marbles dolomite or calcite are the predominant minerals, although the silicate content may be as high as 60 vol. %. The garnet–clinopyroxene rocks mainly consist of garnet (up to 40 vol. %) and K-bearing clinopyroxene (up to 90 vol. %), with calcite, biotite, K-feldspar and quartz up to 10 vol. % each. The garnet–biotite, garnet–clinopyroxene–biotite, garnet–kyanite–biotite and garnet–clinozoisite–biotite gneisses are typically medium-grained. The modal compositions of the gneisses are variable. In addition to garnet porphyroblasts, diopside–augite clinopyroxene (10–40 vol. %) and kyanite (5–15 vol. %) or clinozoisite (5–40 vol. %) porphyroblasts occur in a quartzo-dolomitic matrix (Korsakov et al., 2002). Some samples consist of two different rock types; for example, in sample G11 garnet–biotite layers alternate with garnet–biotite–quartz layers (see Korsakov et al., 2004, for further details).

The diamond crystals in the garnet–biotite, garnet–clinopyroxene–biotite, garnet–kyanite–biotite and garnet–clinozoisite–biotite gneisses are yellowish cuboids with a rough surface (up to 500 μm in length), whereas in the clinozoisite-bearing gneisses the diamonds are perfectly shaped yellowish to colorless octahedral crystals (≤25 μm in size) (Table 1). The characteristic features of these micro-diamonds have been described in detail by Shatsky et al. (1998), De Corte et al. (2000) and Korsakov et al. (2002).

Both cuboid and octahedral diamonds occur as inclusions in refractory minerals (zircon, garnet or K-bearing clinopyroxene). Cuboid diamonds are also observed in the matrix (Fig. 1). Diamond and graphite occur as single crystals or as coexisting phases without showing any preferred spatial distribution within the host porphyroblasts (Fig. 2).

In some samples of kyanite gneiss, large garnet and kyanite porphyroblasts appear to exhibit a zonal distribution in the carbon polymorphs, with abundant preferentially oriented graphite inclusions dominating in the core and diamond mainly occurring in the mantle or the outermost zone of the porphyroblasts (Fig. 3); however, diamond inclusions also occur in the graphite-free cores of the kyanites. Diamonds are also found as inclusions in garnet, which in turn is included in the graphite-rich zone of the kyanite porphyroblasts (Fig. 4). Cuboid diamonds commonly contain numerous semi-transparent, flake-like, graphite-inclusions in their core and outermost rim (Fig. 5). Similar graphite flakes occur in garnet and K-bearing clinopyroxene (Fig. 5a and b). There is a preferred orientation of graphite flakes with respect to the host minerals. Graphite (001) is parallel to (110) of garnet and (100) of K-bearing clinopyroxene. The graphite in cuboid diamonds consists of numerous, uniformly oriented crystal flakes with their (001) faces

### Table 1: Summary of the sample localities, rock types, diamond textures and morphology, and graphite textures

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Sample no.</th>
<th>Diamond morphology</th>
<th>n</th>
<th>Size of diamond crystal (μm)</th>
<th>Graphite Inclusion</th>
<th>Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kumdy-Kol (53° 08' 10&quot; N, 68° 57' 30&quot; E)</td>
<td>Grt–Cpx</td>
<td>G0</td>
<td>3500</td>
<td>30-250</td>
<td>common</td>
<td>almost all</td>
</tr>
<tr>
<td></td>
<td>Grt–Cpx</td>
<td>GAK08-1</td>
<td>2000</td>
<td>30-80</td>
<td>rare</td>
<td>rare</td>
</tr>
<tr>
<td></td>
<td>Grt–Cpx</td>
<td>GAK08-2</td>
<td>2500</td>
<td>30-150</td>
<td>common</td>
<td>rare</td>
</tr>
<tr>
<td></td>
<td>Grt–Cpx and Grt–Bt gneiss</td>
<td>G11</td>
<td>1500</td>
<td>11-40</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Marble</td>
<td>K89-41</td>
<td>870</td>
<td>5-30</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Marble</td>
<td>GA11</td>
<td>1730</td>
<td>5-45</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td>Barchi-Kol (53° 09' 15&quot; N, 68° 42' 20&quot; E)</td>
<td>Zo-gneiss</td>
<td>B95-29</td>
<td>250</td>
<td>10-40</td>
<td>rare</td>
<td>rare</td>
</tr>
<tr>
<td></td>
<td>Zo-gneiss</td>
<td>114-100</td>
<td>140</td>
<td>25-50</td>
<td>common</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Zo-gneiss</td>
<td>B94-83</td>
<td>370</td>
<td>10-50</td>
<td>common</td>
<td>rare</td>
</tr>
<tr>
<td></td>
<td>Zo-gneiss</td>
<td>B95-42</td>
<td>150</td>
<td>10-60</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Grt–Bt gneiss</td>
<td>B33-35</td>
<td>120</td>
<td>15-50</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Ky-gneiss</td>
<td>B29-04</td>
<td>130</td>
<td>10-35</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Ky-gneiss</td>
<td>B9-04</td>
<td>140</td>
<td>10-40</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Ky-gneiss</td>
<td>B34-314</td>
<td>220</td>
<td>10-50</td>
<td>n.i.</td>
<td>rare</td>
</tr>
<tr>
<td></td>
<td>Ky-gneiss</td>
<td>B48-04</td>
<td>260</td>
<td>15-60</td>
<td>n.i.</td>
<td>common</td>
</tr>
<tr>
<td></td>
<td>Marble</td>
<td>B93-49</td>
<td>170</td>
<td>5-35</td>
<td>n.i.</td>
<td>rare</td>
</tr>
<tr>
<td></td>
<td>Grt–Cpx</td>
<td>B94-124</td>
<td>90</td>
<td>30-70</td>
<td>n.i.</td>
<td>rare</td>
</tr>
</tbody>
</table>

