Solid molecular nitrogen (N₂) inclusions in Juina diamonds: exsolution at the base of the transition zone

Oded Navon[1], Richard Wirth[2], Christian Schmidt[2], Brooke Matat Jablon[1], Anja Schreiber[2] and Simon Emmanuel[1]

1) Institute of Earth Sciences, The Hebrew University, Jerusalem, Israel, oded.navon@mail.huji.ac.il, bmjablon@gmail.com, simon.Emmanuel@mail.huji.ac.il.
2) GFZ German Research Centre for Geosciences, Potsdam, Germany, wirth@gfz-potsdam.de, christian.schmidt@gfz-potsdam.de, schreib@gfz-potsdam.de.

Introduction

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 São Luiz, Juina Province, Brazil. The Juina area is known for the high percentage of super-deep diamonds (>300 km), many of these diamonds carry no detectable nitrogen or little nitrogen in a highly aggregated stage (most or all resides in B-centers). The diamonds we examined are nitrogen-rich and expand the known compositional range of super-deep diamonds. We will describe the diamonds and their nitrogen and discuss probable scenarios for their formation and ascent.

Results

The diamonds are opaque. Polish slabs show zoning that is not concentric, with dark, cloudy, inclusion-rich zones and more transparent ones. Secondary electron images show many small inclusions in the cloudy zones. Secondary electron imaging reveal microinclusions (30-300, Average 150 nm). TEM reveals an additional population of nanoinclusions, ~20-30 nm in size (Fig. 1). Chemical analysis of shallow subsurface inclusions with EPMA shows no oxygen or heavier atoms. Infrared spectroscopy of inclusion-rich zones in four diamonds revealed high concentrations of fully aggregated nitrogen (470-1060, average of 900 ppm, all in B centers) and almost no platelets. Hydrogen concentrations (the VN_3H centers) are high.

Raman spectroscopy conducted on three diamonds yielded a spectrum of solid, cubic δ-N_2 at 10.9±0.2 GPa. Figure 2a shows the two lines: a sharp peak at ~2354 cm^{-1} and a weaker one at ~2367 cm^{-1}. The location of these two peaks, their relative intensity and the separation between the two peaks are fully compatible with assignment to the weaker υ_1 and the more intense υ_2 vibrational modes of δ-N_2 as measured in earlier studies. The positions of both peaks closely fit those of δ-N_2 at a pressure of 10.9±0.2 GPa (Figure 2b; Schneider et al., 1992). The corresponding density ia ~1900 kg/m^3. Using the number density and size of the inclusions measured by SEM and TEM, we estimated the nitrogen content of microinclusions at ~100 ppm, while the smaller, but more ubiquitous nanoinclusions carry ~350 ppm N_2 by weight.

