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Nano-inclusion suite and high resolution micro-computed-tomography of polycrystalline diamond (framesite) from Orapa, Botswana

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ABSTRACT

A single polycrystalline diamond aggregate from the Orapa kimberlite (Botswana) contains a syngenetic micro- and nano-inclusion suite of magnetite, pyrrhotite, omphacite, garnet, rutile and C–O–H fluid in order of abundance. This suite of inclusions is distinctly different from those in fibrous diamonds, although the presence of sub-micrometer fluid inclusions provides evidence for a similarly important role of fluids in the genesis of polycrystalline diamond. It is the first study of polycrystalline diamond by High resolution μ-CT (Computed Tomography) reaching a resolution of 1.3 μm using polychromatic X-rays. Combined with Focused Ion Beam assisted Transmission Electron Microscopy the method reveals epigenetic replacement coatings of hematite and late stage sheet silicates around the magnetites showing that magnetites are often (but not always) interstitial to the diamond and, thus, were open to late stage overprinting. It is proposed that the polycrystalline diamond formed by a redox reaction between a small-scale carbonatitic melt and a sulfide-bearing eclogite. The water released from the melt during diamond precipitation fluxed local melting of the surrounding eclogite, and oxidation of sulfide phases to magnetite, which mingled with the carbonatitic melt and (re-)precipitated locally.

1. Introduction

The application of new, high resolution analytical techniques originally developed for material science and condensed matter physics has considerably extended our knowledge of diamond formation and changed our perspective in the direction of fluid-dominated processes. Direct observation of nanometric fluid inclusions and associated crystals in diamond was much facilitated by the innovative Focused Ion Beam (FIB) method for producing thin foils in well-defined areas for analysis by Transmission Electron Microscopy (TEM; e.g. Wirth, 2004, 2009). FIB-assisted TEM analyses of fibrous diamonds, diamonds from placer deposits and kimberlites as well as of metamorphic microdiamonds have led to the discovery of new mineral phases (Brenker et al., 2007) or phases previously only known from experiments (e.g. phase "egg"; Wirth et al., 2007); Uncommon, sometimes "super-deep" mineral parageneses (Hayman et al., 2005; Kaminsky et al., 2009; Klein-BenDavid et al., 2007; Wirth et al., 2009) have been identified, allowing unprecedented glimpses into deep subduction zone processes (e.g. Dobrzhinetskaya et al., 2007).

Our knowledge of the composition of diamond-forming fluids currently mostly stems from analyses of fibrous diamonds which contain thousands of micro- to nanometric fluid inclusions in their turbid coatings (Navon, 1988). These paint a picture of the almost universal presence of carbonates worldwide (Guthrie et al., 1991; Lang and Walmsley, 1983) and halides (Klein-BenDavid et al., 2006; Logvinova et al., 2008) in polyphase inclusions together with fluid compositions varying between carbonatitic, hydrous-silicic and hydrous-saline endmembers, underlining the apparently important role of supercritical fluids rich in alkalis, chlorine, carbonate and water in the formation of diamond (Izraeli et al., 2001; Klein-BenDavid et al., 2004a; Schrauder and Navon, 1994).

Metamorphic microdiamonds, however, have a distinctly different nano-inclusion suite with oxides as the most abundant mineral phases, whereas silicates and carbonates play smaller roles (De Corte et al., 1998; Dobrzhinetskaya et al., 2003, 2006; Sobolev and Shatsky, 1994).

It is well known that the stability field of diamond may stretch over more than 10 log units in oxygen fugacity (fO_2), from conditions of about fO_2 = Iron–Wüstite −6, where moissanite (SiC) is stable (Moore and Gurney, 1989) to distinctly oxidized conditions where carbonate inclusions are present, of an oxygen fugacity about 4 log units above the Iron–Wüstite equilibrium. These conditions are sometimes encountered even within the nanometric inclusion suite of single diamonds (Klein-BenDavid et al., 2007), illustrating some of the variability of diamond formation conditions in chemical space and time (Gurney et al., 2010; Stachel and Harris, 2008).

The innovative studies of O. Navon and co-workers on fibrous diamond have added a new perspective to diamond research, but as

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fibrous diamonds represent only one facet of the variability of diamond formation conditions in the Earth's mantle, it is necessary to extend these pioneering studies to diamonds formed in different environments and at different geological times in order to obtain a complete picture of diamond formation in the Earth's mantle.

We present here the first such study on polycrystalline diamond (PCA, framesite) from the Orapa mine, Botswana. FIB-assisted TEM analyses are combined for the first time with high resolution micro computed tomography (HR-μCT) with state-of-the-art resolution for white X-ray beams which allows examination of both pore space and minerals intergrown with, and included in, diamond continuously in three dimensions from micro- to nanometer scale.

1.1. Polycrystalline diamonds (framesite)-background

Polycrystalline aggregates (PCA) of diamond occur in a few kimberlite pipes in southern Africa (e.g. Venetia, Premier, Jwaneng, and Orapa) and can make up several percent of the diamond production in a mine. They are classified by increasing grain size as framesite (Gurney et al., 1984) or boart (Orlov, 1977) and typically have a porous structure that is classically interpreted to indicate formation from C–O–H fluids. The diamond aggregates can contain silicates of eclogitic and peridotitic affinity, similar (but not identical; Sobolev et al., 1975) to the inclusion suite found in gem-sized diamonds. Micro-inclusions occur mostly in interstices and are intimately intergrown with the diamonds, which, in addition to further structural and geochemical evidence (Jacob et al., 2000, 2004; Kurat and Dobosi, 2000) indicate contemporaneous crystallization within the diamond stability field in the Earth's mantle.