* n, number of investigated crystals; n.i., not identified.
oriented parallel to the (111) diamond face. In contrast to the cuboids, the octahedral crystals contain single graphite inclusions with a plate-like habit (Fig. 5). The graphite crystals are small and idiomorphic (Fig. 5), with their (001) faces oriented sub-parallel to the (111) diamond face. Graphite inclusions in cuboid diamonds are typically accompanied by fractures in the surrounding diamond (Fig. 5f), whereas tiny fractures are rarely visible around graphite inclusions in octahedral diamonds.

Graphite coatings locally surround diamonds, both cuboid and octahedral crystals, but because of their small size their genetic relationship is unclear (Shatsky et al., 1995; De Corte et al., 2000). Using De Corte’s polishing technique for single diamond crystals (De Corte, 2000), several hundred diamonds were polished in thin section and their in situ study has provided crucial information about the relationship between diamond and graphite. The graphite coatings consist of coarse-grained graphite aggregates (sub-individuals up to 50μm in size), locally characterized by radial or spherulite textures (Fig. 6). It is also worth noting that some large euhedral graphite crystals, up to 50μm along the c direction (Fig. 7a and b) form overgrowths and have very thin ‘necks’, which connect them to the graphite-coated diamonds. The thickness of the graphite coatings is highly variable, ranging from
Fig. 2. Photomicrographs (a, b) showing the spatial distribution of graphite, graphite-coated diamond and graphite-free diamond crystals within a garnet porphyroblast (sample B93-38, plane-polarized light).

Fig. 3. Photomicrographs showing (a, b) the spatial distribution of graphite and diamond within a kyanite porphyroblast. I, Graphite-rich kyanite zone, II, Diamond-bearing zone. (c, d) Enlarged view of rectangles in (b) showing diamond inclusions in the core and the rim of the kyanite porphyroblast, respectively. [Sample B09-4; (a, c, d) plane-polarized light; (b) cross-polarized light.]
<1 to 40 μm; however, in diamond crystals of about 100 μm size, the coatings reach an average thickness of about 20 μm. Graphite coatings are estimated to constitute ~40% of the total volume occupied by the graphite + diamond aggregates. Dissolution of the graphite coatings using a mixture of H₂SO₄ + K₂Cr₂O₇ resulted in similar values (37 vol. %). Graphite-coated diamonds are present as inclusions in garnet, K-bearing clinopyroxene, zircon and as intergranular crystals in the carbonate-silicate matrix (Fig. 1). In all cases they lack radial cracks.

In rare cases, composite crystals with a diamond core–graphite mantle zone–diamond rim–external graphite coating are found (Fig. 8). These composite diamond–graphite crystals are very fragile, so it was not possible to prepare doubly polished sections and study the diamond–graphite relationship in detail.

**ANALYTICAL METHODS**

**Scanning electron microscope (SEM) study**

A LEO 1430 VP SEM (Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Science, Novosibirsk), was used to study the morphology of graphite coatings and diamond, the structure of graphite-coated and graphite-free diamond faces and the graphite layers. The probe current ranged from 10⁻¹² to 10⁻⁶ A and the maximum magnification was 20 000. The typical accelerating voltage of the measurements was 20 000 V.

**Laser Raman spectroscopy**

Dispersive laser-Raman spectra were obtained using a Renishaw (Wotton-under-Edge, UK) System-1000
A spectrometer equipped with a 785 nm diode laser (30 mW), a 1200 lines/mm diffraction grating and a Peltier-cooled CCD detector was used at Ghent University, Belgium. The spectrometer is equipped with an Olympus BH-2 microscope, with 5×, 20×, 50× and 80× objective lenses, providing a lateral resolution of 1 μm. Wavenumber calibration was performed by measuring the atomic lines from neon (Hutsebaut et al., 2005). Raman spectra were also obtained on a 30 cm single polychromator (Chromex, 250is), equipped with an optical microscope (Olympus, BX60), Ar⁺ (514.5 or 488 nm; Ion Laser Technology, 5500 Å), and a CCD camera with a resolution of 1024×128 pixels (Andor, DU401-BR) at Tohoku University and the University of Tokyo, Japan. The Rayleigh line was removed by using a holographic supernotch plus filter (Kaiser, HSPF-514.5-1.0). The excitation laser beam was focused on
a spheroidal spot of approximately 1 μm × 1 μm × 5 μm using an Olympus 100 × objective lens (N.A. = 0.95) with a confocal arrangement allowing detection of signals exclusively from the inclusions. A 2D Raman map was recorded with a step size of 1 μm.

