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Earth and Planetary Science Letters 210 (2003) 399–410

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Focused ion beam technique and transmission electron microscope studies of microdiamonds from the Saxonian Erzgebirge, Germany

Larissa F. Dobrzhinetskaya [a,*], Harry W. Green [a,b], Matthew Weschler [c], Mark Darus [c], Young-Chung Wang [c], Hans-Joachim Massonne [d], Bernhard Stöckhert [e]

[a] *Department of Earth Sciences, University of California at Riverside, Riverside, CA 92521, USA*
[b] *Institute of Geophysics and Planetary Physics, University of California at Riverside, Riverside, CA 92521, USA*
[c] *Applications Laboratory, FEI Company, 7451 NW Evergreen Parkway, Hillsboro, OR 97124, USA*
[d] *Institut für Mineralogie und Kristallchemie, Universität Stuttgart, Azenbergstrasse 18, 70174 Stuttgart, Germany*
[e] *Institut Geologie, Mineralogie und Geophysik, Ruhr-Universität, 44801 Bochum, Germany*

Received 19 August 2002; received in revised form 20 January 2003; accepted 21 March 2003

Abstract

A focused ion beam of Ga ions is a relatively new technique that has been developed for microelectronic industries. Now researchers of the Earth sciences find it to be a promising tool for studying various geological materials. Using the FIB technique and an FEI Strata DB 235 dual beam system, we have successfully prepared several electron-transparent foils, which crossed μm-sized diamonds included in host minerals such as zircon and garnet from quartzofeldspathic rocks of the Saxonian Erzgebirge, Germany. Scanning and transmission electron microscopy applied to these foils revealed that the diamonds contain crystalline nanometric inclusions. These inclusions consist of minerals of known stoichiometries such as SiO_2 and Al_2SiO_5, whereas others are characterized by different combinations of Si, K, P, Ti, and Fe in the presence of oxygen (stoichiometries are not clear at this stage of research). One suite of inclusions is assumed to be represented by archerite, KH_2PO_4, which is known to be stable at pressures of 4–22 GPa, and one nanocrystal containing Pb, oxygen and carbon is interpreted to be Pb_xO_y or $PbCO_3$. Along with solid crystalline inclusions, the diamonds contain cavities filled by liquid/gas that escaped during sample preparation. These are associated with dislocations of diamond growth. Our data are consistent with the concept of diamond crystallization from a COH-rich multicomponent supercritical fluid and suggest that the composition of such a fluid is more consistent with a local crustal source rather than that of a mantle origin.

Keywords: focused ion beam; microdiamond; COH fluid

* Corresponding author. Tel.: +1-909-787-2028; Fax: +1-909-787-24324.
E-mail address: larissa@ucrac1.ucr.edu (L.F. Dobrzhinetskaya).

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doi:10.1016/S0012-821X(03)00170-5

1. Introduction

The focused ion beam (FIB) technique was developed in the late 1980s [1,2] from 'device transplantation' techniques to facilitate transmission electron microscope (TEM) specimen preparation for micro-device assembly and repair. Application of this technique to the examination of silicon wafers for semiconductor industries has been described in many publications [3–6] and demonstrates great promise for natural and synthetic geological materials [7,8]. The FIB microscope is based on a Ga^+ (liquid/metal) source and operates along the same principle as the scanning electron microscope (SEM), where a beam of charged particles is scanned across a specimen and the resulting images are constructed. However, unlike SEM, the FIB system may produce a high current density beam, which is used for 'in situ' sectioning of the μm-sized particles. Therefore, the FIB will become a prospective technique for preparation of thin foils transparent for electrons from very tiny mineralogical objects, such as solid inclusions of nanometric size incorporated in rock forming or accessory minerals. We have applied this technique for the first time to TEM studies of nanometric inclusions incorporated in microdiamonds that have recently been discovered by Massonne [9] in the Saxonian Erzgebirge, Germany, within quartzofeldspathic rocks.

Mineral inclusions in diamonds are unique samples of the media in which diamond crystallized. This is because diamond is chemically stable (unless it is converted to graphite) and does not react with any minerals constituting the rocks. Silicate and oxide inclusions from kimberlitic diamonds have been successfully studied by electron microprobe, Raman spectroscopy, and electron microscopy because their sizes are large enough to allow preparation of specimens for analysis by conventional techniques [10–12]. Unfortunately, microdiamonds from Erzgebirge quartzofeldspathic rocks are much smaller, falling in the range of 3–30 μm, and containing inclusions of nanometric size. The small size of such diamonds did not allow for preparation of conventional specimens so that their internal features, such as inclusions of other minerals and dislocations, could be studied. Although the first site of such microdiamonds was discovered more than 15 years ago in the Kokchetav massif, Kazakhstan [13], they have only recently been studied with the FIB and TEM [7]. The FIB technique provided a dramatic advance in the study of these microdiamonds and revealed that many of them contain nanometric inclusions of oxides, silicates, and carbonates, indicating diamond origin from a multicomponent, COH-rich fluid enriched in both crustal and mantle components [7,14].

