

**NANOSTRUCTURES IN ULTRAHIGH-PRESSURE METAMORPHIC COESITE AND DIAMOND:
A GENETIC FINGERPRINT**

by

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Abstract

Metamorphic coesite and diamond were studied in detail by transmission electron microscopy to test whether the high-pressure minerals preserve a nanostructural memory and report of their metamorphic formation and evolution. Metamorphic coesite from Dora Maira contains few, mostly sessile dislocations and is associated with retrograde quartz that nucleated at the margin and along twin boundaries in coesite. This back transformation occurred during exhumation and liberated water that now decorates Brazil twins in retrograde quartz. Metamorphic diamonds from the Kokchetav and Erzgebirge massifs are absolutely defect-free. The Erzgebirge diamonds are surrounded by a shell of hydrous minerals, suggesting a formation by precipitation from a C-O-H fluid. The lack of retrograde graphite indicates that metamorphic diamond is obviously more resistant to back transformation than coesite. These nanostructural characteristics contrast with those observed in coesite and diamond from kimberlite and impact rocks, substantiating that the defect structure provides a valuable genetic fingerprint.

Introduction

Relictic coesite and microdiamonds are increasingly recognized in rocks from ultra-high pressure (UHP) metamorphic terranes (SCHREYER & STÖCKHERT, 1997; LIOU ET AL., 1998 and 2002). Both high-pressure minerals provide evidence for rapid exhumation of subducted slabs from hitherto unexpected depths greater than 100 km. The uplift of UHP metamorphites apparently occurs when the continents collide and the subducted oceanic slab breaks off in the mantle (LIOU ET AL., 1998). The study of coesite- and diamond-bearing UHP metamorphites has revolutionized our understanding of such continent collisions and allows to gain unique insight into the geodynamical processes and conditions prevailing in deep levels of subduction zones.

To reconstruct the metamorphic evolution, particle trajectories and pressure-temperature conditions of UHP rocks, petrologists usually study the phase relations and mineralogical compositions of constituent phases and employ thermodynamic concepts. However, little is known about the nanostructural characteristics (i.e., lattice defects, exsolutions, anti-phase domains and other nanoscale phenomena) of high-pressure minerals and their potential information about the metamorphic and structural history of the host rocks and geodynamics at convergent plate boundaries. This paper focuses on transmission electron microscopic (TEM) observations of metamorphic coesite and microdiamonds. The aim of the presented TEM study was to explore the potential of nanostructures in these high-pressure minerals by addressing two fundamental questions: (1) Do the high-pressure minerals preserve a nanostructural memory of their formation till the exhumation to the surface, and (2) is this nanostructural signature a fingerprint of the metamorphic origin or, in other words, is the defect structure of metamorphic coesite and microdiamond different from that of coesite and diamond from other geological environments? To address the second question, coesite and diamond from kimberlite and impact rocks were studied, as well.

The TEM observations substantiate that lattice defects in metamorphic high-pressure minerals are preserved, providing indeed valuable and diagnostic information about geodynamic pathway and metamorphic evolution of UHP rocks.

Samples and experimental techniques

Coesite crystals of various natural origin were available from three localities: (1) Dora Maira massif in the Western Alps, Italy (CHOPIN, 1984), (2) Roberts Victor kimberlite pipe, Kimberley, South Africa (SMYTH & HUTTON, 1977) and (3) Ries impact crater, Germany.

Diamonds of various genesis were studied from the following natural occurrences: (1) Kumdy-Kol, Kokchetav Massif, Northern Kazakhstan (SOBOLEV & SHATSKY, 1990), and Saidenbach reservoir, Saxonian Erzgebirge, Germany (MASSONNE, 1999), (2) Popigai impact crater, North Siberia (DEUTSCH ET AL., 2000), and (3) Premier kimberlite pipe, Pretoria, South Africa. Samples were ion-beam thinned in a GATAN DUOMILL machine and were then studied with an analytical PHILIPS CM20 FEG scanning transmission electron microscope (TEM) at the Bayerisches Geoinstitut, University of Bayreuth, operating at 200 kV. Imaging and diffraction techniques employed to characterize the defect structures in coesite and diamond were bright-field (BF), dark-field (DF) and high resolution TEM imaging (HRTEM), as well as selected area electron diffraction (SAED). Burgers vectors of dislocations were determined using the $g \cdot b$ criterion.

