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Direct observation and analysis of a trapped COH fluid growth medium in metamorphic diamond

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ABSTRACT

The mechanism by which diamonds grow in Earth's mantle has been a subject of discussion for many years. Arguments have been advanced for growth from a melt, from a COH fluid, and in the solid state. The discovery of microdiamonds within ultra-high pressure terranes of continental collision settings re-energized this debate because of their very different but well-defined continental crust environment. We report here the discovery of filled nanometric fluid bubbles in diamonds from marble of the Kokchetav massif, Kazakhstan, and the serendipitous measurement of their contents due to bursting of a bubble very shortly after a measurement of chemical composition in the transmission electron microscope, thereby allowing immediate re-analysis with exactly the same settings of all parameters of the microscope. The chemical composition of the fluid is C, H, O, Cl, S, Ca, Fe and K. The direct observation and composition of a low-viscosity trapped fluid in microdiamond unambiguously establish their fluid growth medium.

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Introduction

Diamonds from kimberlites and related eruptions (diamond pipes) have been known and studied for many years and are now known from all continents (e.g. Haggerty, 1999). They were long thought to be the only primary source of diamonds in the Earth. However, discovery of microdiamonds in metasediments in continental collision terranes (Sobolev and Shatsky, 1990; Xu *et al*., 1992; Dobrzhinetskaya *et al*., 1995; Massonne, 1999; Nasdala and Massonne, 2000) demonstrated that continental material can be subducted to depth appropriate to diamond stability (>120–150 km) and tectonically returned to the surface, providing an additional diamond source. Perhaps not surprisingly, metamorphic diamonds differ from their kimberlitic cousins in several important respects. For example, their morphology, while having similarities to kimberlitic diamonds, is generally different, as are their solid inclusion suites (Dobrzhinetskaya *et al*., 2001, 2003a,b, 2004b). Similarly, whereas the light and variable carbon isotopes in some kimberlitic diamonds have suggested a biogenic source for the carbon, that proposal has met with spirited debate (Haggerty, 1999; Schulze *et al*., 2003, 2004). In contrast, the light carbon isotopes source for metamorphic microdiamonds (Cartigny *et al*., 2001) is clear, because they are found in metamorphosed Si–Al-rich (pellite-like) continental rocks and marine carbonates.

Nevertheless, debate also persists concerning the mechanism by which metamorphic microdiamonds grow (de Corte *et al*., 1998; Dobrzhinetskaya *et al*., 2001, 2003a,b, 2004b; Hwang *et al*., 2001, 2003; Stöckhert *et al*., 2001; Massonne, 2003). Evidence for growth from a fluid medium is strong, but discussion continues over whether the fluid was a melt or a COH fluid (Ogasawara *et al*., 2000; Dobrzhinetskaya *et al*., 2001, 2003a,b, 2004b; Hwang *et al*., 2001, 2003; Stöckhert *et al*., 2001; Massonne, 2003). High-pressure experiments are consistent with either growth medium (e.g. Taniguchi *et al*., 1996; Akaishi and Yamaoka, 2000; Pal'yanov *et al*., 2001, 2002; Dobrzhinetskaya *et al*., 2004a) and therefore help little to clarify this issue. Direct observation and analysis of fluid inclusions incorporated in these diamonds could offer a resolution of the controversy and potentially cast light on the origin of these diamonds. Few data exist on the composition of fluid inclusions in kimberlitic diamonds (Navon *et al*., 1988; Navon, 1991; Schrauder and Navon, 1994), in part, because of their rarity and, in the case of metamorphic microdiamonds, their small size and therefore possibility of fluid escape during analytical procedures. Here we report direct observation of nanometer-sized bubbles in metamorphic microdiamonds from dolomitic marbles from the Kumdikol diamond deposit in Kazakhstan. Bubbles are spatially associated with platelets, crystal defects common in diamonds (Gross *et al*., 2003), and contain a low-viscosity, oxygen-rich fluid containing small amounts of Ca, K, Fe, Cl, S, and commonly including aragonite crystals. The observations demonstrate that COH fluid is the medium from which diamonds grew in these rocks and most probably is the medium by which they grow in other deeply subducted sediments.