Our current studies are focused on the examination of the nanometric inclusions in the Erzgebirge microdiamonds by combinations of FIB, SEM, and TEM techniques. Because FIB milling is a new method in geological sciences and is not appropriately tailored to each mineral class yet, we describe here some important details of sample preparation as well as the first results of TEM inspection of nanometric inclusions and dislocation suites observed in the diamonds. Our results indicate that some of these nanometric inclusions are represented by solid compounds of known stoichiometries such as SiO_2 and Al_2SiO_5, whereas others may be characterized by different combinations of Si, K, P, Ti, and Fe in the presence of oxygen. Additionally, abundant tiny cavities (former fluid/gas) are situated along diamond growth dislocations. Our new observations support the concept of microdiamond crystallization from a COH-bearing fluid, as suggested earlier [7,14–17].

2. Geological background and sampling

The crystalline massif of the Erzgebirge is located in Saxony, Germany and the northern part of the Czech Republic. Like other basement areas in Central Europe, it is part of the Variscides, which are widely covered by younger strata. In the central part of the Erzgebirge massif, the so-called 'gneiss–eclogite unit' (GEU), ortho- and paragneisses dominate, containing numerous lenses of eclogite and a few lenses of garnet peridotite. Eclogites have experienced peak metamorphic temperatures of 800°C [18] or 900°C [19]. Relics of coesite and aggregates consisting of K-

feldspar and quartz, interpreted as pseudomorphs after K-cymrite, are enclosed in omphacite and garnet [20]. They point to ultra-high pressure metamorphism (UHPM). More recently, microdiamonds were discovered in quartzofeldspathic rocks of the GEU near the eastern shore of Saidenbach Reservoir, about 1.5 km NW of the village of Forchheim [9,21].

For our current research, we have collected diamondiferous quartzofeldspathic rock samples from this area. Abundant microdiamonds of 3–30 μm size are included in garnets and zircons. They are associated with other minerals such as phengite, phlogopite, apatite, rutile, K-feldspar and others [17], forming multiple inclusion pockets. Polished thin sections viewed petrographically revealed that both garnets and zircons contain microdiamonds. One of these sections was used further for FIB–SEM–TEM research on diamonds included in garnets. Zircons were retrieved by conventional magnetic separation following hand-picking under the binocular microscope. Zircon crystals were mounted on standard petrographic glass by epoxy and polished until diamond crystals became visible on the flat zircon surface. Then final electron-transparent foils were prepared by the FIB technique.

3. Diamond sample preparation

Most TEM studies of kimberlitic and synthetic diamonds have been accomplished by standard sample preparation techniques utilizing conventional argon milling [22]. These diamonds are easily cut into wafers, typically a few tens of μm thick and 1–2 mm on a side, then placed on standard holders for subsequent dimpling and precise ion polishing. The microdiamonds from UHPM rocks are generally found in situ within softer minerals such as zircon and garnet in petrographic thin sections and polished sections. There are extreme differential ion milling rates between diamond and the host minerals that make it difficult to produce a successful foil by conventional ion milling techniques. We have exploited two independent techniques for TEM diamond foil preparations: (i) a conventional argon milling with a specific sample mounting technique [23] using a precise ion polishing system (PIPS, Gatan Inc.) and (ii) a focused ion beam (FEI Company). The latter is a new alternative to the conventional argon ion thinning [24].

Standard PIPS foil preparation [22] applied to diamonds demands more than 150 h of conventional Ar milling before electron transparency is achieved. Because diamonds of interest to us are very small, we have to mount dozens of crystals together using a special Gatan-10 glue and extract 3 mm disks so that they are compatible with the size of standard TEM copper grids, which are used as holders for samples [12,23,24]. With this technique, however, the heterogeneity of the prepared specimens is due to differential ion thinning between host and diamond, resulting in frequent loss of diamond particles.

Compared with PIPS, the FIB technique allows preservation of samples by minimizing manual handling, reduces the possibility of physical and chemical damage of the material, and, most importantly, allows preparation of a foil at any point of interest within any polished or petrographic thin section of standard size. FIB also provides a greatly enhanced opportunity to correlate observations on the host minerals, mineral inclusions, dislocation patterns and any other characteristics over a wide range of scales: from optical microscope to SEM and TEM. In addition, the trace of the FIB cutting remains on the polished surface of the thin section, thereby facilitating repeated FIB milling and additional TEM examination of the precise area of interest in cases where it is needed for resolution of controversial or confusing data. This exceptional precision is offered by the FIB technique because the volume of removed material is very small. It is clear that the FIB microsampling technique represents a powerful new application for a broad range of geological problems that involve solid micro-inclusions in host minerals and/or line defects in crystalline structures. It holds tremendous promise for analysis of samples from high-pressure experiments in which the size of synthesized mineral phases is usually very small.