In case of metamorphic diamond it was important to determine the compositions and iron oxidation state of surrounding minerals by means of two attached spectrometers: (1) a VANTAGE ThermoNoran energy-dispersive X-ray (EDX) analyser, equipped with an ultra-thin NORVAR window and a germanium detector and (2) a GATAN parallel electron energy loss spectrometer (PEELS) 666. The quantification of EDX spectra is based on the principle of electroneutrality (VANCAPPELEN & DOUKHAN, 1994) and is in detail described in LANGENHORST ET AL. (1995). Combined with the scanning unit of the TEM, the EDX system was also used to produce elemental distribution maps. $Fe^{3+}/\Sigma Fe$ ratios were determined with the PEELS following the method by van AKEN ET AL. (1998).

Crystal structures and resultant lattice defects

The crystal structures largely determine which lattice defects can form and operate in solids. Therefore, a brief inspection of the crystal structures of coesite and diamond enables us to understand and predict possible lattice defects in these minerals. This brief discussion will disregard dislocations, since they occur in every solid.

Coesite is monoclinic but has almost hexagonal dimensions: $a = 7.14 \text{ \AA}$, $b = 12.37 \text{ \AA}$, $c = 7.17 \text{ \AA}$, and $\beta = 120.3^\circ$ (LEVIEN & PREWITT, 1981; SMYTH ET AL., 1987). Despite these pseudo-hexagonal dimensions, coesite could never have hexagonal symmetry because its crystal structure does not contain any 3- or 6-membered structural elements. The $[\text{SiO}_4]$ -tetrahedra form 4-membered rings that are connected along the c axis (Fig. 1). A consequence of the pseudo-hexagonal dimensions (i.e., the a , c and $[101]$ vectors are of almost equal length) is the tendency of coesite to twin. Two types of reflection twins have been described with the mirror planes (021) and (100) (RAMSDELL, 1955). A peculiarity is that the (100) twins have (010) as composition plane. These twins could also be imagined as rotation twins about the b axis but according to BOURRET ET AL. (1986), the a and c axes of host and twin do not exactly form a 120° angle. It follows from these crystal-structural considerations that twinning in coesite is a pure growth effect and cannot be explained by a displacive transformation.

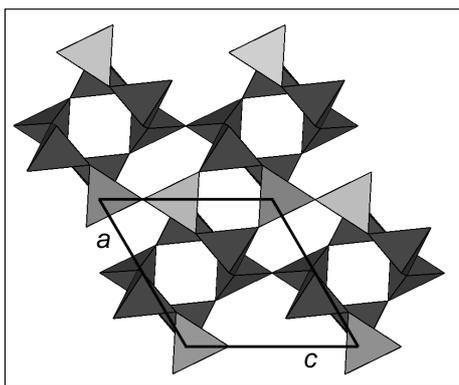
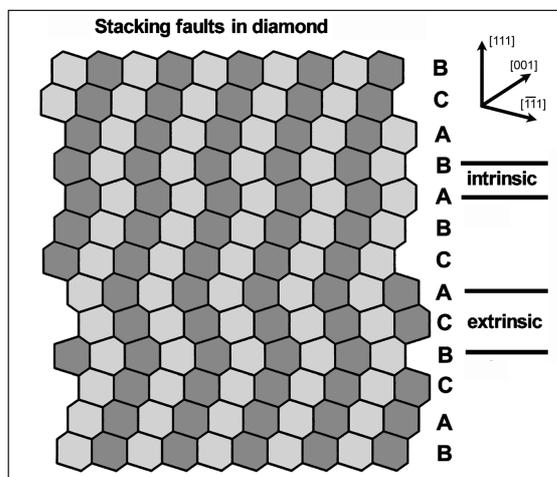


Fig. 1
Crystal structure of coesite projected along the monoclinic b axis. The structure contains rings of four SiO_4 tetrahedra that are linked along the c axis.