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Diamond occurrences in ultra-high pressure metamorphic terranes

Diamonds were discovered within metasedimentary rocks of continental affinity in the Kokchetav massif, Kazakhstan in the 1980s (e.g. Rozen *et al*., 1972), but their identification *in situ* and demonstration of their growth under condition of diamond stability occurred only a decade ago (Sobolev and Shatsky, 1990). Since the original discovery, the occurrence of similar microdiamonds in several other localities in the Euroasian continent has been confirmed: Central Orogenic Belt of China (Xu *et al*.,

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1992; Yang *et al.*, 2003); Western Gneiss Region of Norway (Dobrzhinetskaya *et al.*, 1995; van Roermund *et al.*, 2002); Erzgebirge massif of Germany (Massonne, 1999); Ural Mountains of Russia (Bostick *et al.*, 2003); and the Greek Rhodope (Mposkos and Kostopoulos, 2001, 2003; Beyssac and Chopin, 2003). All of these localities include metamorphic rocks that mark the location of former continental collisions and imply the subduction of continental materials to depths of at least 120 km before return to the surface. A new startling discovery of microdiamonds, with characteristics of N-aggregations and N-isotopes similar to diamonds from Kokchetav massif, within the Akluilak minette dykes (Nunavut, Canada) has been recently reported by Cartigny *et al.* (2004). The authors believe that Akluilak diamonds were formed in Early Proterozoic time during deep subduction metamorphism of their primary host rocks and later were sampled by minett dike and delivered to the surface. The discovery opens a new avenue for discussion of the deep Early Proterozoic subduction and extends the occurrence of ultra-high pressure metamorphism from 0.6 billion years to before 1.8 billion years ago.

Diamonds from ultra-high pressure metamorphic rocks show many differences from the well-known diamonds from kimberlitic and lamproitic pipes: (i) They are characterized by a very narrow range of carbon isotopes ($\delta^{13}C = -10$ to $-15‰$) in comparison with the wide variation of $\delta^{13}C$ ($+2$ to $-25‰$) in diamonds from mantle sources (Cartigny *et al.*, 2001). (ii) The size of diamonds hosted by metamorphic rocks is restricted mostly to 10–100 μm diameter, and their morphology is dominated by skeletal-like and imperfect cuboid forms rather than the common octahedral morphology of the larger diamonds from kimberlitic sources. (iii) Metamorphic diamonds in many cases contain solid nanometric oxide and rare silicate inclusions that reflect the local chemistry of the host minerals and rocks (Dobrzhinetskaya *et al.*, 2001, 2003a,b). For example, our recent studies (Dobrzhinetskaya *et al.*, 2003a) show that in the Kokchetav massif, Kazakhstan, diamonds from felsic rocks contain abundant inclusions of SiO_2 whereas diamonds from carbonate rocks contain mostly $CaCO_3$ inclusions (Dobrzhinetskaya *et al.*, 2004b).

The number of hypotheses to explain the origin of these unusual diamonds has now been diminished to two, with experimental production of diamonds from both COH fluid and alkaline-carbonate or/and carbonate-silicate and silicate melts (Taniguchi *et al.*, 1996; de Corte *et al.*, 1998; Akaishi and Yamaoka, 2000; Hwang *et al.*, 2001, 2003; Pal'yanov *et al.*, 2001, 2002; Stöckhert *et al.*, 2001; Dobrzhinetskaya *et al.*, 2003a,b, 2004a,b; Massonne, 2003). Nevertheless, no consensus has been achieved as to which of these growth media is correct or, indeed, if they both can be correct under different circumstances (e.g. de Corte *et al.*, 1998; Hwang *et al.*, 2001, 2003; Massonne, 2003). We have now directly observed more than four fluid bubbles in one foil from diamond hosted by dolomitic marbles, that we believe, resolves this issue, at least for the Kokchetav diamond-bearing locality.

Electron microscope studies

A specimen of marble consisting of dolomite, garnet, K-rich diopside and phlogopite that contains diamond in concentrations >2000 carat/tonne (Kumdikol, Kazakhstan) was polished and electron-transparent slices of diamonds included in diopside and garnet were 'cut' by focused ion beam (FIB); several 30-nm thick foils were prepared (e.g. Dobrzhinetskaya *et al.*, 2003b; Seydoux-Guillaume and Wirth, 2003; Wirth, 2004) for examination by transmission electron microscopy (TEM). FIB, the innovative technology for TEM sample preparation from small specimens or from precisely chosen locations in bulk material, has been applied previously to diamonds from felsic gneisses of Kazakhstan and Germany (Dobrzhinetskaya *et al.*, 2001, 2003a,b, 2004b), but this is the first such application for diamonds from carbonate rocks. Electron transparent foils were cut from microdiamonds in polished thin sections *in situ* using a FEI FIB 200TEM at GeoForschungsZentrum Potsdam with a Ga ion source and accelerating voltage 30 kV (Wirth, 2004). At the final step a TEM ready foil is produced with the dimensions $15 \times 10 \times 0.150$ μm, which needs no further carbon coating. Homogeneity and thickness of the foils are automatically controlled by the FIB milling system. TEM studies were performed in a Philips CM200 TEM operating at 200 kV with a LaB6 filament as electron source. The TEM is equipped with a Gatan imaging filter GIF® and an energy-dispersive X-ray analyzer (EDAX). The GIF was used for acquisition of energy-filtered images applying a 20 eV window to the zero loss peak of the energy-loss spectrum. Analytical electron microscopy was performed by means of an energy dispersive analyzer (Si–Li) with ultra-thin window. Beam size is 4 nm; standard counting time is usually 200 s, but during our studies of the entire fluid bubble the counting time was shortened to 100 s to avoid a complete loss of its integrity and disappearance in the vacuum chamber of TEM.