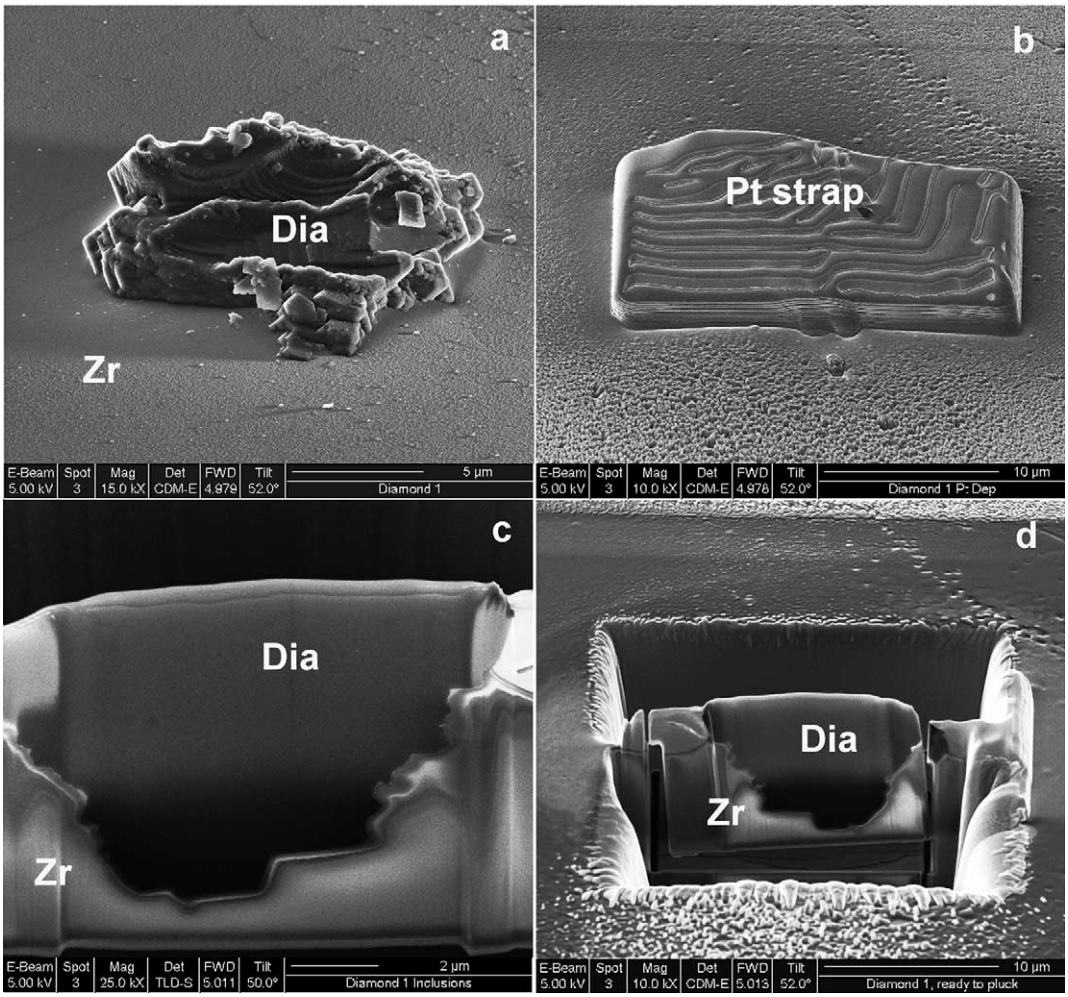

Fig. 1. Sequence of SEM images illustrating extraction by FIB during TEM specimen preparation of diamond-1 included in zircon. The FEI Strata DB235 dual beam system at 5 kV: (a–d) secondary electron images revealing the diamond surface after the following preparation stages: (a) polished surface of zircon host with the diamond inclusion standing out from the host; (b) deposition of the Pt 'strap' on the surface of the diamond crystal; (c) detail of ion-milled specimen showing the intricate and irregular interface between diamond host zircon; (d) a fully thinned and partially cut diamond foil: on the right side of the foil a connecting 'bridge' is already cut, while at the left side the foil is still connected to the sample. The foil is ready for 'lifting out' and placement onto the supportive grid.

4. FIB cutting/milling technique

The FIB microsample cutting/milling technique uses a dense beam of Ga^+ to mill deep trenches adjacent to the area of interest, thereby allowing exhumation of a small plate of the sample ($10\times5\times0.1$ μm) using an ex situ 'lift-out' micromanipulator or an in situ manipulator to remove the sample and to transfer it to a standard TEM grid [25,26]. We have applied a Strata DB 235 dual beam system manufactured by the FEI Company to prepare foils of microdiamonds included in zircons and garnets. The FEI Strata DB 235 system combines scanning electron beam and ion beam modes as two units of a single instrument. Such a combination allows scanning the surface

of the sample, obtaining high-resolution images (electron beam mode) to select the area from which to prepare the TEM foil. The foil is then prepared in an orientation perpendicular to the specimen surface by excavating on both sides of it with the ion beam of Ga^+ (FIB mode). Using 30 kV of Ga^+ ion beam with 20 nA maximum current, we were able to extract several electron-transparent diamond cross-sections. Transfer of the foils from the mineral host to the 3 mm diameter carbon-coated standard TEM copper grid was performed outside of the FIB vacuum chamber with the aid of the Mitutoyo high-resolution large-working-distance optical microscope and Narishige micromanipulator available at the FEI Company. For such an operation, a sharpened glass needle, prepared by direct heating of the glass rod, is placed at the excavation site by a hydraulic minimanipulator, and the thin foil of diamond is extracted. The foil attaches to the glass needle due to strong electrostatic attraction. The same strong electrostatic attraction makes the diamond foils adhere to the carbon-coated surface of the standard TEM copper grid without requiring additional mounting media.