**X-ray diffraction study**

Four diamond (100–300 μm) crystal fragments (with irregular shape) covered by graphite, were studied by X-ray single-crystal diffraction at the Dipartimento di Scienze della Terra, Università di Firenze, Italy. Preliminary experiments, carried out on an automated Bruker P4 diffractometer equipped with a conventional point-detector using graphite-monochromatized MoKα radiation, showed the absence of diffraction peaks belonging to any crystalline phase other than diamond. The same samples were then analyzed with an Oxford Diffraction Xcalibur 2 diffractometer, fitted with a Sapphire 2 CCD detector. The crystals underwent 360° rotation around the Φ-axis, which was perpendicular to the incident X-ray beam. However, overexposed rotation photographs showed only weakly visible rings as a result of disoriented polycrystalline graphite together with strong and relatively sharp reflections belonging to the diamond structure. For this reason, a diamond sample was selected and analyzed using the powder diffraction technique, which was carried out by means of a 114.6-mm Gandolfi camera using Ni-filtered CuKα radiation.

**RESULTS**

**SEM study of graphite and diamond**

Graphite coatings form both polycrystalline aggregates and isolated single grains (Fig. 7). The size of the graphite crystals varies significantly from 1 to 50 μm (Figs 7 and 9). In most cases, small graphite crystals (Gr-S) cover the...
diamond surface, whereas the large graphite (Gr-L) crystals overgrow the fine-grained graphite. Some large euhedral graphite crystals (up to 100 μm along the c direction) form overgrowths and have very thin 'necks', which connect them to the graphite-coated diamonds (Fig. 7a).

Growth layers, up to 0.01 μm thick, occur on some graphite crystals on the {001} surface (Fig. 7c and d).

Graphite-coated and graphite-free diamond surfaces were studied by SEM to check for any possible difference in their surface morphologies. As has been shown...
diamond morphology varies significantly within the samples. Both graphite-free and graphite-coated diamonds form a continuous range from perfect octahedral to skeletal crystals in clinozoisite-bearing gneisses and from cuboid to skeletal crystals in garnet-clinopyroxene rocks (Fig. 10). The morphology of surfaces $\{111\}$ and $\{100\}$ remains the same for both graphite-free and graphite-coated diamonds. No dissolution features, such as trigons and rounded ribs (for further details see Sunagawa, 2005), were observed in the diamond crystals.

Fig. 8. (a–c) Photomicrographs of composite crystal with diamond core–graphite mantle zone–diamond rim–external graphite coating. It should be noted that this composite crystal is an inclusion in a garnet porphyroblast.
Raman spectroscopy of carbon polymorphs

Diamond

The rough surface of the diamond cuboids causes some difficulties with *in situ* Raman spectroscopy. Two faces were polished to serve as ‘windows’ on all cuboid crystals, whereas octahedral crystals have their own ‘windows’ through flat {111} faces.

The main diamond Raman band (Solin & Ramdas, 1970) of the single diamonds studied here appears as a sharp band at 1329–1336 cm\(^{-1}\) with a full width at half maximum height (FWHM) in the range of 3.6–9.2 cm\(^{-1}\). There is no general correlation between the Raman shift and the FWHM as seen in metamorphic microdiamonds from other locations (Ishida et al., 2003; Yang et al., 2003; Godard et al., 2005; Korsakov et al., 2005; Perraki et al., 2006, 2009; Menneken et al., 2007).

Graphite inclusions and coatings

The Raman spectrum of carbonaceous material is highly sensitive to its crystallinity. In the first-order region, a single Raman mode (G band) is expected at around 1580 cm\(^{-1}\) (Tuinstra & Koenig, 1970; Nemanich & Solin, 1979; Ferrari & Robertson, 2000). An additional laser wavelength-dependent band appears at around 1350 cm\(^{-1}\) (\(D^0\)) when excited with a 514.5 nm Ar\(^+\) laser [or 1306 or 1357 cm\(^{-1}\) when respectively the 785 nm or 488 nm excitation laser line was used (Matthews et al., 1999)]. The \(D^0\) band and a shoulder at around 1620 cm\(^{-1}\) (\(D^{00}\)) are typically observed in disordered carbonaceous material (Lespade et al., 1982; Wang et al., 1990; Pasteris & Wopenka, 1991; Wopenka & Pasteris, 1993). In the second-order region, several bands (also laser-dependent, corresponding to overtone and combination scattering) appear at around 2400, 2700, 2900 and 3300 cm\(^{-1}\) (Nemanich & Solin, 1979; Wopenka & Pasteris, 1993).