The crystal structure of diamond is characterized by strong covalent bonds between the tetrahedrally coordinated carbon atoms. Diamond shows a honeycombed structure with open channels when viewed along the $[110]$ direction (Fig. 2). In this projection, the diamond structure can be considered as a cubic closest packing of A, B and C layers (ABCABC...), stacked along the $[111]$ direction. Disorder in the cubic stacking sequence results in stacking faults and microtwins (ANGUS ET AL., 1992). In case of a missing C layer the stacking sequence shows a local hexagonal symmetry with ABAB. This structural arrangement is called intrinsic stacking fault. On the other hand, an extrinsic stacking fault can be imagined to result from an additional C layer between A and B layers. Both stacking faults show locally a twin configuration. The intrinsic stacking fault produces a twin extending over one layer, whereas the extrinsic stacking fault extends over two layers. If the fault in the stacking sequence extends over more than two layers, the defect is, by definition, called a microtwin. Thus, there is a close structural relationship between stacking faults and twins, both oriented parallel to (111). The formation of these planar defects can be attributed to both growth or deformation. The presence of partial dislocations indicates a mechanical nature of the twins.

Fig. 2
Simplified structure model of diamond with stacking faults, projected along the $\langle 110 \rangle$ direction. The structure shows channels in this projection, whereby the carbon atoms occupy the corners of sketched cells. An ordered diamond would show a cubic stacking sequence (ABCABC...) along the $\langle 111 \rangle$ direction but the cubic arrangement is locally disturbed by stacking faults.

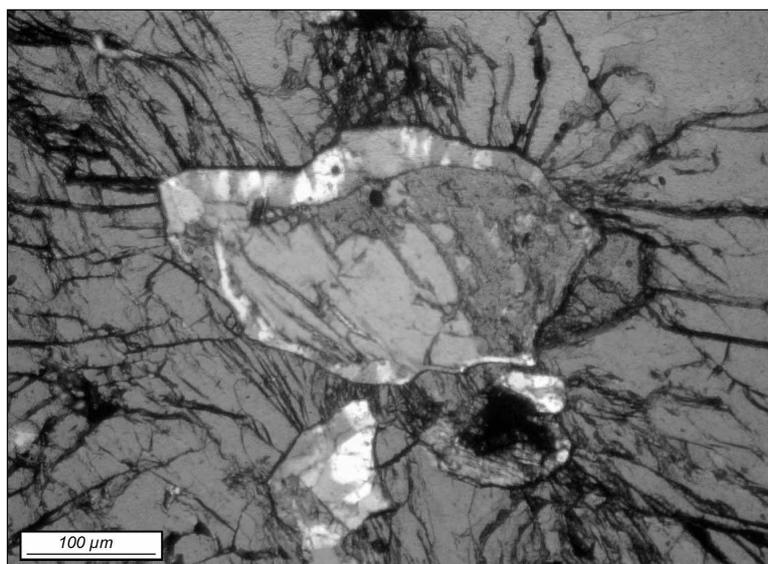


Optical and TEM observations

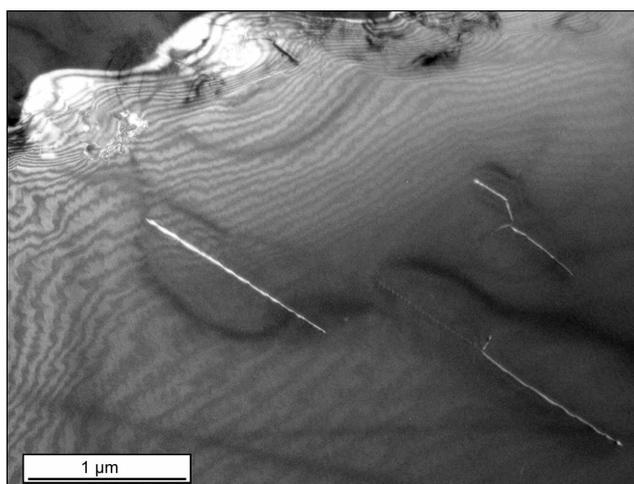
Coesite from the UHP-metamorphic Dora Maira massif

