Thematic Article

Diamond growth during ultrahigh-pressure metamorphism of the Kokchetav Massif, northern Kazakhstan

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Abstract Characteristic features of in situ diamonds can be used to retrace diamond formation during ultrahigh pressure (UHP) metamorphism of the Kokchetav Massif, Kazakhstan. These features include the nitrogen aggregation state in diamond, dissolution features observed on diamond surfaces, and the carbon and nitrogen isotopic composition of the diamonds. The minerals in which the diamonds are included provide additional information and support the view that at least some of the Kokchetav microdiamonds are the products of prograde or peak UHP metamorphism. The coexistence of diamond and graphite is evaluated within this framework.

Key words: diamond, graphite, ultrahigh-pressure metamorphism.

INTRODUCTION

Approximately 10 years ago, microdiamonds (<1 mm) were recognized in metamorphic rocks of crustal affinity in the Kokchetav Massif of Northern Kazakhstan (Sobolev & Shatsky 1990). However, their formation requires much higher pressure–temperature (P–T) conditions than those expected within the Earth’s crust. Three fundamentally different models have been proposed to explain their occurrence.

The premetamorphic relict model postulates that the diamonds are of kimberlitic origin (Marakushev et al. 1995). Diamonds of mantle origin were brought by kimberlites or lamproites to the Earth’s surface. They were incorporated into crustal sediments as placer deposits that were later metamorphosed. It is thought that diamonds would have survived the metamorphism because they were enclosed in refractory minerals that grew early in the metamorphic history.

The metastability model claims diamond genesis by condensation from a reduced mantle fluid at temperatures of 600–1050 °C and pressures that are below their equilibrium pressure in local shear zones. Diamonds are formed at conditions of crustal metamorphism and there is no requirement for ultrahigh-pressures (UHP), which are characteristic of the upper mantle (e.g. Nadejdina & Posukhova 1990; Dobrzhinetskaya et al. 1994; F. A. Letnikov, unpubl. data, 1995; Simakov 1995; Lavrova et al. 1997).

The ultrahigh-pressure metamorphism (UHPM) model states that diamonds grew steadily within their stable equilibrium as a result of a major metamorphic event (Sobolev & Shatsky 1990). Crustal rocks subducted to depths of over 150 km were metamorphosed and returned to the Earth’s surface. Microdiamonds crystallized at pressures of >4 GPa and temperatures ≥900–1000 °C.

Studies of the external morphology of diamonds found in situ within metamorphic rocks of the Kokchetav Massif (hereafter described as in situ diamonds) strongly suggest that the diamonds crystallized in the diamond stability field (Shatsky et al. 1989; De Corte et al. 1999). The presence
of diamond populations linked to the host rock; their characteristic cuboid morphology; the complete absence of diamond abrasion features; the preservation of Ib diamond; and the isotopic composition of the diamonds, which reflect a crustal signature and the tectonic setting all support microdiamond genesis during UHPM. However, the diamonds may have crystallized during the latter part of the prograde path, at peak metamorphic conditions, and/or during the early retrograde path of UHPM.

Metamorphic conditions that led to the formation of the diamondiferous UHPM rocks in the Kokchetav Massif peaked at temperatures of 900–1000°C and pressures of more than 4 GPa (Shatsky et al. 1995; Zhang et al. 1997; Fig. 1). These P–T estimates are based on relict high-P–T minerals that are included in garnet and zircon because whole-rock mineral assemblages have been affected to varying degrees by retrograde metamorphism. Recently, new peak pressure estimates of at least 5 GPa have been proposed (V. S. Shatsky pers. comm., 1999) on the basis of magnesite and magnesite–calcite inclusions in zircon from Kumd–Kol marble (sample K91-16). These inclusions are inferred to be high-P breakdown products of dolomite, which is unstable in comparison with aragonite and magnesite at pressures exceeding 5 GPa (Martinez et al. 1996). Okamoto et al. (2000) suggest peak pressures of 6 GPa for eclogites and adjacent garnet peridotites. They further suggested that SiO2 rods and rutile lamellae in clinopyroxene would require even higher pressures (7 GPa and higher).