Semitransparent flakes of graphite in diamond, garnet and clinopyroxene (Fig. 5) were analyzed *in situ* (Fig. 11). The intensity of the G band strongly depends on the thickness of the graphite flakes. The external part of the graphite inclusions in diamond is characterized by weak disordering; no disordering appears in the core of the...
graphite inclusions. Disordered bands were obtained in the Raman spectra of the graphite coatings around diamond crystals. Surface graphite also exhibits disordering. Graphite inclusions in garnet and K-bearing clinopyroxene are highly ordered as shown by the presence of the $G$ band at $\sim 1580 \text{ cm}^{-1}$ and the absence of any disordered band (Fig. 11).

The order-disorder pattern of a graphite inclusion in microdiamond can be shown in a plot of the graphite/diamond ratio vs the main graphite band at around $\sim 1580 \text{ cm}^{-1}$ (Fig. 12). As mentioned above, for all the collected spectra in the outermost zone of the graphite inclusions the $D'$ mode appears at $1641 \text{ cm}^{-1}$, exhibiting a significant shift from $1620 \text{ cm}^{-1}$ at ambient pressure; any other disordered band is totally absent. The second-order spectrum ($2500–3000 \text{ cm}^{-1}$) for the rim zone of the graphite inclusions yielded two broad bands at around $2700$ (S1) and $2900$ (S2) cm$^{-1}$.

In summary, disordering occurs in the external part of the graphite inclusions in diamonds as well as in some graphite coatings around diamond exposed at the polished surface. The core of the graphite inclusions in diamonds, garnet and K-bearing clinopyroxene are highly ordered.

X-ray diffraction results
An X-ray powder diffraction pattern of a graphite-coated diamond from garnet-clinopyroxene sample G0, in which the intensities were measured with an automated densitometer, shows that the peaks for pure diamond are located at $2\Theta=43.9^\circ$ and $75.4^\circ$ (Fig. 13). The intensity of the sharp graphite (002) peak is located at $2\Theta=26.6^\circ$. The diffraction pattern is similar to that reported by Qian et al. (2004) (spectrum d in their fig. 1) for graphite formed after a synthetic nanodiamond was heated at $1173 \text{ K}$ and $2 \text{ GPa}$. The sharp (002) graphite peak is believed to derive from the strong sample texture (Qian et al., 2004) as it does not occur with other peaks. Because of its strong anisotropic nature, graphite grew preferentially along the (002) plane. As a result of the low quality of the diffraction pattern, determining the volume percentage of graphite from the X-ray pattern by fitting using the Rietveld method was not possible.

DISCUSSION
Coesite- and/or diamond-bearing UHPM complexes are considered to be very good indicators of subduction of continental crustal materials to depths $\geq 120 \text{ km}$ (see Chopin, 2003; Ernst, 2006). Quartz-coesite and graphite-diamond equilibria are generally used to subdivide the eclogite-facies metamorphic rocks into quartz- or coesite-subfacies, and graphite- or diamond-subfacies. The presence of diamond and graphite within the same sample was first interpreted as evidence for their formation near to the diamond–graphite equilibrium boundary (Sobolev & Shatsky, 1990). However, higher pressure peak metamorphic conditions were subsequently estimated for these rocks (Hermann, 2003; Massonne, 2003) implying that graphite can be metastably preserved at a pressure as high as $6 \text{ GPa}$ and a temperature of $1000–1100^\circ\text{C}$.
Although more research on both experimental and natural systems needs to be undertaken, the possibility of metastable graphite growth has gained ground in recent experimental studies (Sokol et al., 2001a, 2001b; Pal’yanov et al., 2002; Yamaoka et al., 2002a). The simple diamond graphitization model fails to take into consideration an increasing number of puzzling observations in natural systems. The two possible scenarios for graphite formation in the Kokchetav rocks are discussed below.

Graphitization model versus metastable graphite growth

In the case of a graphitization model, the following features are expected.

1. Graphite crystals in diamond coatings decrease in size away from the diamond–graphite interface (see Pearson et al., 1995, fig. 13.5).

2. Graphite exhibits a strong preferred orientation in the case of partial diamond-to-graphite transformation (Grenville-Wells, 1952; Lonsdale & Milledge, 1965; Korsakov et al., 2008). This observation has been confirmed by HP–HT experiments (Pantea et al., 2002; Qian et al., 2004, and references therein). A strong preferred orientation of graphite crystals has also been documented for graphite pseudomorphs after diamond from the Beni Bousera and Ronda peridotite massifs (Slodkevich, 1982; Pearson et al., 1989, 1995).

3. Crystals of disordered graphite with a preferred orientation are expected to form after diamond. As experimentally shown, even at high temperatures (>1500°C), amorphous carbon appears on different defects in diamond crystals such as inclusion walls, dislocations and subgrain boundaries when low-quality diamond is partly graphitized (Willems et al., 2004).

4. There is a limit of 25% to the amount of graphite that is produced from diamond graphitization (Qian et al., 2001).

5. The morphology of the diamond relic is affected by the diamond-to-graphite transformation. The graphitization rates of {111} and {100} diamond faces are different (e.g. Pantea et al., 2002, and references therein), and should be reflected in the morphology of the graphitized diamonds.