The metamorphic Dora Maira coesite occurs in the prominent pyrope quartzite from the Parigi outcrop, about 60 km SSW of Turino. Coesite was first discovered there by CHOPIN (1984), as relictic inclusions in garnet. Recent petrologic studies suggest peak metamorphic conditions of 36 kbar at 720°C (GEBAUER ET AL., 1997; NOWLAN ET AL., 2000), which implies exhumation from a depth of about 120 km. Relictic coesite inclusions are usually surrounded by radial cracks in garnet and exhibit a margin of retrograde quartz with a palisade structure (Fig. 3). Additionally, lamellae or veins of quartz can transect the coesite. In a previous TEM study, these quartz veins were interpreted to result from penetration of H_2O-SiO_2 fluids along preexisting cracks rather than from retrograde transformation of coesite (INGRIN & GILLET, 1986).

Fig. 3
Optical micrograph of a coesite inclusion in garnet from Dora Maira, Western Alps, Italy. Coesite is surrounded by retrograde palisade quartz and is additionally pervaded by quartz veins; crossed Nicols and gypsum plate.



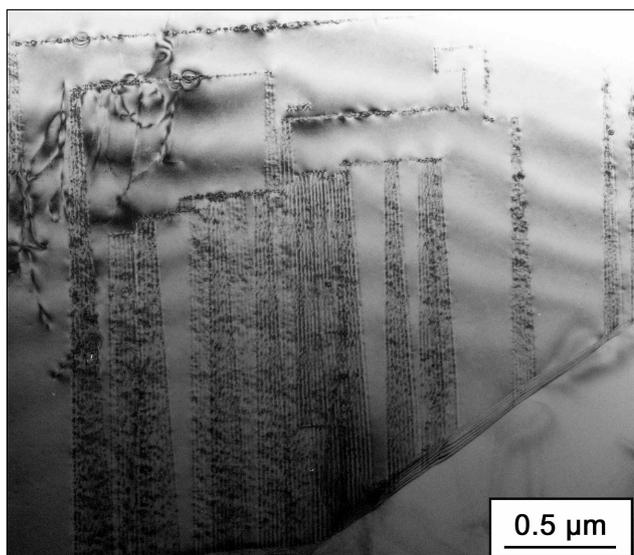
Detailed TEM observations on relictic coesite and associated retrograde quartz were recently presented by LANGENHORST & POIRIER (2002) and can be summarized as follows. Coesite from Dora Maira exhibits very few signs of plastic deformation; dislocation densities are always less than 10^{11} m^{-2} . Most dislocations are straight and presumably sessile but there are also few examples of dislocation loops, nodes and dipoles in the vicinity of palisade and lamellar quartz (Fig. 4). The Burgers vectors of dislocations in monoclinic coesite are $[100]$, $[001]$, $[110]$ (i.e., a , c , and $a+b$) and other symmetrically almost identical vectors. In the hexagonal setting, these



Burgers vectors correspond to a and $a+c$. The (110) plane could be identified as a slip plane. Small prismatic dislocation loops with Burgers vector $[010]$ (c in the hexagonal setting) are also observed and are possibly formed by water-related defects.

Fig. 4
Dark-field TEM image of coesite with dislocations adjacent to palisade quartz (upper left).

Retrograde palisade quartz exhibits a high dislocation density of dislocations pinned on bubbles and Brazil twins parallel to $\{10\bar{1}1\}$ planes (Fig. 5). The twin planes are decorated with a large number of water-related bubbles. Similar twins have also been observed in amethyst grown in the presence of water (MCLAREN & PITKETHLY, 1982). The discrete quartz veins display a midrib and are aligned parallel to the (100) and (021) composition planes of twins in coesite.



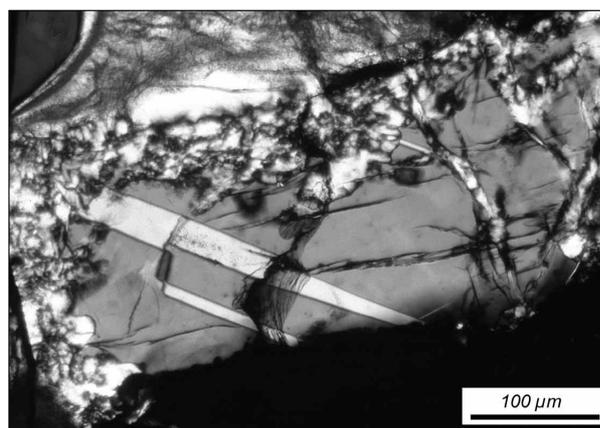
These observations indicate that palisade and lamellar quartz nucleate at grain and twin boundaries. This retrograde transformation liberates the water from coesite, which then accumulates at the boundaries of Brazil twins in quartz.