In seeking to unravel the formation history of diamond and, hence, the complexities of the P–T–time path, the genesis of the Kokchetav microdiamonds will be discussed with reference to the nitrogen aggregation state, its morphological features and the isotopic composition of the in situ microdiamonds. The characteristics of some host minerals are used to further constrain their histories. This information is used to evaluate the observed coexistence of graphite and diamond in some samples.

NITROGEN AGGREGATION STATE

Based on Sm–Nd and U–Pb ages, the Kokchetav microdiamonds spent no longer than 25 Ma at depths greater than mid-crustal levels and temperatures >600°C (Claoué-Long et al. 1991; Shatsky et al. 1995; Hermann et al. 1999). The nitrogen aggregation state of diamond is the only method that gives precise information about the prevailing T during nitrogen aggregation and the time (t) diamonds spent at high temperature.

Diamonds can be classified into two types on the basis of their infrared (IR) spectra and the form in which substitutional nitrogen impurities (i.e. N substituting for C atoms) occur in them. Type II diamonds have essentially no IR-active substitutional nitrogen, while type I diamonds contain >10 ppm of substitutional nitrogen incorporated at the time of their formation. Type I diamonds are further characterized by the presence of a dominant form of a nitrogen defect center. The main subgroups are type Ib, IaA and IaB. In type Ib diamonds, nitrogen substitutes in the form of single atoms (the C defect center). In type Ia diamonds, nitrogen-related defect centers are present in aggregated forms. Type IaA diamond contains nitrogen atoms arranged in pairs (the A defect center), whereas in type IaB diamond four nitrogen atoms occur in a tetrahedral arrangement around a vacancy (the B defect center). The various nitrogen defects are related to each other by diffusion, and an aggregation sequence of C to A to B has been established (Chrenko et al. 1977; Evans & Qi 1982). Chrenko et al. (1977) showed experimentally that type Ib diamond could be transformed into type IaA. The aggregation reaction was shown to follow second order kinetics.

The degree of nitrogen aggregation (or the nitrogen aggregation state) depends mainly on the initial nitrogen content, the prevailing T during aggregation and the time spent at this temperature (Chrenko et al. 1977; Evans & Qi 1982; Taylor et al. 1996). The activation energy of the Ib to IaA transformation is relatively low and is dependent on crystallographic orientation. The activation energy has been determined experimentally to be 4.4 eV for octahedral growth sectors and 6.0 eV for cube (cuboidal) sectors (Taylor et al. 1996). Cathodoluminescence studies of in situ diamonds of the Kokchetav Massif revealed the presence of dominating cubic growth sectoring; hence, the activation energy of 6.0 eV is used.

Singly substituted nitrogen atoms (type Ib diamonds) are preserved in all studied in situ diamonds of the Kokchetav Massif (De Corte et al. 1998a, 1999), which indicates a short residence time at high pressure and/or a low prevailing temperature (Chrenko et al. 1977; Evans & Qi 1982; Taylor et al. 1996). However, the temperature to which the diamonds were exposed must have been more than 750°C as below this temperature nitro-
gen aggregation does not proceed for reasonable geologic times (i.e. 750°C is the blocking temperature of nitrogen aggregation; Taylor et al. 1996). Temperature–time calculations based on nitrogen content and the aggregation state of nitrogen in diamonds obtained from garnet-clinopyroxene rocks all yield average aggregation temperatures of 900–950°C for a geologic acceptable residence time of 5 Ma (i.e. the time spent by the diamond in the high-P environment at T > 750°C; De Corte et al. 1998a). It should be noted that the nitrogen aggregation temperature is a time-averaged value of the nitrogen aggregation temperature as defined by (i) Shatsky et al. (1995) and Zhang et al. (1997); (ii) Shatsky et al. (unpubl. data); and (iii) Okamoto et al. (2000). (iv) Considering Si rods in clinopyroxene and rutile lamellae, more than 7 GPa is required (Okamoto et al. 2000). The figure is adapted from Zhang et al. (1997).
that depends on the postformation thermal history of the diamond because all time spent at temperatures >750°C will contribute, to some degree, toward the final aggregation state of the diamond. Calculations using probable prograde and retrograde T–t paths (Taylor et al. 1996) indicate the peak metamorphic temperature will be some 25–50°C higher than the nitrogen aggregation temperature range given earlier. Furthermore, the problem can be inverted so that the residence time can be calculated based on input temperature. A residence time of approximately 10 Ma is required if average formation plus postformation temperatures were 900°C, while only 0.097 Ma is needed if average temperatures were 1000°C.