Figs. 1 and 2 illustrate the most important steps of sample preparation, skipping details of the 'lift-out' manipulation. Fig. 1a shows a diamond inclusion from a thin section of garnet–phengite quartzofeldspathic rock specimen ER-5-LD-00. The diamond (diamond-1) stands out of the flat surface of the zircon host due to the final gentle polishing with colloidal silica (see details in [7]). The sample, mounted on a standard glass slide, was placed in the FIB vacuum chamber and observed in SEM mode to locate the area of interest and then to mark it for automated foil preparation by the ion beam. The diamond crystal of about 10 μm size was covered by deposition of a Pt 'strap' (Fig. 1b) to protect the top surface of the diamond from unnecessary beam damage. The Ga^+ ion beam 'cuts' the diamond crystals by excavating two parallel trenches perpendicular to the surface of the thin section (Fig. 1c) and two additional 'cuts' are made at the left and right sides of the foil to prepare it for subsequent extraction from the host (Fig. 1d). The FIB that was used enabled the TEM sample preparation to be automated and thus the electron-transparent foils could be made to be very consistent from sample to sample. Fig. 1d shows the stage at which the clean and electron-transparent cross-section, including material from both the diamond crystal and its host zircon, is ready to be 'lifted out' for TEM examination. The cross-section through the second diamond crystal (diamond-2) included in zircon (Fig. 2a) shows details of the rough surface developed at the first stage of ion milling (Fig. 2b) and the diamond crystal configuration in two dimensions (Fig. 2c). The trace of the ion beam on the surface of the sample is shown in Fig. 2d, indicating that the sample may be used in the future for additional microscopic research; the place of foil excavation may be found easily, even with an optical microscope.

5. TEM observations

Transmission electron microscopy of the foils was performed with a Philips CM300 TEM with twin lens and LaB_6 cathode operated at 200 and 300 kV in the Central Facility for Advanced Microscopy and Microanalysis of the University of California, Riverside. A carbon-coated copper grid with foil was mounted on a Philips low-background double-tilt holder for examination in the TEM. The Philips CM300 TEM analytical equipment consists of an EDAX system for acquisition and processing of energy dispersive X-ray (EDX) spectra, equipped with a Si detector with resolution of 135 eV at Mn Kα, an ultra-thin window, and MX-TEM software. EDX spectra were collected with specimen tilt of about 25° towards the detector, resulting in an effective take-off angle of 38°. Part of the research on the foils was completed at the FEI Company using a Tecnai F20 scanning transmission electron microscope (STEM) combining EDX and electron energy loss spectroscope (EELS) systems. The Tecnai F20 STEM with S-Twin objective lenses and field emission gun (Shottky field emitter) operates at a beam current of 20–200 nA, providing a high probe current (>0.6 nA on a 1 nm spot). It is equipped with a fully embedded digital scan system; bright-field and annular dark-field modes are