Fig. 5
Bright field TEM image of a quartz grain in the palisade rim around coesite. The grain contains numerous Brazil twins parallel to $\{10\ 1\}$ planes.

Coesite from kimberlite and impact rocks

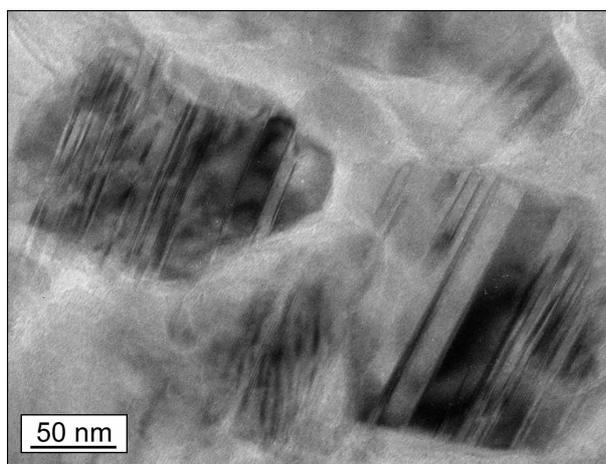
Comparative TEM results have been obtained on coesite from the Roberts Victor mine, South Africa and the Ries impact crater, Germany. The Roberts Victor coesite can be regarded as a rock-forming constituent in the studied host rock, a mantle-derived grosspydite that contains up to 6 vol.% of coesite (SMYTH & HUTTON, 1977). Coesite mostly occurs as up to 3 mm large crystals in the matrix of the host rock and is surrounded by a thin rim of polycrystalline quartz. The few, up to 50 μm wide growth twins in Roberts Victor coesite are usually well preserved (Fig. 6). Preliminary TEM observations show that the coesite underwent plastic deformation. Dislocations are glissile and have interacted with each other, as is shown by numerous dipoles and nodes; dislocation densities are up to 10^{12} m^{-2} .

Fig. 6
Optical micrograph of a twinned coesite grain in a mantle-derived grosspydite from the Roberts Victor mine, South Africa. Back transformation to quartz has started at the rim.



Coesite from the Ries crater was discovered by SHOEMAKER & CHAO (1961), leading to the final acceptance of this circular structure as an impact crater. Coesite occurs in strongly shocked (shock stage 3) crystalline clasts in suevite, the typical polymict impact melt breccia at the Ries crater. The coesite forms strings of polycrystalline aggregates within diaplectic quartz glass. Under TEM, the grain size of individual crystals turns out to be on order of 100 to 300 nm (Fig. 7). These tiny crystals are intensely twinned on (100) with the composition plane (010); the twins are often distinctly thinner than 50 nm. Additionally, it is important to note that the Ries coesite is devoid of dislocations. These nanostructural characteristics are in accordance with TEM observations on coesite from other impact craters (LEROUX ET AL., 1994).

Fig. 7
Bright-field TEM image of a polycrystalline coesite aggregate in diaplectic quartz glass from a suevite, Ries impact crater, Germany. The coesite grains show polysynthetic twinning parallel to the composition plane (010).



Microdiamonds from the UHP-metamorphic Kokchetav and Erzgebirge massifs

Diamonds of metamorphic origin were first discovered at the type locality Kokchetav, Northern Kazakhstan (SOBOLEV & SHATSKY, 1990). The diamondiferous source rocks usually contain relict diamond as inclusions in garnet. Most Kokchetav diamonds studied here were extracted by acid dissolution and were thus available as loose grains with grain sizes on the order of a few tens of micrometers. The diamond grains show a facet-rich, sometimes skeletal morphology and are commonly bound by octahedral faces (Fig. 8). Most importantly, high-resolution TEM reveals that the metamorphic diamonds are absolutely defect-free. This observation provides evidence for the absence of substantial back transformation and deformation. Due to limited sample material direct study of diamonds in thin sections was so far only possible in one case,

where diamond showed a thin (100 nm) coating with a chlorite layer.