The petrographic and spectroscopic findings of this study are inconsistent with the above-mentioned graphitization features.

Size of graphite

Graphite coatings form either polycrystalline aggregates or isolated single grains. The graphite crystals increase in size away from the diamond–graphite interface. One could argue for two generations of graphite replacing diamond, both within the stability field of graphite. In this scenario, the first one is represented by the large crystals that started to grow at the diamond surface within the stability field of graphite while temperatures were still high. The second generation of graphite, represented by the fine-grained crystals, continued growing by replacing diamond at lower temperatures. This feature could be the result of a process analogous to symplectite formation. However, in the case of possible ‘diamond symplectitization’, one would expect strong preferred orientation of the (001) graphite crystals with respect to the diamond (111) (Slodkevich, 1982, fig. 2a) typical of symplectite formation (e.g. Dégì et al., 2009); this feature is not observed in the samples studied here.

Another possibility is that the large graphite crystals (Fig. 7a and b) could be recrystallized from original poorly ordered graphite via an Ostwald ripening mechanism. Recrystallization of graphite needs either a very long time or the presence of fluid or melt to act as catalyst. Geochronological data indicate that the UHPM rocks of the Kokchetav massif reached peak metamorphic...
Fig. 12. (a) Euhedral graphite inclusion in diamond within garnet. (b, c) Raman maps: (b) surface distribution of the $I_{Gr}/I_{Dia}$ ratio where $I_{Gr}$ is the intensity of the main graphite band (1580 cm$^{-1}$) and $I_{Dia}$ the intensity of the main diamond band (1332 cm$^{-1}$). (c) Integrated area of the main graphite band at 1580 cm$^{-1}$. (d–l) First- and second-order Raman spectra of this graphite inclusion collected at points I–III (Ar+ laser, 488 nm). Additional bands appear at 1372–1377 cm$^{-1}$.
conditions at 530 Ma (Shatsky et al., 1995; Hermann et al., 2001) and were exhumed to mid-crustal level in less than 6 Myr (Hermann et al., 2001, 2006). The aggregation state of nitrogen in the Kokchetav diamonds also supports a short residence time at high-temperature conditions (De Corte et al., 1998, 2000). At such short times, recrystallization of graphite could happen only in the presence of a fluid or melt. Because there is no systematic relationship between the thickness of the graphite coatings around diamond and the presence of melt products, a mechanism of graphite recrystallization into larger crystals seems unlikely. Furthermore, undisturbed lamellae of K-feldspar and phengite around graphite-coated diamond crystals in K-bearing clinopyroxene indicate that the clinopyroxene acts as a pressure vessel, which would effectively slow the diamond-to-graphite transformation as well as any grain coarsening phenomenon in graphite (Gillet et al., 1984; Van der Molen & van Roermund, 1986).

Some large euhedral graphite crystals, up to 100 μm along the c direction (Fig. 7a and b), form overgrowths and have very thin 'necks' that connect them to the graphite-coated diamonds. It is unlikely that such large single graphite crystals are pseudomorphs after diamond. Graphite crystals, deposited from a carbon-rich fluid during the early postcumulus stage of crystallization, as a component of the intercumulus association, were found in anorthosites from the Korsun-Novomfugorod pluton in Ukraine by Kvasnitsa et al. (1999), who supported a possible mechanism of spiral-layer and polycrystalline growth of the rare graphite crystals in the presence of negative wedge disclinations. Growth layers, up to 0.01 μm thick (Fig. 7c and d), occur on the (001) surface of some of the graphite crystals studied here, possibly indicating a similar spiral-layer graphite growth. The size of the graphite crystals increases from the diamond surface outwards (Fig. 8), suggesting that the growth of graphite proceeded from the diamond–graphite interface towards the host mineral (K-bearing clinopyroxene or garnet, Fig. 6).

**Orientation of graphite**

The orientation of graphite is a key point in deciphering its formation mechanism. The graphite coatings around diamonds studied here exhibit no preferred orientation; thus it is unlikely that these graphite coatings represent pseudomorphs after diamond.

Single graphite flakes included in garnet, K-bearing clinopyroxene and kyanite show strong preferred orientation with respect to the host minerals; this indicates either that graphite precipitated from an originally homogeneous solid solution, or that it represents an epitaxial intergrowth (i.e. co-crystallization with the UHP minerals). Alternatively, oriented graphite crystals formed during a prograde metamorphic stage were captured by the host porphyroblasts (garnet, K-bearing clinopyroxene, kyanite) grown at UHP conditions. Unfortunately, the solubility of carbon at UHPM conditions in silicate minerals is not well known. The solubility of carbon (12 ppm wt at T = 900–1400°C and P = 11 GPa) in silicates has been documented only for olivine (Shcheka et al., 2006). If the graphite flakes corresponded to a former schistosity, the graphite crystals would be expected to show morphological damage and structural disorder (Jaszczak, 1995), given that the short duration of the UHPM stage (De Corte et al., 1998; Hermann et al., 2001) would have prevented graphite from being annealed. However, the graphite morphology is well formed as shown in Fig. 7. Thus, the cases of graphite precipitation from an originally homogeneous solid solution and of oriented graphite captured during a prograde metamorphic stage are unlikely scenarios. The case of epitaxial graphite–host mineral intergrowth explains the preferred orientation of the graphite flakes. Recent experiments have revealed that K-bearing clinopyroxene (with K2O of about 1 wt %) forms only at a P > 5 GPa (Hermann & Green, 2002; Perchuk et al., 2002).