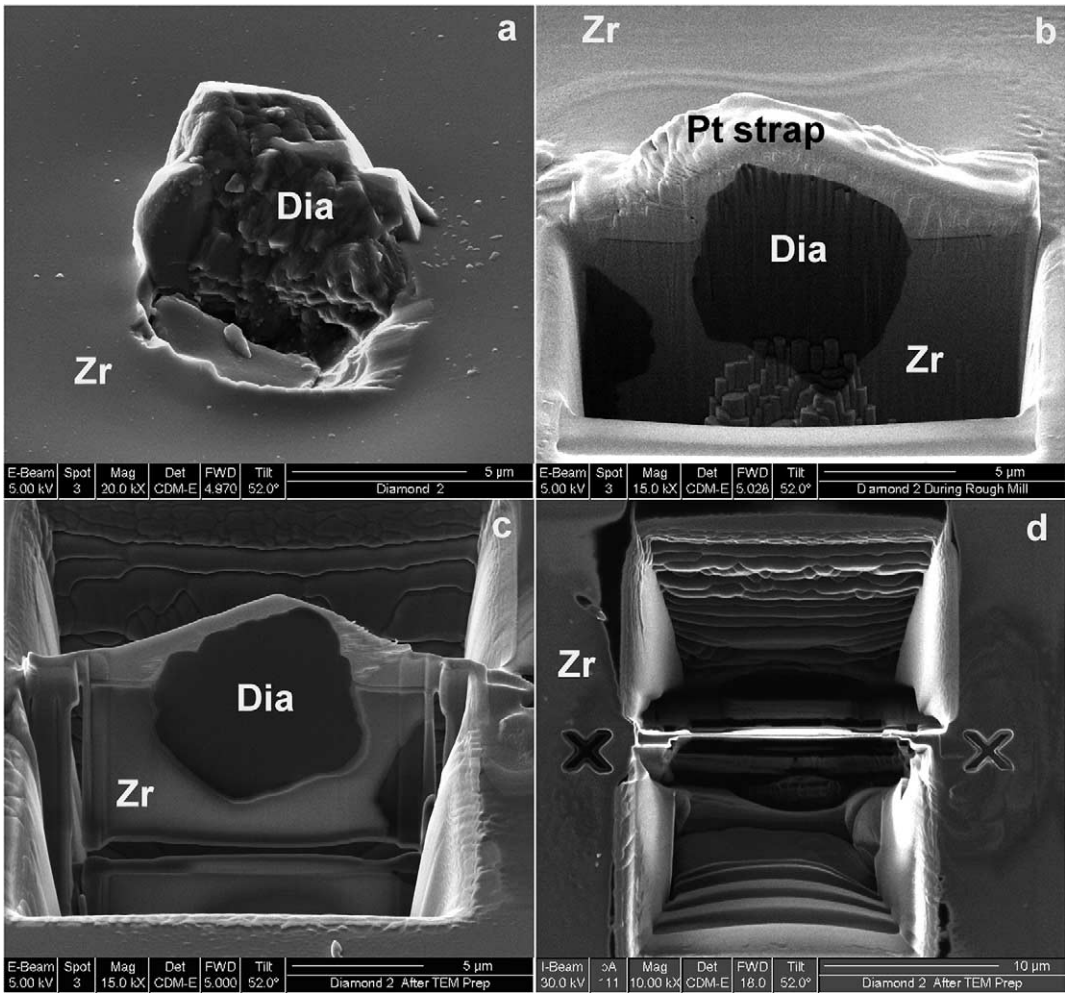

Fig. 2. Secondary electron images of diamond-2 included in zircon showing the FIB milling sequences. (a) Polished cross-section of zircon host with a diamond inclusion. (b) A FIB section through the diamond crystal; vertical 'column-like' patterns are due to 'rough' milling. Pt strap covers top of the diamond crystal. (c) FIB foil of diamond-2 showing two-dimensional geometry of diamond and the grain boundary between diamond and zircon host. (d) The internal details of the 'trench' remaining after foil excavation, viewed from above. All images obtained using secondary electrons in the FEI Strata DB235 dual beam system at 5 kV.

provided by ultra-high resolution high-angle annular dark-field (HAADF) detector. STEM allows measuring the composition of the nanometric inclusions directly without tilting of the sample. Our inspection of the FIB-prepared diamond foils at TEM/STEM shows that they are transparent to the electron beam at an operating voltage of 200 kV, the specimen thickness is uniform, and the amorphization zone induced by milling is about 15 nm thick.

6. Results

6.1. Diamond-1 included in zircon

The studied diamond foil reveals sharp selected area electron diffraction (SAED) patterns, which correspond to the diamond structure. A series of nanometric solid inclusions, empty cavities, and defect structures were observed in the core of the diamond crystal (Fig. 3a,b) in bright-field im-