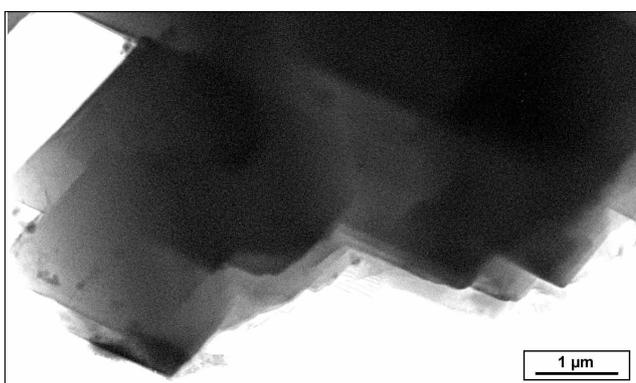


Fig. 8
Bright-field TEM image of chemically extracted metamorphic diamond from the Kokchetav massif, Northern Kazakhstan. The crystal is bounded by octahedral faces.

The diamonds from the Saxonian Erzgebirge abundantly occur in thin sections of certain gneisses from the so-called "Gneiss-Eclogite Unit" and can be easily recognized by a special preparation technique (MASSONNE ET AL., 1998). They were first discovered by MASSONNE (1999). The phase assemblages associated with diamond were subsequently described by STÖCKHERT ET AL. (2001), leading to a model for the formation of these diamonds from supercritical C-O-H fluids. HWANG ET AL. (2001) report similar phase assemblages but conclude that the diamonds formed by crystallization from partial melts.

The diamondiferous gneisses studied here are composed of garnet, potassic white mica, quartz, kyanite, plagioclase, rutile, zircon, diamond, and graphite. The tiny diamonds occur primarily as inclusions in the host minerals garnet and zircon but also in kyanite and clinopyroxene. In agreement with the observations on Kokchetav diamonds, TEM study did not show any structural imperfections in diamonds from the Erzgebirge (Fig. 9).

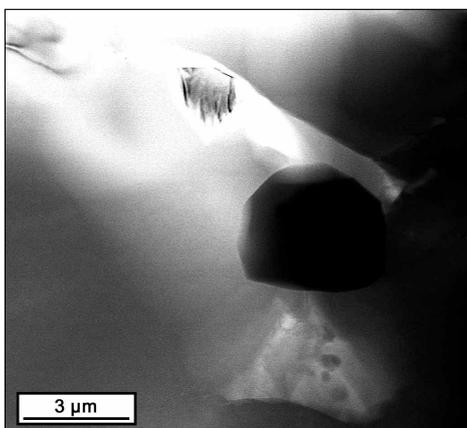
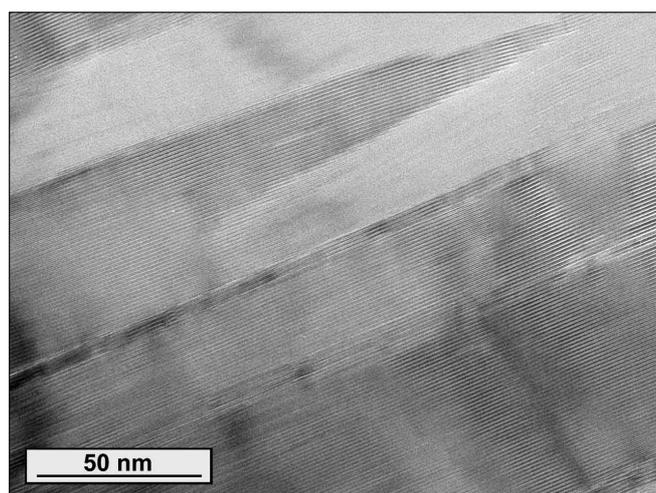


Fig. 9
Bright-field scanning TEM image of a diamond-bearing inclusion in garnet from a gneiss, Saldenbach reservoir, Erzgebirge, Germany. The single crystal diamond (black) is defect-free and displays a cubo-octahedral morphology.

