Solid molecular nitrogen (δ-N$_2$) inclusions in Juina diamonds: Exsolution at the base of the transition zone

Oded Navon [a,*], Richard Wirth [b], Christian Schmidt [b], Brooke Matat Jablon [a], Anja Schreiber [b], Simon Emmanuel [a]

[a] *Institute of Earth Sciences, The Hebrew University, Jerusalem 91904, Israel*
[b] *GFZ German Research Centre for Geosciences, Section 4.3: Chemistry and Physics of Earth Materials, Telegrafenberg, 14473 Potsdam, Germany*

ABSTRACT

Diamonds originating from the transition zone or lower mantle were previously identified based on the chemistry of their silicate or oxide mineral inclusions. Here we present data for such a super-deep origin based on the internal pressure of nitrogen in sub-micrometer inclusions in diamonds from Juina, Brazil. Infrared spectroscopy of four diamonds, rich in such inclusions revealed high concentrations of fully aggregated nitrogen (average of 900 ppm, all in B centers) and almost no platelets. Raman spectroscopy indicated the presence of solid, cubic δ-N$_2$ at 10.9 ± 0.2 GPa (corresponding to a density of 1900 kg/m^3). Transmission electron microscopy of two diamonds found two generations of octahedral inclusions: microinclusions (average size: 150 nm, average concentration: 100 ppm) and nanoinclusions (20–30 nm, 350 ppm). EELS detected nitrogen and a diffraction pattern of one nanoinclusion yielded a tetragonal phase, which resembles γ-N$_2$ with a density of 1400 kg/m^3 (internal pressure = 2.7 GPa). We also observed up-warping of small areas ($\sim$150 nm in size) on the polished surface of one diamond. The $\sim$2 nm rise can be explained by a shallow subsurface microinclusion, pressurized internally to more than 10 GPa.

Using available equations of state for nitrogen and diamond, we calculated the pressures and temperatures of mechanical equilibrium of the inclusions and their diamond host at the mantle geotherm. The inclusions originated at the deepest part of the transition zone at pressures of $\sim$22 GPa (630 km) and temperatures of $\sim$1640 °C. We suggest that both generations are the result of exsolution of nitrogen from B centers and that growth took a few million years in a subducting mantle current. The microinclusions nucleated first, followed by the nanoinclusions. Shortly after the exsolution events, the diamonds were trapped in a plume or an ascending melt and were transported to the base of the lithosphere and later to the surface.

1. Introduction

1.1. Juina super-deep diamonds

The Juina area (Mato Grosso, Brazil) is the source of many super-deep diamonds. The mineral inclusions in these diamonds fit experimental prediction of lower mantle (>660 km) and transition zone (410–660 km) mineralogy. This is in contrast to most natural diamonds, which originate at the sub-continental lithospheric mantle or the upper asthenosphere at depths of 150–240 km. The various zones differ in the mineralogy of the major silicates and oxides, and the assignment of depth of origin relies

on these differences, as reflected in the mineral chemistry of the inclusions (see Harte, 2010; Walter et al., 2011; Harte and Richardson, 2012 and Kaminsky, 2012 for reviews). The Juina diamonds are found in alluvial deposits and in a few kimberlites scattered over an area of a few thousand square kilometers west and southwest of the town of Juina in the Amazonian Craton. Peridotitic and eclogitic lithospheric mantle xenoliths as well as the exposed upper crustal rocks yield mid-Proterozoic ages. The alluvial deposits of the São Luiz tributary are located in the center of this area (see map in Bulanova et al., 2010). Two Juina kimberlites were dated at 92–95 Ma (Heaman et al., 1998). A 101 ± 7 Ma, ^{206}Pb/^{238}U age of a CaTiSi–perovskite inclusion in a Juina diamond (Bulanova et al., 2010) suggests very short mantle residence time for these deep diamonds. This is also consistent with Sm/Nd and Rb/Sr isotope systematics (Harte and Richardson, 2012) and the survival of nitrogen in A centers in some deep diamonds. At temperatures

>1500 °C, the A centers should convert to B centers in just a few million years (see the section below for nomenclature and systematics of nitrogen aggregation in diamond). Harte and Richardson (2012) summarized this evidence and suggested a model for the formation of the Juina deep diamonds in an oceanic crust that was subducted to the upper–lower mantle boundary at 660 km. Subsequently, the diamonds were picked up by an ascending plume that transported them to the base of the lithosphere, where they were later picked up by kimberlites that transported them to the surface.

1.2. Nitrogen aggregation

The deep source of many Juina diamonds is also reflected in the aggregation of their nitrogen. Nitrogen enters the diamond lattice as single atoms substituting for single carbon atoms (C center). The single nitrogen atom migrates and pairs are formed (A centers). At typical lithospheric temperatures of 1000–1200 °C, this process is completed over a time scale of a few million years (Taylor et al., 1990, 1996). The couplets join to form B centers (four nitrogen atoms around a vacancy) at a much slower pace. At lithospheric temperatures, this process takes a few billion years to reach completion. Most lithospheric diamonds carry both A and B centers and show a correlation between the concentration of B centers and the height of a sharp absorption peak at ~1370 cm^{-1} (B′). This peak is attributed to platelets, a planar defect of nanometer to micrometer size, consisting of monoatomic layers of interstitial carbon atoms (Woods, 1986) with some nitrogen (Kiflawi et al., 1998). Some diamonds fall below the correlation line due to degradation of their platelets (Evans et al., 1995; Kiflawi and Bruley, 2000).