Tens of solid crystalline inclusions of 10–100 nm diameter were observed in diamond foils. Most of them are pure $CaCO_3$, or $CaCO_3$ with minor cation substitution of Fe and Mg. Electron diffraction patterns identify such inclusions as aragonite, a high-pressure polymorph of calcite. Many aragonite inclusions were surrounded by empty space, and numerous completely empty cavities also were observed similar to those from felsic gneisses shown in earlier publications (Dobrzhinetskaya *et al.*, 2001, 2003a,b), suggesting the former presence of fluid or gas, or fluid + gas inclusions that burst during foil preparation.

Fortunately, two foils (nos 427 and 430) also contained some bubbles that were smaller than the foil thickness. An intact fluid bubble spatially associated with platelets is shown in Fig. 1. The bubble was discovered by appearance movement of absorption contrast because of density variation within the foil which resulted from electron beam heating. Examination at higher magnification showed the contrast to vary with time (Fig. 1a,b), culminating after 2 min with sudden loss of fluid, inducing a sudden change to bright contrast in the entire area between the two larger platelets and a

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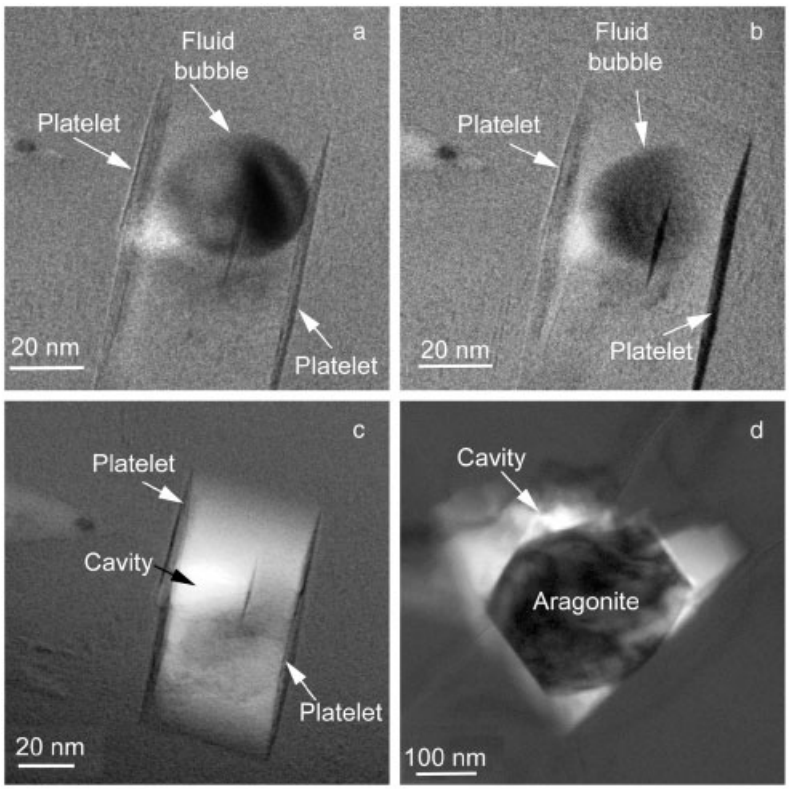