However, at the optical scale, it is already obvious that the tiny, few micrometers sized diamonds are surrounded by a shell of birefringent phases, whose thickness is on the order of the size of diamonds. TEM-EDX analyses show that the shell around diamond is composed of intercalated sheet silicates (potassic and sodic micas, chlorite; Fig. 10), anatase, quartz, plagioclase, apatite and other rare earth element phosphates. All these phases monitor distinctly lower pressures than diamond, which suggests their formation during the ascent.

Fig. 10
HRTEM image of intercalating sheet silicates (chlorite and mica), forming a shell around diamond inclusions in garnet from a gneiss of the Saldenbach reservoir, Erzgebirge, Germany.



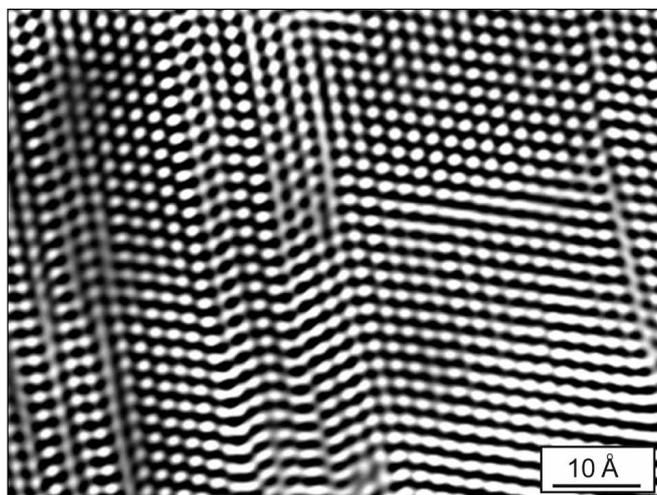
The iron oxidation state of surrounding sheet silicates was measured to resolve the question of the redox reaction that led to the precipitation of elemental carbon in form of diamond. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the most Fe-rich phase chlorite is with 0.48 unusually high, whereas in the surrounding garnet only 10 % of the iron is ferric. Thus, the EELS data suggest an oxidation of iron, compensated by the reduction of the carbon-bearing substance (possibly CO_2) to diamond. Another important observation is that the same garnet containing diamond also bears inclusions with primary graphite. The primary nature of graphite is obvious from the hexagonal, flaky morphology of the single crystals. EDX mapping shows that diamond-bearing inclusions are usually rich in sodium, whereas graphite-bearing inclusions are depleted in alkaline elements.

Diamonds from kimberlite and impact rocks

Comparative TEM observations show that kimberlite and impact diamonds exhibit different nanostructural characteristics than the defect-free metamorphic diamonds. Mantle-derived kimberlite diamonds are also relatively poor in lattice defects but usually contain dislocations at densities of 10^{12} m^{-2} . The slip system is $\frac{1}{2} \langle 110 \rangle \{ 111 \}$ (HORNSTRA, 1958), whereby dislocation lines are mostly aligned along $\langle 110 \rangle$ directions, i.e. dislocations are of screw or 60° character. Sometimes dislocation lines can show helical configurations due to interaction with point defects (LANGENHORST ET AL., 2001).

Among all types of diamonds, impact diamonds show the most complicated defect structure (LANGENHORST ET AL., 1999 and 2002). Impact diamonds can be regarded as pseudomorphs after graphite because they usually show a tabular shape and sometimes even preserve growth twins of the precursor mineral graphite (MASAITIS ET AL., 1990). Internally, the diamonds exhibit lattice defects at two different scales. At the micrometer scale, impact diamonds are transected by numerous, up to 1 μm wide twin bands (LANGENHORST ET AL., 2002).

These twin bands are inherited from the precursor graphite that, prior to transformation, was deformed by shock compression. At the nanometer scale, one observes a large number of stacking faults and microtwins bounded by partial dislocations (Fig. 11). Both the preservation of graphite twins and the planar faulting of the diamond lattice are a consequence of the rapid solid-state



transformation, preventing the formation of a well ordered diamond.

Fig. 11
Fourier-transformed and filtered HRTEM image of an impact diamond from the Popigai impact crater, Siberia. In this view along the [110] axis, the diamond crystal shows numerous stacking faults and microtwins. Bright dots represent the channels in the diamond structure (see figure 2).