Many Juina diamonds have very low levels of nitrogen (Type II diamonds). Where nitrogen is present, it is highly or fully aggregated (showing mostly or only B centers). In most cases, there is no detectable platelet peak, probably due to complete degradation of the platelets at high temperature. The Juina super-deep diamonds spent little time in the mantle (Bulanova et al., 2010; Harte and Richardson, 2012). Their very high aggregation state coupled with the low concentration of nitrogen and the short residence time point to high residence temperatures. For example, Thomson et al. (2014) estimated temperatures of 1400–1550 °C for a suite of Juina diamonds, assuming a residence time of 10–100 Myr. In many other cases where temporal constraints are not strict, the temperature cannot be determined.

1.3. Voidites

Further development of nitrogen aggregation was observed in a few diamonds where platelets degraded into dislocation loops that were sometimes accompanied by voidites. Voidites were first studied by Barry (1986), Hirsch et al. (1986) and Barry et al. (1987). They described small (<10 nm) octahedral bodies, residing inside or near dislocation loops associated with the destruction of platelets. Far from being void, the voidites are, in fact, filled with a solid phase. Based on Moiré patterns, Barry (1986) and Hirsch et al. (1986) identified it as crystalline NH$_3$. Later, electron energy-loss spectroscopy (EELS) revealed a sharp line at 400 eV, indicating the presence of nitrogen (Bruley and Brown, 1989). Nitrogen was also detected by energy dispersive X-ray spectroscopy (EDX) in both small (20–30 nm) and large (100–200 nm) octahedral inclusions in diamonds from Juina (Rudloff-Grund et al., 2016a, 2016b). Inclusions of similar appearance and size ranges were also described in Juina diamonds carrying a deep transition zone or lower mantle assemblage of ferropericlase, clinoenstatite and olivine (Kagi et al., 2016). The density of nitrogen calculated based on the EELS

spectra was found to be quite high, about half that of the diamond, leading Bruley and Brown (1989) to suggest that the solid phase is N$_2$. On one hand, such high density indicates high internal pressure. On the other hand, it also calls for the involvement of vacancies in converting B centers with a density close to that of the diamond into lower density N$_2$ (van Tendeloo et al., 1990). Evans et al. (1995) and Kiflawi and Bruley (2000) observed nitrogen-bearing voidites within or very close to dislocation loops left after destruction of platelets in platelet-bearing diamonds that were heated to 2650–2750 °C.

The connection between voidites and platelets was broken when van Tendeloo et al. (1990) found larger voidites (~20 nm) randomly distributed in diamonds that showed no platelet peaks and very few dislocation loops. They suggested that such voidites were formed in vacancy-rich diamonds, where the formation of B-centers was not accompanied by platelet formation. Luyten et al. (1994) examined the solid phase in these voidites using transmission electron microscopy (TEM). Moiré patterns observed in some voidites were explained as rising from the overlap of diamond (111) and molecular nitrogen (200) planes and their different d-spacing rotated against each other. Selected area diffraction patterns suggested a tetragonal phase with unit cell parameters of $a = 4.47$ and $c = 4.79$ Å, in contrast with earlier determination of a cubic lattice (Barry et al., 1987). With four nitrogen molecules per unit cell, the calculated density is 1940 kg/m^3, in agreement with former estimates of about half the density of diamond (3520 kg/m^3).

The 1940 kg/m^3 density of the nitrogen in the voidites indicates high internal pressures of 12.1 GPa (Olijnyk, 1990). However, the phase expected at such pressure or density is δ-N$_2$, a cubic phase. A tetragonal phase, γ-N$_2$, is stable only at low temperatures and pressures (< 100 K, <2 GPa, see phase diagram in Fig. 9) and is less dense (Buchsbaum et al., 1984). It is possible that the cubic symmetry is broken by the strain field exerted by the diamond (Luyten et al., 1994) or by the C–N interaction at the voidite interface. Alternatively, because the cubic symmetry of δ-N$_2$ depends on the free rotation of the N$_2$ molecules, it is also possible that the tetragonal phase is δ_{loc}, which is stable at room temperature at pressures higher than 10 GPa (Bini et al., 2000; Hanfland et al., 1998).

Nitrogen was also found, mixed with CO$_2$ in fluid inclusions in diamonds (Smith et al., 2014), but these are larger inclusions along healed cracks in diamonds that carry both A and B centers and originate from shallower depth.

Here, we describe the inclusions we found in five opaque diamonds from São Luiz. Slabs of these diamonds were studied using optical, scanning electron (SEM), transmitted electron (TEM) and atomic force microscopy (AFM), and by Fourier transform infrared (FTIR) and Raman spectroscopy. The examinations reveal the presence of octahedral inclusions with a range of sizes. Raman spectroscopy indicates the presence of solid molecular nitrogen in the inclusions and, together with TEM and AFM, indicates that the internal pressure in the inclusions is high and that the diamonds originated at high temperatures and great depth.

2. Methods

2.1. Sample preparation and characterization

The five diamonds are opaque, irregular in shape, a few mm in size and weigh 69–126 mg. All were laser-cut to produce 0.8–1.1 mm thick slabs with parallel surfaces. Following polishing on a diamond wheel at the Hebrew University of Jerusalem (HUJ), they were cleaned ultrasonically in a mixture of 69% HNO$_3$ and 60% HF to remove all surface contamination and leave only diamond at the surface, and rinsed in water and alcohol.