Temperature–time calculations thus indicate that temperatures much higher than 800°C are required during the aggregation process, so that diamond crystallization during most of the retrograde phase of metamorphism (i.e. at T less than about 900°C) can be excluded.

**MORPHOLOGY**

The diamond stability field covers a wide P/T range. Once diamonds are formed, they remain very stable as long as: (i) they are preserved in favorable P–T and oxygen fugacity (fO₂) conditions; and (ii) they do not come into contact with resorptive agents. Some information about P–T regimens can be obtained from diamond dissolution features. Signs of pronounced bulk dissolution (e.g. tetrahexahedroid forms) have not yet been observed among the Kokchetav diamonds but surface features indicative of early stages of resorption are observed (De Corte et al. 1999). From the 672 in situ diamonds investigated using scanning electron microscopy, more than 45% crystals exhibit at least one of the following dissolution characteristics: (i) surface etch pit and frosting; (ii) a relatively small, irregular-shaped hole; (iii) a rounded face and edge; (iv) a mottled or blocky {100} face; (v) trigon, hexagon or tetragon; and (vi) a rough octahedral face (Robinson 1979; Sunagawa 1984). The negatively oriented etch features seen on Kokchetav microdiamonds (Fig. 2) are of special interest as they provide evidence of temperatures in excess of 950°C (Robinson 1979). Hence, this temperature must have been reached during UHPM. Water- and carbon dioxide-bearing fluids are the etchants most likely to be responsible (Robinson 1979), and these fluids must have had access to the diamonds after their formation.

The process by which fluids reached the diamond surfaces is not fully understood. Three models can be proposed: (i) the present host minerals crystallized at the same time or just after the diamonds, so that the etchants had free access to the diamonds; (ii) the diamonds were trapped together with a coexisting fluid which, under different P/T conditions, was out of equilibrium with the diamond and caused etching; and (iii) as soon as the diamonds were formed they were captured by minerals but etchants came in contact with the diamonds via fractures in the host minerals. Although we do not have evidence, the first or second model seems more realistic and either implies that at least some of the diamonds were present before their host minerals.

For crystals with the same habit and from the same host rock (200 g), surface features of diamond are highly varied, as illustrated for octahedra in Fig. 3. This can be explained by local changes in P–T–fO₂ conditions, by different diamond growth events, by a distinct time of
crystal capturing by the host minerals, and/or by the non-uniform presence of active etchants.

HOST MINERALS

Microdiamonds are found today as inclusions in garnet and clinopyroxene (and their secondary minerals), zircon, kyanite, zoisite, biotite and quartz included in garnet. Because the diamonds are included in these minerals, the diamonds crystallized before or synchronously with the host minerals. In this section we will explore some constraints on the conditions of diamond formation provided by the host minerals.

GARNET

Experimental work by Poli and Schmidt (1995) demonstrates that the grossular component in garnet decreases with decreasing pressure. Approximately 80% of the matrix garnets of diamond-bearing rocks are characterized by a Ca-rich core compared to their rim (Fig. 4a). Therefore, the garnet must have formed at or near the peak of UHPM and continued its growth during retrograde metamorphism. Hermann and Green (1999) support garnet growth during retrograde metamorphic conditions based on piston cylinder experiments.
experiments in the range 700–1100°C and 2.0–3.5 GPa using gneissic to pelitic compositions.