The K-bearing clinopyroxene in our samples could have formed at peak metamorphic conditions or during the initial stage of exhumation within the diamond stability field (Sobolev & Shatsky, 1990; Shatsky et al., 1995; Perchuk et al., 2002; Korsakov & Hermann, 2006). Because the host minerals formed at UHPM conditions, as indicated by the diamond inclusions in garnet and kyanite and the K-bearing clinopyroxene, a metastable growth of graphite within the diamond stability field is favored.

**Ordering degree in graphite**

As revealed by their Raman spectra, the graphites studied here show very weak disordering, contrary to the highly disordered graphite found in experiments (Willems et al., 2004).

**Amount of graphite**

The transformation rate of diamond to graphite depends on the size of the diamond crystals and is different for the
various faces (Qian et al., 2001). In the Kokchetav Massif, the thickest graphite coatings are observed around diamond crystals > 100 µm in size. The high estimated volume fraction of graphite in our samples (about 40 vol. %) and the presence of large graphite crystals composing the graphite coatings are inconsistent with a simple diamond-to-graphite solid-state transformation. An extra carbon source such as carbonate or carbon-bearing fluids might provide additional C; however, no relics of fluids have been detected. The possibility of the host mineral being the carbon source has been shown to be unlikely (Harris & Vance, 1972). The presence of diamond inclusions in dolomite included in garnet (Korsakov et al., 2005, see Fig. 2) is inconsistent with the idea that carbonate could be the carbon source via a solid-state transformation. However, carbonates could produce carbonate melts and thus be very important for diamond formation.

Recent work on pressure-volume-temperature (P-V-T) relationships and mineral equilibria in minerals (Guiraud & Powell, 2006) has shown that those inclusions that do not react with the host mineral tend to be preserved during an exhumation path in the form that they were included and not be transformed into their stable polymorphs. As shown in their Fig. 8a and b, diamond inclusions in pyrope reach the Earth’s surface mainly as diamond (less than 20% of the diamond is converted into graphite). As noted above, the graphite coatings around diamonds from the Kokchetav Massif represent up to 40% of the ‘original’ diamond crystals. A coupled dissolution–reprecipitation mechanism can preserve the diamond morphology and transfer crystallographic information from the parent to the product by epitaxial nucleation (Putnis & Putnis, 2007). In the presence of a solvent, a metastable phase is dissolved and a more stable phase then nucleates and forms independently from solution, a mechanism called solvent-mediated phase transformation (Cardew & Davey, 1985). In the case of the Kokchetav diamonds, some crystals may have been captured with a trace amount of fluid or melt, and have grown even in an environment with very low solubility of carbon in the C-O-H fluid or melt, making this a possible mechanism of diamond–graphite transformation (Papyanov et al., 2002, and references therein). The formation of porosity in the product phase is a prerequisite for such a mechanism as it allows the fluid to maintain contact with a reaction interface that moves through the parent phase from the original surface. Porosity is unlikely to develop at the pressure conditions inferred; thus the absence of porosity in our samples cannot be used as an argument against this model. The lack of experimental results on fluid-mediated diamond–graphite transformation and on the dissolution–reprecipitation mechanism at high-pressure conditions do not allow us to confirm or reject this model.

**Diamond morphology**

The graphitization rates of \{111\} and \{100\} diamond faces are different (e.g. Pantea et al., 2002, and references therein) and this should be reflected in the morphology of graphitized diamonds. This is not the case for the samples studied here. The morphology of surfaces \{111\} and \{100\} remains the same for both graphite-free and graphite-coated diamonds. In the context of the graphitization model it is difficult to explain why the diamond-to-graphite transformation did not affect the diamond morphology. A model of co-crystallization of diamond and metastable graphite within the diamond stability field better explains the presence of only growth features in both diamond types.

Semi-transparent graphite flakes in the cores of the diamond crystals can be interpreted either as protogenic (recrystallization of precursor carbonaceous material during the prograde UHPM stage) or as synogenic (simultaneous crystallization of the diamond core and graphite) inclusions or as products of diamond-to-graphite partial transformation. Katayama et al. (1998) interpreted an overgrowth of single graphite crystals by polycrystalline diamonds in a garnet–biotite gneiss as a solid-state transformation of pre-existing graphite into diamond. The presence of skeletal crystals of diamond in this rock type, however, weakens this hypothesis because they contain many cavities; thus, if a later graphite coating formed, the same texture would be observed.