Discussion

Formation and evolution of metamorphic coesite and diamond

The nanostructural characteristics of metamorphic coesite and diamond provide fundamental clues to the formation and evolution of these high-pressure minerals and the conditions prevailing in host rocks. UHP metamorphism takes place in a deep geological environment, where both coesite and diamond can grow as almost perfect crystals and do not undergo any deformation. The lack of deformation can be attributed to incorporation in and protection by the stable cages of container minerals such as garnet. Modifications in nanostructure and phase assemblage in the vicinity of the high-pressure minerals occur during the ascent, as is outlined in the following. Metamorphic coesite from Dora Maira first developed few (021) and (100) twins during growth at great depth and then underwent partial retrograde transformation to quartz during exhumation. The retrograde transformation proceeded at the margin and along the twin planes of coesite, forming a palisade rim and veins of quartz. This process was accompanied by the precipitation of water, which is no longer dissolvable in coesite due to the pressure decay (MOSENFELDER, 2000). The water precipitates in form of tiny voids that decorate the Brazil twins in retrograde quartz. The key to understanding the formation of metamorphic diamonds from the Erzgebirge is the characterization and knowledge of the hydrous phase assemblage around it. The defect-free diamond itself does not tell much about its genesis. In agreement with STÖCKHERT ET AL. (2001), the numerous hydrous phases around diamond can only be explained by trapping of a supercritical C-O-H fluid, which subsequently reacted with the host mineral garnet. EELS determination of $Fe^{3+}/\Sigma Fe$ ratios suggests that diamond precipitated from this supercritical fluid by a redox reaction which involves the oxidation of iron from the garnet and the reduction of CO_2 . This presumed redox reaction implies also that the source for carbon might be dissociated carbonates from the subducted lithospheric slab.

Furthermore, the TEM analyses show a heterogeneous composition of inclusions with variable concentrations of alkaline elements. This observation can explain the coexistence of primary graphite and diamond in the same garnet because alkaline elements and, in particular, sodium are known to have a catalytic effect on diamond nucleation (BURNS & DAVIES, 1992). In the absence of sodium, the nucleation of the carbon phase might be prolonged into the stability field of graphite, i.e. precipitation of graphite occurs later than diamond formation when the host rock already ascended and pressure significantly decreased. During further ascent, the remaining fluid continued to react with garnet and to form the observed hydrous mineral assemblage, which is composed of indicators for low pressures such as chlorite, plagioclase and anatase. Whether or not these considerations, in particular the formation of diamond from supercritical fluids, also apply to Kokchetav diamonds, is not yet sufficiently investigated.

Comparison to coesite and diamond from kimberlite and impact rocks

The present comparison of coesite and diamond from various geological environments substantiates that the nanostructural characteristics are indeed indicative of the geological process that produced them, i.e. the lattice defects provide a clear genetic fingerprint.

A brief discussion of the nanostructural signatures of coesite and diamond from kimberlite and impact rocks may underline this basic conclusion. Mantle-derived coesite and diamond usually contain dislocations in glide configuration but show less retrograde alteration than their counterparts from the metamorphic environment. Hence, high-pressure minerals from kimberlite rocks have been deformed to some extent in the mantle and, according to expectations, ascended much faster to the surface than metamorphic high-pressure minerals.

Coesite and diamond from impact rocks have the most diagnostic defect structure, indicative for the short time and dynamics of the impact process. The polycrystalline, fine-grained appearance and the extremely high density of twins are characteristic of impact coesite, because it forms by rapid crystallization from an undercooled high-pressure silica melt at a time scale shorter than one second. A similar duration can be assumed for the solid-state transformation of graphite to diamond. As a consequence, impact diamonds preserve the morphological characteristics of the precursor mineral graphite and develop numerous structural imperfections such as stacking faults and microtwins.

Finally, it can be concluded that detailed TEM studies may provide profound insights into the origin and evolution of natural high-pressure minerals and their host rocks. The results of this paper suggest that even investigations on loose grains of high-pressure minerals from placer deposits would indicate as to whether they are of metamorphic, kimberlitic, or impact origin.

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