As diamonds are observed both in the core and in the rim of garnet, diamonds must have formed before or during garnet formation. At least some of the diamonds crystallized later during prograde path and/or peak UHPM.

ZIRCON

Zircon is extremely stable and resistant over a wide temperature and pressure interval (Chopin & Sobolev 1995) and, therefore, is considered to be the best UHP mineral container. Garnet, clinopyroxene, phengite, diamond, coesite, graphite, chlorite, quartz, plagioclase, K-feldspar, kyanite and amphibole have been identified as inclusions in zircon. From zoisite-bearing gneiss sample B93-6 the inclusion content of 860 zircon grains was studied. Except for one case, all zircon grains contained either low P (quartz, graphite) or high P minerals (coesite, diamond) and not much information could be obtained. Only in one zircon grain of the sample set were both low P and high P mineral assemblages identified. The low P minerals are located close to the zircon core, while the high P minerals lie close to the zircon rim. A similar arrangement of inclusions in zircon was also described by Katayama et al. (1998). These authors concluded that the zircon grew along the prograde path and at peak metamorphism. The present study supports the growth of some zircons during prograde metamorphism, as distinct mineral assemblages are present in well-defined zones of the zircons.

In zoisite-bearing gneiss sample B-94-83 from the Barchi locality, a zircon with a garnet inclusion each in its core and rim has been observed. The composition of both garnets is depleted in Ca compared to the core and even the rim of matrix garnet (Fig. 4b). Therefore, we suggest that the zircon grow prior to garnet crystallization and thus during prograde metamorphism.

ZOISITE

Diamond inclusions in zoisite occur in core samples of zoisite-bearing gneiss from the Barchi locality. Diamonds occur more commonly in symplectitic zoisite–quartz intergrowths, but again only in zoisite gneisses from Barchi. The morphology of the diamonds from these rocks seems to be related to the presence of symplectitic zoisite. Diamonds with an octahedral habit are only observed in zoisite-bearing gneisses that are devoid of symplectitic zoisite, while zoisite-bearing gneisses with symplectitic zoisite are dominated by diamonds of cuboidal morphology (De Corte et al. 1999).

Infrared spectroscopy studies have shown that cuboid microdiamonds from symplectitic zoisite gneisses contain inclusions of carbonates and water, as is the case for other in situ diamonds (De Corte et al. 1999). The presence of these inclusions is interpreted to be the result of the trapping of fluids during the rapid crystallization of the diamonds (De Corte et al. 1998a). In a fluid-bearing system the experimental work of Boettcher (1970) showed that the assemblage zoisite–quartz in the system CaO–Al₂O₃–SiO₂–H₂O is not stable at temperatures >800–850°C at pressures around 3 GPa. However, in the coesite stability field, the assemblage Zo+Coe is stable up to 850–900°C. If the system is dry or at low H₂O activity, much higher temperatures are possible. The nature of zoisite–quartz symplectites is not clear. As evidence of melting is absent in the rocks, the symplectites are interpreted to be the products of decomposition of a UHP phase during retrograde metamorphism.

MICA

Biotite containing cubo–octahedral microdiamonds has been found as an inclusion in garnet from a biotite gneiss at Kumdy–Kol. The biotite occurs in close relationship regarding locality with quartz. In only one sample were diamonds identified as inclusions in matrix biotite of biotite gneiss. The origin of the biotite is not yet fully understood.

Diamond has been found as an inclusion in phengite, which itself is included in garnet from zoisite gneiss (Fig. 5). The phengite inclusion is partly transformed into chlorite. Phengite is stable at pressures >2.4 GPa (Schmidt 1996) but chlorite is not stable above 600°C (Schmidt 1996). Two theories may explain the coexistence of chlorite and phengite as inclusions in garnet.

(1) Phengite was present at a UHPM phase and grew during or after diamond formation. However, the phengite stayed uncaptured until 600°C so that it partly reverted to chlorite. Only then was the phengite trapped by garnet, which implies that the garnet is a retrograde product.