The formation of composite crystals with a diamond core, graphite mantle zone, diamond rim and external graphite coating (Fig. 8) is another puzzling feature that challenges the model of diamond partial graphitization. If the diamond and graphite had each formed in their own stability field either temperature or pressure would have to have oscillated, which is inconsistent with the existing petrological data. Recent experiments on diamond synthesis in non-metallic systems have revealed that oxygen fugacity plays an important role in the formation of diamond and graphite. In a reduced system, only graphite forms even in the diamond stability field, whereas diamond grows in relatively oxidized conditions (Sokol et al., 2000, and references therein). Local variation in f(O₂) might, therefore, also control the crystallization of different carbon polymorphs in UHPM rocks.

**Internal pressures in C inclusions based on their Raman shifts**

The observed shifts in the characteristic Raman bands of diamond and graphite provide important information on the remnant internal overpressure in the C inclusions. The shift of the diamond F2g band to 1336 cm⁻¹ could be assigned to high internal pressure in graphite inclusions in diamonds. The maximum upshift of 4 cm⁻¹ of the main diamond band indicates a remnant pressure of \(\sim 1.5 \text{ GPa}\).
Similar pressure estimates were discussed by Nasdala et al. (2005) for a single protogenetic graphite inclusion in a kimberlitic diamond. Using the elastic model proposed by Zhang (1998), the estimated pressure at which this inclusion was trapped is 6–6.5 GPa for a temperature of 950–1000°C. These pressure values are slightly higher than the peak metamorphic conditions of 4.5–6 GPa and 950–1000°C calculated by Hermann et al. (2001), Hermann (2003) and Korsakov & Hermann (2006). Ota et al. (2000) and Massonne (2003) reported even higher peak pressure of 7 GPa and a temperature up to 1100°C. In this case, either the diamonds formed below the peak pressure conditions or the pressure values derived by Raman diamond band upshift correspond to the minimum pressure.

The downshift of the main diamond band to 1329 cm⁻¹ is difficult to explain. Laser heating could theoretically cause this (Zhao et al., 1998); however, in our experiments the laser power was low enough to prevent any spectral change caused by local temperature increase. The shift of the D' mode of graphite is probably related to overpressure (up to 4 GPa, Liu et al., 1990) concentrated along the diamond-host graphite-inclusion interface. An overpressure of 1–2.6 GPa has been estimated assuming a pressure dependence of the main graphite G-band (Fig. 14; Liu et al., 1990).

**Growth stages of graphite and diamond**

Based on the different textural relationships between diamond and graphite, at least two growth stages of graphite are inferred. The growth of graphite coatings and diamonds began simultaneously; subsequently the graphite coatings continued growing after the diamonds stopped growing. The last stage of crystallization of the graphite coatings occurred under UHPM conditions (PT > 5 GPa and T ~ 1000°C) as signified by the presence of undisturbed K-feldspar and phengite lamellae in K-bearing clinopyroxene surrounding both graphite-coated and graphite-free diamond (Fig. 5b).

The typical growth morphologies of diamonds are the octahedron and the cuboid. The mechanisms of growth of these two varieties differ in their kinetics (Moore & Lang, 1972; Sunagawa, 1990); a change in growth conditions may result in a change in the growth mechanism and resultant re-shaping of crystals. The presence of graphite inclusions and graphite coatings around both octahedral and cuboid diamonds indicates that differences in diamond morphology, as well as perfection of their structure, did not control the formation of graphite.

The discrepancy between the effectiveness of the diamond-to-graphite phase transformation and the amount of water present clearly indicates the catalytic effect of water. From ‘wet’ to ‘dry’ experiments on the partial graphitization of diamond at P = 2.0 GPa and T = 1473 K, the amount of graphite produced dropped from 22% to 1%, respectively (Qian et al., 2001). Supercritical water is known to dissolve diamonds and heal their surfaces (Qian et al., 2001). No traces of fluid associated with graphite inclusions in diamond and other UHPM minerals were observed in this study, thus excluding any possible catalytic effect of water.

TEM study of both diamond-inclusion pockets and graphite-inclusion pockets in garnets from the Kokchetav Massif has revealed that they are randomly distributed and not associated with each other within the same garnet crystals (Hwang et al., 2003). Furthermore, in the diamond-inclusion pockets, microdiamond aggregates were always found to be associated with phlogopite. Submicron-sized metal sulphide inclusions were observed at the diamond grain boundaries and the diamond–garnet boundary, but not inside the diamond crystals. Metal sulphides were not found in association with graphite–phlogopite inclusions in which the graphite flakes are bifurcated and bent but not rolled, and, generally, less than 100 nm in thickness with the layer planes slightly rotated around the c-axis with respect to each other. These graphite flakes are highly defective and corrugated but not intergrown with other carbon phases such as diamond. The interplanar spacing of the graphite in the graphite-inclusion pockets is significantly larger (~0.344 nm) than that of ideal graphite (0.334 nm). There is no specific crystallographic relationship between the graphite and phlogopite, although their basal planes appear to be parallel (Hwang et al., 2003).