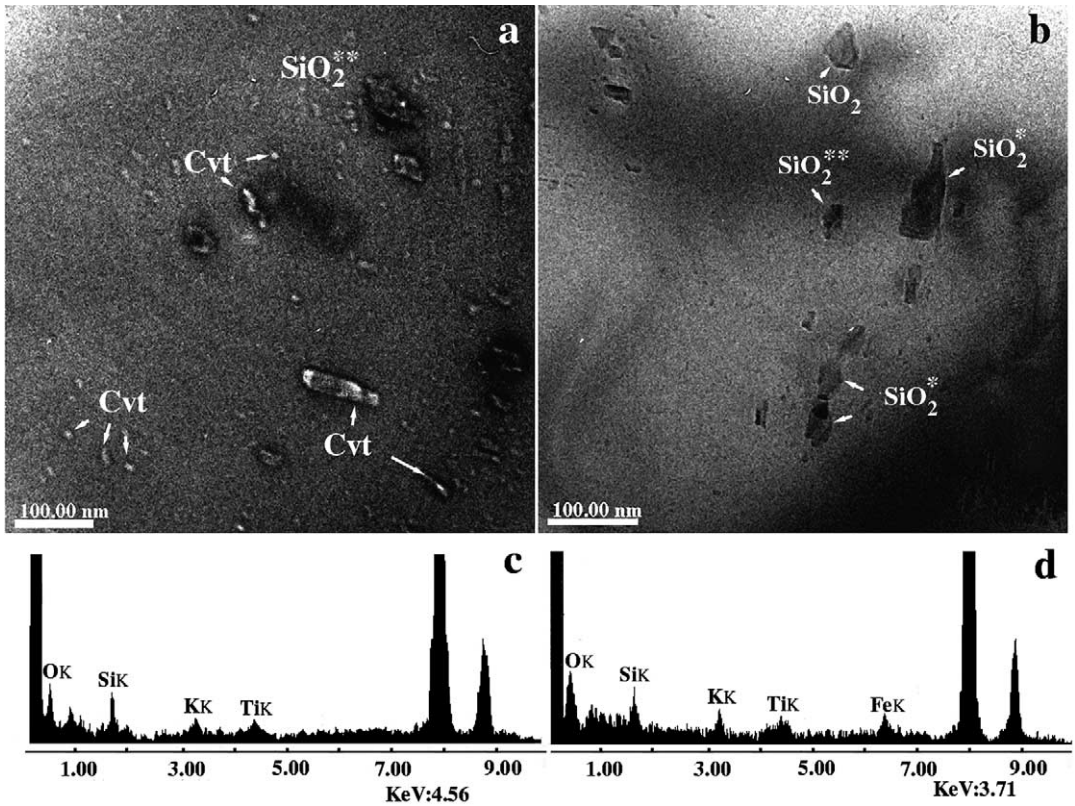

Fig. 3. (a,b) TEM bright-field images of diamond-1 foil containing nanometric-size solid inclusions of SiO_2 with varying minor components and cavities (Cvt) that were filled by fluid or gas liberated during foil preparation. SiO_2 represents pure silica, SiO_2*, silica with admixture of K and Ti, which may indicate a signal coming from any tinier fluid or solid inclusions enriched in K and Ti and spatially associated with SiO_2. SiO_2** indicates silica with admixture of K, Ti and Fe. (c,d) EDX spectra of two representative inclusions labeled SiO_2* and SiO_2**. Cu peaks at 8 and ~8.7 on the EDX diagrams correspond to the signal coming from the standard supportive grid. On EDX spectrum diagrams, the vertical axis indicates counts while the horizontal axis corresponds to energy in keV. Time of counting is 100 s. All data were obtained with a Philips CM300 FEG TEM.

ages at TEM. The solid inclusions intermixed with cavities typically occur randomly (Fig. 3a,b), although some exhibit apparent association with diamond growth dislocations (Fig. 4). The size of the inclusions and cavities is in the range 20–80 nm. EDX inspection demonstrated that the solid inclusions are, in most cases, pure SiO_2, although some of the spectra, in addition to the Si peak, also show peaks for K and Ti (Fig. 3c), or K, Ti, and Fe (Fig. 3d); another spectrum contains O, Si, and Al, with a cation ratio corresponding to kyanite, Al_2SiO_5. Within pockets of Si–K and Si-rich nano-inclusions, we have detected one inclusion containing Pb. On the EDX diagram, the Pb peak is associated with Si and K peaks, which likely reflect a background composition from neighboring inclusions. We assume that the Pb phase could be represented by either Pb_xO_y or $PbCO_3$. This is only a guess, however, because the carbon peak is very strong on each EDX diagram, reflecting a background signal originating from the diamond host. We interpret the cavities as indicating the former presence of fluid/gas, which escaped during foil preparation. Electron diffraction patterns of all inclusions labeled in Figs. 3 and 5 confirm that they are crystalline. However, we have not been able to determine structures because the inclusions are very small,

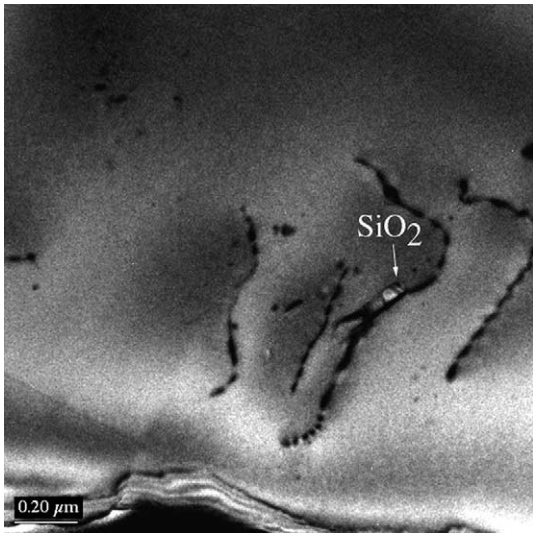

Fig. 4. Bright-field image of dislocation patterns in diamond-1 obtained with a Philips CM300 FEG TEM. The solid inclusion seen associated with the dislocations is SiO_2.

and their orientations have not been such that diagnostic zone axes could be accessed by tilting in the electron beam.

6.2. Diamond-2 included in zircon

The foil provides a clear picture of the diamond shape, revealing that it is a rounded single crystal with a weak development of octahedral faces (Fig. 2b). The dark-field image obtained by HAADF detector at STEM revealed a series of nanometric inclusions (Fig. 5a,b) that are situated in the part of the diamond section that is close to its boundary with the zircon host. The sizes of the inclusions are ~20–150 nm. The EDX spectrum of inclusion #1 indicates that it contains SiO_2 with a trace of Fe (Fig. 5a,c), whereas the neighboring inclusion #2 consists of pure SiO_2 (Fig. 5a,e). The EDX spectrum of inclusion #3 is characterized by peaks of O, K, and P (Fig. 5b,d). EDX spectra with similar combinations of K, P, and O are very common for Kokchetav diamonds [7]. We assume that a possible mineral phase might be an anhydrous acid phosphate, archerite–KH_2PO_4 [27]. Although EDX cannot detect hydrogen, the foundation of such an assumption is supported by the fact that the KH_2PO_4 phase has been reported to be stable from $P<1$ to >14 GPa [28]. Because KH_2PO_4 is the most typical hydrogen-bonded ferroelectric phase widely used in modern technologies, many experiments have been performed on this material. They indicate a wide stability field for KH_2PO_4 and its polymorphs, from several hundred MPa to more than 14 GPa at different temperatures [28]. Stability of the KH_2PO_4 phase was experimentally tested over a wide range of pressures from <1 to >14 GPa but only over a limited range of temperatures, 25–450°C; we assume that at very high pressures the KH_2PO_4 phase may remain stable to high temperature (~900°C). Therefore, we expect that the possibility of finding such phases incorporated in diamond is high, if the bulk chemistry is appropriate.