(2) Garnet enclosed phengite but, via a fracture, the phengite reacted to become chlorite at lower P–T conditions. Detailed investigations of the garnet composition support the second hypothesis.
as the garnet core is enriched in Ca, indicating garnet crystallization at peak metamorphism.

**ISOTOPIC COMPOSITION**

Carbonate and water inclusions in *in situ* cuboids give evidence that the metamorphic diamonds are crystallized from a C–O–H fluid (De Corte et al. 1998a, 1999). The main nitrogen and carbon source of the diamonds is identified as recycled nitrogen and carbon of metasedimentary origin (Cartigny et al. 1998). Diamonds from garnet–clinopyroxene rock (formerly described as ‘garnet clinopyroxenites’ by De Corte et al. 1998a, 1999 based on the work of Shatsky et al. 1995; sample 2-4) and marble (also known as ‘garnet–clinopyroxene dolomitic rock’; sample K92-99) are characterized by positive mean $\delta^{15}N$ values of $+5.9$ and $+8.5\%_{o}$, respectively. Their mean carbon isotopic composition corresponds to $-10.5$ and $-10.2\%_{o}$, respectively. The nitrogen isotopic composition of the diamonds is in accordance with the positive values of metasediments. The carbon isotopic composition of the diamonds is consistent with a mixture of crustal carbonates and biogenic material, which are characterized by initial mean $\delta^{13}C$ values of 0 (e.g. Veizer & Hoefs 1976) and $-25\%_{o}$ (e.g. Schidlowski 1983), respectively. A contribution of mantle carbon and nitrogen (with $\delta^{13}C=-4.5\%_{o}$ and $\delta^{15}N=-6\%_{o}$, e.g. Javoy & Pineau 1991; Cartigny 1997) is thought to be negligible but can not be completely ruled out from the present data set.

Additional support for the mixing of mainly crustal carbonate and biogenic carbon is provided by the presence of the diamonds in the area. In eclogites or any other rock type that is unlikely to contain a pre-existing carbonaceous component (biogenic carbon), no single diamond has been found to date (Shatsky et al. 1995). In rocks containing none or only minor carbonate contents, diamonds have also not been found (I. Katayama, pers. comm., 1999). Hence, the following diamond reaction is favored:

$$\text{CH}_4 + \text{CO}_2 = 2\text{C} + 2\text{H}_2\text{O}$$

Decarbonatization of carbonates producing CO$_2$-rich fluids is believed to have interacted with reduced carbon phases bearing a biogenic component to form diamond. The reduced phase is represented here by CH$_4$ although its precise nature is unknown (bituminous material, CH$_4$ and/or any reduced hydrocarbon-rich fluids) and requires further research. In a reduced carbonaceous sediment layer H$_2$O released by a dehydration reaction could lead to CH$_4$ formation via the reaction:

$$\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{O}_2$$

A low intrinsic fO$_2$ value for the rock will drive the reaction to the right. In the framework of the diamond genesis model proposed earlier, the coexistence of diamond and graphite is evaluated.

**COEXISTING DIAMOND AND GRAPHITE**

In the Kokchetav rocks, as a rule graphite and diamond coexist (Fig. 6). Graphite is observed both in intergranular sites and as inclusions in minerals that also contain diamond. The latter case is of
The transformation of diamond into graphite involves the breaking of C–C bonds in the diamond structure. As the number of bonds to be broken is highest for \{111\} faces, the activation energy for graphitization is theoretically the highest for \{111\} faces (1060 kJ/mol; Pearson & Nixon 1996). The activation energy for \{110\} faces is 760 kJ/mol (Davies & Evans 1972). Experimental work has demonstrated that the rate of graphitization on \{100\} surfaces is much slower than that of \{110\} surfaces and, therefore, the activation energy for \{100\} faces is greater than 760 kJ/mol (Evans 1979). At present no data about the precise activation energy for graphitization of \{100\} faces are available. The presence of some gases in natural systems may catalyze graphitization, and hence lower the activation energy.