Fig. 1 Energy filtered bright field TEM (Philips, 200 kV, LaB6 filament, Gatan GIF®) images of diamond foil. (a–c) Step-by-step record of changing contrast of a single fluid inclusion during illumination by the electron beam. Fluid inclusion is situated between two platelets, thin lamellar defects of diamond structure. Although many authors have assumed that platelets are structural defects caused by nitrogen aggregation around carbon atoms, recent infrared research and computer simulations suggest that they are largely carbonaceous defects and actually contain little nitrogen (Gross *et al.*, 2003). Panels (a) and (b) show the fluid inclusion intact; the dark contrast moved from the right part of the bubble (a) to its left side (b). The brighter area at the left side of the fluid bubble (a and b) corresponds to a less dense volume in diamond foil caused by interaction of the electron beam and fluid, but no perforation of the foil has occurred yet at the moment when images were taken. Panel (c) demonstrates that this inclusion became perforated: note small elongate cavity (a bright area with diffuse boundaries) at left in the brightest part of image that is related to the less thickness of the foil. Panel (d) shows another inclusion containing an aragonite crystal surrounded by bright contrast space previously occupied by fluid that was lost during foil preparation. A detail description of this foil will be published elsewhere.

stable image thereafter (Fig. 1c). A similar inclusion that had been perforated during foil preparation and that contains an aragonite crystal is shown in Fig. 1d. On this image, the bright contrast existing around the well-shaped aragonite crystal is because of a reduced sample thickness at that location, and records the former presence of fluid that was liberated during thinning to electron transparency. The residual film on the surface originally in contact with the fluid exhibits weak Ca and K peaks (not shown here but to be published elsewhere). Figure 2 shows the chemical signature obtained from the fluid inclusion shown in Fig. 1 by energy dispersive X-ray analysis (EDX) before and after rupture. Prior to rupture, small peaks for Ca, K, Fe, Cl, S were present, accompanied by a larger O peak (Fig. 2a). A second EDX analysis taken 36 s later, after the sudden change in image contrast, shows the same small Ca, K and Fe peaks, but the oxygen peak is greatly reduced and the Cl and S peaks have disappeared (Fig. 2b). There was no tilting of the specimen between the two analyses, hence the lessened peak of oxygen cannot be attributed to change of sample orientation with respect to geometry of the detector. The observations strongly suggest that, when the bubble lost its integrity, the trapped high pressure fluid escaped, along with the dissolved components (probably HCl and H_2SO_4 or SO_2), leaving only a thin amorphous film containing Ca, K and Fe oxides). We also have performed dozen energy dispersive X-ray spot analyses on the surface of diamond foil at the distance 10–100 nm outside of the fluid bubble (Fig. 1c) after its perforation as well as around aragonite inclusion enveloped by former fluid (Fig. 1d), and no other peaks than pure carbon and Cu, Ga and Pt corresponding to supportive grid and induced by milling process were detected.

Based upon the absence of Si within the residual film inside the bubbles, we exclude their origin as droplets of alkaline-carbonate, carbonate-silicate melt as was proposed by others (e.g. Hwang *et al.*, 2001, 2003; Pal'yanov *et al.*, 2001, 2002; Massonne, 2003). If such bubbles represented a former melt of any composition, they would now consist of crystalline materials developed on cooling preceding tectonic uplift of diamond-bearing rocks to the Earth's surface, or conceivably they could have been quenched to a glass. Moreover, the sudden escape of fluid through the tiny orifice shown in Fig. 1c, leaving only traces of oxide behind clearly implies a low-viscosity fluid at room temperature, ruling out a melt. Comparison of the EDX analyses before and after rupture also inescapably tell us that the fluid was principally oxygen but does not distinguish between CO_2, H_2O, or a combined, COH, fluid. The composition of the host rock (dolomitic marble), the fact that diamond grew from the fluid, and the common presence of aragonite in the inclusions all indicate that CO_2 was likely a major component of the fluid. However, the loss of Cl strongly suggests that the fluid also had a hydrous component, and elsewhere in these diamonds we have found inclusions of high-pressure amphibole. Moreover, spectroscopic