The EDX spectrum of inclusion #4 indicates the presence of K_2O with a trace of Ti (Fig. 5f). Si and Zr peaks in this spectrum probably originate from the zircon host but the presence of nanocrystals of zircon is not unusual, at least in Kokchetav diamonds [7,14]. Because only out-of-zone-axis-orientation SAED patterns were obtained due to the unfavorable orientation and very small size of both SiO_2 inclusions, we may conclude that they are crystalline, though their structures remain undetermined.

6.3. Diamond-3 included in garnet

Bright-field images in the TEM reveal a high density of dislocations situated in the inner part of the diamond crystal (Fig. 6a,b). Their morphologies suggest that they were formed during diamond growth rather than due to its deformation. No solid inclusions were observed in this cross-section. However, many 'dot'-like subnanometric cavities are located along the dislocations, indicating that the former liquid/gas inclusions and dislocations are related to the process of diamond crystallization from a fluid phase.

7. Discussion and conclusions

From the technical aspect, our results demonstrate that FIB milling offers exceptional precision in preparing selected areas of a sample for exami-

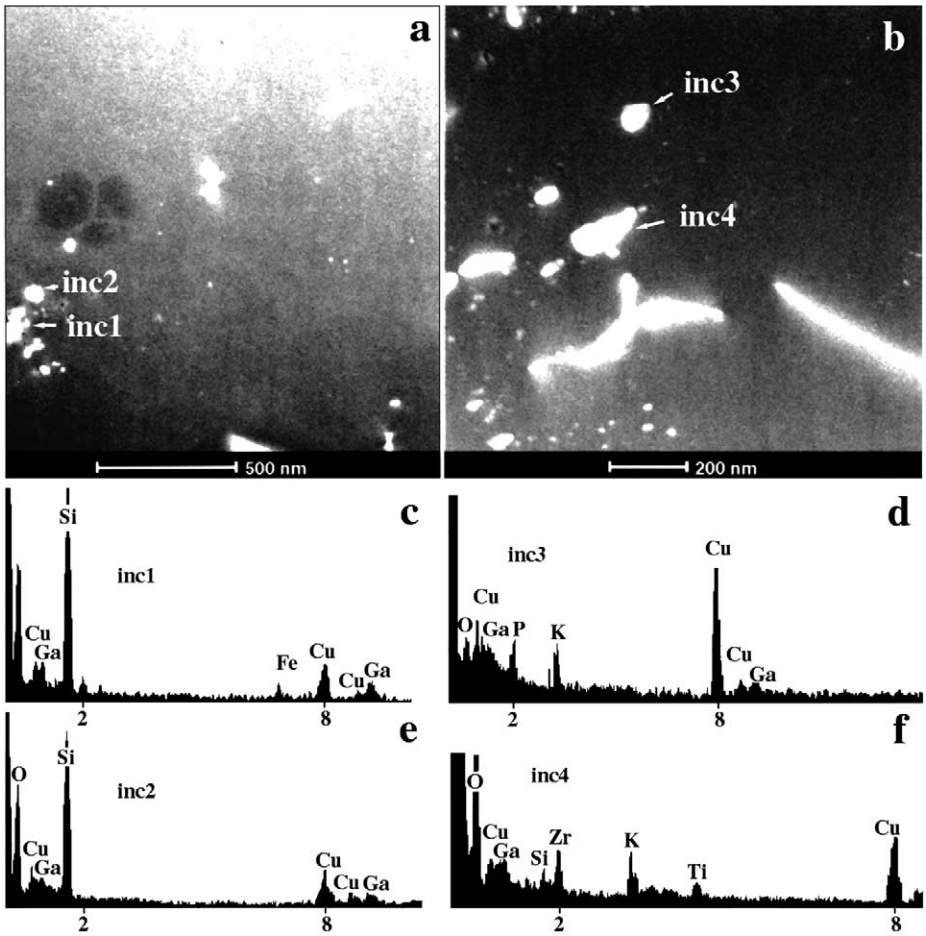

Fig. 5. Images of diamond-2 foil with solid nanometric crystalline inclusions (a,b) and EDX spectra of four representative inclusions (c–f) obtained by HAADF detector using STEM technique (Technai F20). On EDX spectrum diagrams, the vertical axis indicates counts while the horizontal axis corresponds to energy in keV. Time of counting is 100 s. Cu peaks originate from supportive standard TEM grid; Ga peaks are due to the Ga^+ beam used for foil preparation.

nation by TEM. The technique provides analytical access to very small-scale features that are usually lost if the specimen is prepared by conventional argon milling using PIPS. The investigation of nanometric inclusions in microdiamonds utilizing FIB–SEM–TEM techniques shows that they contain crystalline particles of SiO_2 and Al_2SiO_5 stoichiometries, whereas many other crystalline inclusions are characterized by the presence of Si, K, P, Ti, or Si and Fe, along with pronounced oxygen peaks in their EDX spectra. The stoichiometries of many of them (other than SiO_2 and Al_2SiO_5) are not well known yet. One suite of such inclusions is interpreted to be archerite, KH_2PO_4, which is known to be stable at pressures from <1 to >14 GPa, and one nanocrystal containing Pb is interpreted as Pb_xO_y or $PbCO_3$.