It can be shown that the rate of graphitization per unit time can be expressed as

\[
\frac{Dx}{dt} = Ce^{-(\Delta E + \Delta V)/RT}
\]

with C a constant, \(\Delta V\) the activation volume and \(\Delta E\) the activation energy. The low activation volume for graphitization (~10 cm³/mol) means that the influence of the pressure on the reaction is small and that the graphitization rate is thus largely dependent on temperature (Pearson et al. 1995). The transformation of diamond to graphite has been used (e.g. Pearson et al. 1995; Leech & Ernst 1998) to place constraints on the temperature conditions experienced by rocks bearing such graphitized diamonds.

The experimentally determined activation energy for \{110\} faces is used as an indication of the maximum graphitization rate of the Kokchetav diamonds. Calculations show (Fig. 7) that the conversion of an \textit{in situ} diamond of average 15 μm size (Shatsky et al. 1995)—which corresponds to a mass of approximately 1 \times 10^{-11} g—to graphite would require a time scale of less than 10⁶ years at 1000 °C and less than 100 years at 1200 °C. At temperatures below 900 °C, graphitization takes more than 10 million years, which is an unrealistic situation in the Kokchetav case. Hence, the graphite crystals and coats may, in principle, be the result of graphitization during prograde path, peak or the early (T > 900°C) retrograde UHPM path.

Graphite found in close relationship with diamond or other UHPM indicators, could be: (i) graphite formed during prograde metamorphism in the graphite stability field and preserved as metastable phase in the diamond stability field; (ii) graphite formed by complete graphitization of dia-

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**Fig. 6** (a) Graphite crystals (arrow) coexisting with 20 μm octahedral diamonds from zoisite gneiss sample b-94-331. Bar = 100 μm. (b) Graphite coating (arrow) on a 105 μm diamond (garnet–clinopyroxene rock sample 2-4). Bar = 100 μm.

[Special interest. Three subgroups are recognized: (i) intergrowth of diamond and graphite; (ii) separate graphite crystals (without adjacent diamond) and; (iii) graphite forming a coating on diamond.

Diamond and graphite are often intergrown. Katayama et al. (1998) describe the particular case of graphite rimmed by diamond. We believe that a small influx of CO₂-rich fluid reacted with bituminous material or CH₄-rich fluid, which resulted in diamond crystallization. The opposite case, that is, in which a large amount of CO₂-rich fluid reacted with a low volume of bituminous material or CH₄-rich fluid, is believed to form separate diamond crystals (without adjacent graphite).

Graphite-coated diamonds are present in all rock types and no correlation between the coated diamond and its size has been observed. Graphite coats are observed on diamonds from any morphology. The graphite coats can either be explained as late overgrowths forming in the graphite stability field (hence, during the retrograde path), or as the result of diamond graphiti-
pared with their rims. This is considered to be evidence for garnet growth during the peak (core) and retrograde (rim) conditions. Because diamonds are observed in both garnet cores and rims, at least some of the diamonds must have formed during prograde or peak metamorphism. The study of diamond included in zircon confirms this finding.

The nitrogen isotopic compositions of the diamonds reveal that the source of nitrogen was metasedimentary. Their carbon isotopic signature is consistent with a carbon source derived from a mixture of crustal carbonates and reduced carbonaceous material. A reaction between CO$_2$ and CH$_4$ to form diamond and H$_2$O is proposed as the dominant mechanism for diamond formation.

ACKNOWLEDGEMENTS

The authors express their sincere thanks to Prof. V. S. Shatsky, Prof. J. Klerkx and Ac N. Dobretsov for their interest and discussions. Dr A. Zayakovskiy, Dr K. Theunissen and Dr O. Navon are thanked for their constructive comments. This research was made possible by a grant received from the Flemish Institute for Support of Scientific and Technological Research in the Industry (Belgium).

REFERENCES