In addition to silicates, rarer phases such as Fe-carbide can sometimes be found in framesites, recording unusually low local oxygen fugacity at the time of their formation (Jacob et al., 2004). Furthermore, while many gem-sized diamonds have old, often Archean formation ages, polycrystalline diamond aggregates from the Venetia Diamond Mine (South Africa) containing eclogitic minerals have been shown to have formed by very young remobilization processes within the cratonic lithosphere that directly preceded kimberlite eruption (Jacob et al., 2000).

2. Sample and analytical techniques

Sample PHN 4596/22 stems from a collection of P. Nixon from the Orapa kimberlite pipe and is about 8 mm in size. Diamond is very fine-grained (less than 1 mm on average). The sample is magnetic and contains a number of black to reddish inclusions at the surface. The polycrystalline diamond aggregate was studied in a completely untreated condition, ensuring an original composition unchanged by chemical treatment. After laser cutting and polishing (carried out at the Research Laboratory of the De Beers Diamond Trading Company, Maidenhead, UK), the sample was mounted in epoxy and major element analyses of the exposed inclusions were carried out using JEOL 8900R electron microprobes at the Georg-August University in Göttingen and the Johannes Gutenberg-University in Mainz by wavelength-dispersive analysis with a beam diameter of 2 μm. Standardization was carried out with a range of natural and synthetic standards and the data were corrected using the CITZAF procedure.

Micro-Computed X-ray-Tomography was carried out at the Department of Geosciences, Johannes Gutenberg-University using a CT-Alpha instrument (ProCon X-ray) equipped with a YXLON FXE 160.51 X-ray tube and a Hamamatsu flat panel sensor detector. Since resolution of the method depends on the sample size, two individual analyses were carried out, one on the ca. 6 mm large polished piece and a second one on a smaller freshly cut slice of about 2 mm length. The samples were irradiated with a white X-ray cone beam (acceleration voltage of 60 kV, tube current of 250 μA). The X-ray beam is pre-filtered by an aluminum foil with a thickness of 0.15 mm to reduce beam-hardening effects. Projections were taken with an integration time of 1.5 s. For the measurement, 800 projections were acquired during a 360° rotation of the sample resulting in a spatial resolution of 9.5 μm per voxel (volume pixel) for the larger sample and 1.3 μm per voxel for the smaller sample. Reconstruction of the raw data was carried out using in-house MATLAB (Mathworks Inc.) codes and visualization was performed with the software amira 5.2.2 (Visage Imaging Inc.).

For Transmission Electron Microscope analyses (TEM), twenty-five ultra-thin foils of ca. 15 by 10 μm and 0.150–0.200 μm thicknesses were prepared using the focused ion beam device (FIB) of a FEI FIB200 instrument following procedures given by Wirth (2004, 2009). After milling, the foil was cut free, extracted, and placed on a carbon-coated Cu grid. No further carbon coating was necessary. During TEM analysis, FIB-foils cut from the polished sample surface showed cavity fillings clearly consisting of polishing material and sample debris. Therefore, before preparing further FIB-foils, a new surface was generated by laser cutting. These turned out to be free of polishing contamination and were useful in identifying uncontaminated analyses in some of the early foils cut from the polished surface. Four of the twenty-five FIB-foils turned out to be completely inclusion-free; another seven showed extensive contamination by polishing material and were not used for data collection and interpretation.

TEM imaging and analysis were undertaken with a FEI Tecnai™G2 F20 X-Twin transmission electron microscope with a FEG electron source at the GeoForschungsZentrum, Potsdam. The TEM was operated at 200 kV acceleration voltage. A Gatan Tridiem™ filter allowed energy-filtered imaging applying a 20 eV window to the zero loss peak. Analytical electron microscopy (AEM) was performed with an energy dispersive X-ray analyzer (EDX). Analyses usually were carried out in scanning transmission mode (STEM) scanning the beam in a preselected window thus avoiding mass loss during the spectrum acquisition. Counting time was 60–120 s. Beam size was approximately 1 nm in diameter. Images in the STEM mode were acquired with a high angle annular dark field detector (HAADF). Electron energy-loss spectra (EELS) were recorded in diffraction mode with a dispersion of 0.1 eV/channel. Acquisition time was 1 s. The resolution of the energy filter was 0.9 eV at half width, at full maximum of the zero loss peak. The spectra were processed (background subtraction, removal of multiple scattering, Fourier ratio deconvolution) using the Digital Micrograph software package.

The FIB-milling method is carried out by sputtering the material surrounding the target area with gallium ions. Platinum coating protects the target area itself. Heating of the sample during sputtering has been shown to be less than 10 K, due to the very low angle between Ga beam and sample (Ishitani and Yaguchi, 1996). However, it is well known that FIB-milling generates a thin amorphous layer of 10–20 nm thickness on both sides of the foil and that its thickness shows a strict linear relationship to the accelerating voltage of the Ga beam (e.g. Kato, 2004) The thickness of this layer is much less than the total thickness of the foil (150–200 nm) and causes nothing more than a slight blurring effect in high resolution TEM images, if not removed. Amorphization introduced by FIB milling across the complete thickness (or considerable parts) of the foil has never been observed in more than 2600 FIB foils cut in this laboratory. We consider it therefore highly unlikely that the amorphous phase studied here was introduced by the FIB-milling procedure. Furthermore, the surface of the amorphous carbon phase (Fig. 4a) is wedge-like and rough. These features cannot have been produced by the gallium ion beam, because of its very small angle during milling (sub-parallel) to the surface of the foil.

3. Phase composition

3.1. Diamond

As is typical for polycrystalline diamond aggregates, sample PHN4596 consists of >90 vol.% diamond. TEM analyses of the diamond