Previous studies on diamond-bearing multiphase inclusions in garnets [17,29] and in zircons [14] suggested that Erzgebirge diamonds crystallized from a supercritical COH fluid rich in Si, K, Na, Ti, P, and other components. They have reported that diamond-bearing multiple inclusions in garnets and zircons contain phengite, quartz, phlogopite, apatite, rutile and K-feldspar in addition to diamond. However, these assemblages might not reflect the actual bulk composition of the original fluid, because it appears that the fluid

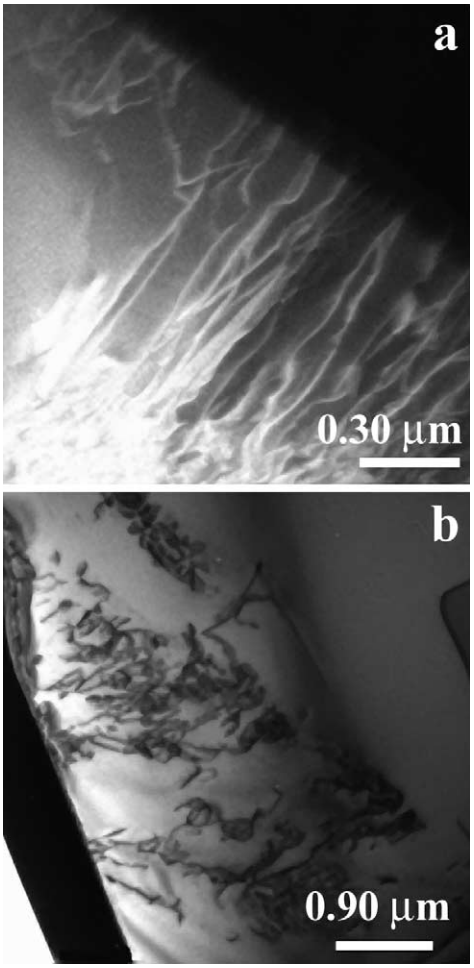

Fig. 6. Dark-field (a) and bright-field (b) TEM images of diamond-3 included in garnet, demonstrating growth dislocations (Philips CM300 FEG TEM).

has reacted with the enclosing garnet host upon cooling [17]. It is also possible that a new fluid of another composition could migrate through zircons along cracks, providing various components for the formation of the present solid assemblages associated with diamond [7].

The diversity of the nanometric inclusions in diamonds, their morphologies and spatial association with dislocations of diamond growth revealed by our current FIB–SEM–TEM studies, support the concept of diamond crystallization from a COH-rich multicomponent fluid. Moreover, only the nanometric inclusions in diamonds keep a record of the actual composition of such a fluid because diamond is a perfect inert container protecting inclusions from chemical reactions. This statement is also supported by the fact that all nanometric crystals in individual inclusions in diamond are clearly syngenetic. The comparison of the mineralogical assemblages incorporated in diamonds and those that associate with diamonds in polycrystalline pockets included in garnets and zircons shows that no Mg and Ca components are recorded within diamonds, whereas both these components are abundant within the multiphase pockets in garnet. This suggests that, during diamond growth, the COH-rich multicomponent fluid was probably depleted in Mg and Ca and relatively rich in Si, Al, K, P, Ti, and Fe. The presence of Zr and Na cations in such a fluid needs to be clarified by additional studies, because they may be camouflaged by a strong signal of Zr from the zircon host, and a strong Cu peak from the supportive grid that might overlap the real Na peak in the EDX spectra.

Overall, the diversity of the components occurring within the inclusions in Erzgebirge diamonds is more consistent with a crustal origin than that of a mantle origin. Conversely, diamonds from the Kokchetav massif, Kazakhstan – another classical site of microdiamonds from UHPM rocks – have been found to contain inclusions suggesting that they originated from a COH-rich supercritical fluid carrying components from both crustal and mantle sources [7]. It may be interpreted that the Kokchetav diamond-bearing rocks followed a different trajectory with a different spatial relation to the mantle wedge, or that they had a longer residence time in the subduction zone, facilitating access of fluid enriched in mantle components.

The inclusions found in Erzgebirge diamonds provide useful insights into the chemical characteristics of the system in which the diamonds formed. However, this point needs to be developed further to place tighter constraints on the two existing models ‘fluid vs. melt’ suggested for crystallization of diamonds in UHPM terranes (e.g. [13,16,17]). Our recent studies of Kokchetav rocks based on a comparison of the chemical compositions of nanometric inclusions in diamonds with the bulk chemistry of the entire pockets consisting of diamond and other associated

silicates and oxides, included in both garnet and zircons, strongly suggest that the diamond origin in Kokchetav is consistent with the COH multicomponent fluid concept rather than with a silicate melt model [30]. Similar comparative analysis for Erzgebirge diamonds in the future would be very helpful.

Acknowledgements

The laboratory research was supported by National Science Foundation Grant EAR-0107118 to L.F.D. and H.W.G. We thank Mr. Frank Hansen for his help with zircon separations from the rocks and K.N. Bozhilov for obtaining TEM images. Efforts by Mr. Tony Carpenter of the FEI Company are greatly appreciated for cooperation in exploiting the FEI Strata DB 235 dual beam system. L.F.D. is grateful to Stuttgart University for travel support during her field trip to the Erzgebirge diamond site. We also thank G. Ernst and W. Glassley for their constructive comments on this paper.*[BOYLE]*

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