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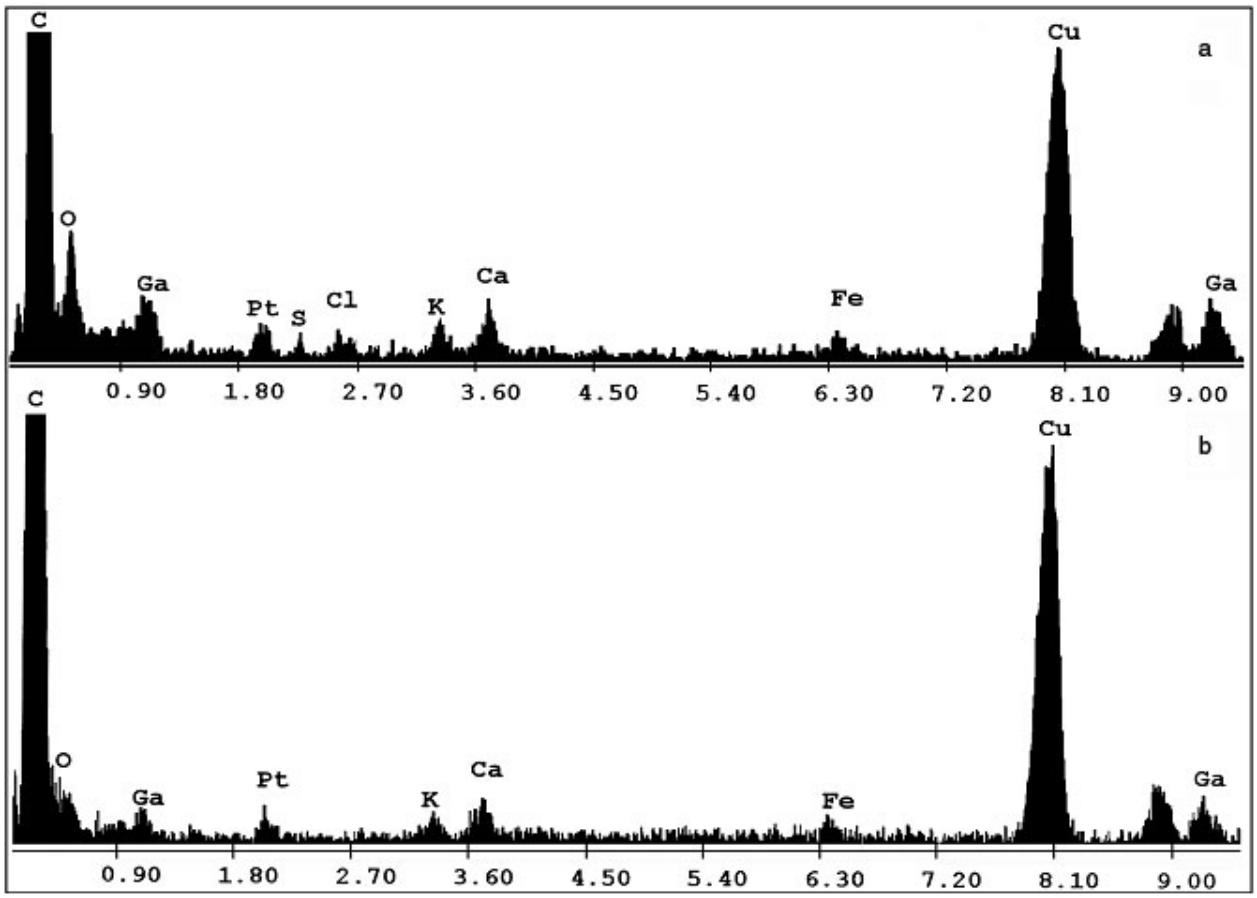

Fig. 2 EDX spectra of bubble. Spectrum (a), obtained prior to perforation of the bubble, shows small X-ray intensities of several elements as indicated and a significant O peak in addition to the strong C peak from the diamond as well as Ga, Pt and Cu secondary fluorescence from specimen preparation and TEM grid, respectively. Spectrum (b), obtained 36 s after spectrum (a) and subsequent to perforation of the bubble lacks peaks for S and Cl and shows a greatly reduced O peak, reflecting loss of bubble constituents but retention of a thin amorphous oxide surface film. Counting time for both spectra is 100 s. Unlabelled peak of Cu–Kb is situated between Cu and Ga peaks on both spectra (a and b).

evidence (de Corte *et al.*, 1998) from diamonds in other lithologies has indicated that the presence of H_2O and the wide variety of crystalline oxides in diamonds from felsic gneisses (Dobrzhinetskaya *et al.*, 2001, 2003a,b, 2004b) likely required a significant H_2O component in the fluid. Therefore, we conclude that the Kokchetav microdiamonds grew from a COH fluid enriched in local components of the host rocks.

The direct observation of fluid inclusions in diamond from ultra-high pressure metamorphic terranes underlines the significance of diamond as a natural 'sampling capsule'. Its great strength and chemical inertness allows delivery of deep-seated fluid to the Earth's surface in continental subduction zones and pristine preservation for geologically meaningful times. Such fluid trapped by diamonds provides the only opportunity to researchers for direct access to high-pressure natural fluids. This demonstration of the growth fluid in metasediments may have relevance for the fluid medium responsible for growth of kimberlitic diamonds (Navon *et al.*, 1988; Navon, 1991; Schrauder and Navon, 1994; Schulze *et al.*, 2003, 2004), which is still a subject of debate.

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