TEM study of micrometre- to nanometre-sized fluid inclusions in diamonds from the Kokchetav massif, Kazakhstan and the Erzgebirge massif, Germany (Hwang et al., 2001, 2006; Dobrzhinetskaya et al., 2005) showed that the pockets are typically 5–300 nm in size and usually bounded by {111} faces of diamond. Except for the blinking Bragg contrast arising from the presence of nanometric precipitates, the inclusion pockets typically showed no contrast variation upon sample tilting, consistent with their non-crystalline nature.

High-resolution TEM study of metamorphic microdiamonds from the Kokchetav massif and the Erzgebirge massif revealed that metamorphic microdiamonds are defect-free, suggesting the absence of substantial back transformation and deformation (Langenhorst, 2003).

Analytical electron microscope (AEM) study of metamorphic microdiamonds from a garnet–quartz–pyroxene rock from the Kokchetav massif has revealed the presence of nanometre-sized inclusions of saline fluid (Hwang et al., 2005). TEM study of diamonds from dolomite marbles from the Kokchetav Massif has identified filled nanometric fluid bubbles with the chemical composition C, H, O, Cl, S, Ca, Fe and K (Dobrzhinetskaya et al., 2005). None of the studies to date have reported graphite precipitated on the walls of the fluid inclusions. The lack of graphite...
precipitates might indicate that the presence of a C–O–H fluid does not accelerate the diamond-to-graphite transformation in UHPM rocks.

Intergranular matrix diamonds without any evidence of resorption and graphitization were described by Korsakov et al. (2004). This observation indicates that even in the matrix, graphitization is not a predominant process. The transformation of diamond into graphite in inclusions is even more difficult to interpret because of the large difference in the densities of diamond and graphite. The elastic properties of the host mineral would prevent the diamond-to-graphite transformation (Zhang, 1998). This conclusion is also supported by TEM studies of diamond-bearing polyphase inclusions in garnets from the Erzgebirge, Germany (Hwang et al., 2001; Stockhert et al., 2001) in which no systematic relationship was identified between diamond and graphite surrounded by the crystallization products of a UHP melt or fluid.

The alternation of carbon polymorphs within the graphite-coated diamond crystals suggests a succession in the crystallization of the carbon polymorphs. Semitransparent graphite flakes formed at high pressure and temperature (most probably in the diamond stability field). At that time, crystallization of diamond was sluggish. Long induction periods for diamond growth and nucleation have been documented for the carbon–carbonate and carbon–C–O–H fluid systems by Pal’yanov et al. (2002) and Sokol et al. (2000, 2001b). The in situ X-ray study of the kinetics of the graphite–diamond transformation in a C–O–H fluid have confirmed the existence of a long incubation time for diamond growth, which increases with decreasing temperature (Okada et al., 2004).

Diamond growth was successively initiated and a mantle zone free of graphite inclusions formed in the diamond crystals. The main parameters (temperature, pressure, fluid composition) controlling the growth of this zone are unknown. During a later stage, graphite started to grow simultaneously with diamond. Most probably, the presence of graphite on the surface of the diamond terminated diamond growth. The kinetics of graphite crystallization are faster than those of diamond (e.g. Pal’yanov et al., 2002, and references therein). Information concerning the induction period of graphite growth or nucleation in the diamond stability field is lacking. Furthermore, experiments in carbon–carbonate or C–O–H systems (Sokol et al., 2001a, 2001b; Pal’yanov et al., 2002; Yamaoka et al., 2002a) have revealed that in the diamond stability field graphite is the first C-polymorph to crystallize.

Contemporaneous diamond and graphite crystallization may also occur under extremely high carbon supersaturation in a fluid or melt. In this case, the presence of both carbon polymorphs would indicate a very rapid eduction process.

CONCLUSIONS

The findings of this study suggest the possibility of a metastable growth of graphite within the diamond stability field.

Petrographical, morphological and spectroscopical observations, such as (1) the presence of coarse-grained graphite around metamorphic microdiamonds and the increasing size of the graphite crystals from the diamond–graphite interface to the external part of the graphite coatings, (2) the high volume fraction of graphite in the graphite coatings, (3) the presence of composite crystals of successively formed diamond core–graphite mantle zone–diamond rim–external graphite coating, (4) the formation of both ordered and disordered graphite, (5) the presence of oriented graphite flakes in K-bearing clinopyroxene and (6) the absence of any fluid associated with the graphite inclusions in diamond, garnet and clinopyroxene, lead to the following scheme for the C-polymorph succession.

1. Graphite was the first C-polymorph formed in the diamond stability field, as a result of the long induction period for diamond growth and nucleation.

2. Diamond was the next phase that grew.

3. Graphite coatings around diamond were formed during the final stage of UHP conditions.
The remnant pressure for the diamond was about 1.5 GPa based on the shift of the main Raman diamond band. Calculated pressure values at which graphite inclusions were captured are $P=6-6.5$ GPa; these values are in good agreement with previous estimates of peak metamorphic conditions of $T \approx 950-1000$ °C and $P=4-5-6$ GPa.

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