EELS also 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). In this case, the corresponding pressure at room temperature lies outside the stability field of the γ-N_2 phase, which is limited to T<100K. Using AFM, we also observed up-warping of small areas (~150 nm in size) on the polished surface of one diamond. The ~2 nm rise can be explained by a shallow subsurface microinclusion, pressurized internally to more than 10 GPa
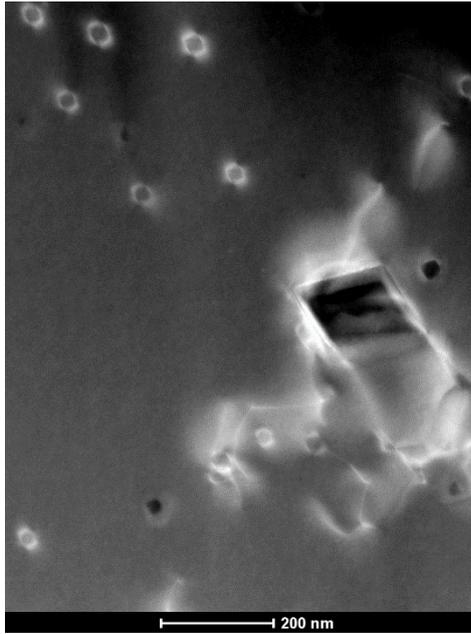
Fig. 1. TEM bright-field images of diamond ON-SLZ-392. The large microinclusion (120 nm) is surrounded by dislocations, together with many small nanoinclusions (~20 nm). All the inclusions are octahedral in shape and aligned parallel to the diamond's major crystallographic axes. The microinclusion is exposed to the polished surface, as are some of the nanoinclusions (dark ones), but many are still closed and under pressure, as indicated by the strain contrast at their sides.
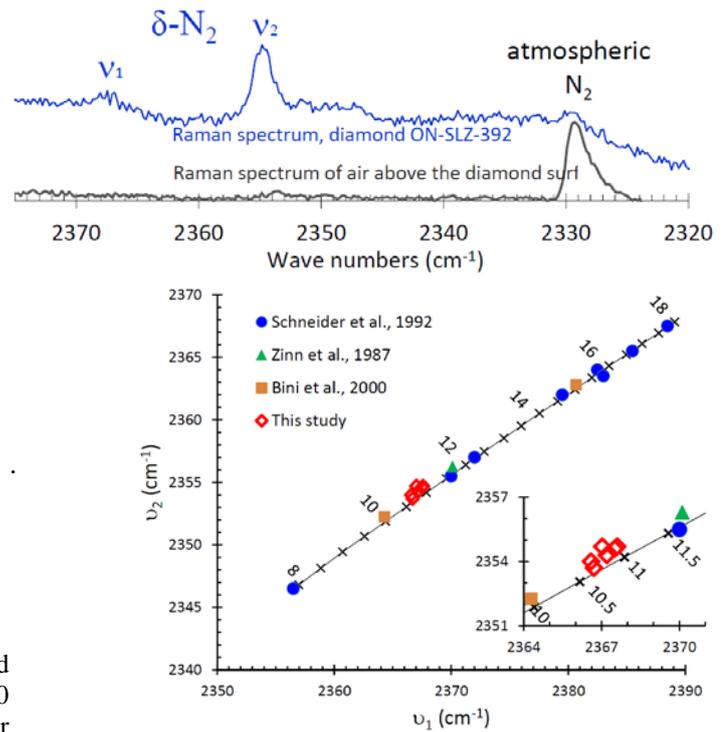

Fig. 2. a. Spectrum of inclusion-rich zone in diamond ON-SLZ-392 shows the two characteristic peaks of δ-N_2 and compared with a spectrum of atmospheric nitrogen. b. The position of the two peaks (open red diamonds) compared with high pressure measurements (solid symbols) and the best fit line for the results (Schneider et al., 1992, black crosses and line). All spectra yield similar pressure of 10.9±0.2 GPa.

Discussion

We adopt the clear fit of the Raman data with δ-N_2 over the structural data of the single inclusion obtained by TEM and conclude that the inclusions carry δ-N_2 at pressure of 10.9±0.2 GPa at room temperature. Most of the nitrogen of the diamond resides in B centers (~900 ppm) but the micro- and nanoinclusions also carry an appreciable amount of ~100 and 350 ppm, respectively. Similar inclusins where described more than 20 years ago by Loyten et al. (1994) and recently by Rudloff-Grund et al. (2016) and Kagi et al. (2016), but none reported a clear evidence for the nature of the included phase. At mantle temperatures, the nitrogen in the inclusions was in a fluid state. Using available equations of state for fluid 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 ~22 GPa (630 km) and temperatures of ~1640°C. Further support for such deep source comes from the identification of a deep transition zone or lower mantle assemblage of ferropericlase, clinoenstatite and olivine in Juina diamonds that carry similar nanoinclusions (Kagi et al., 2016).

We suggest that the formation of both micro- and nanoinclusions are the result of exsolution of nitrogen from B centers and from platelets during their degradation. Evans et al. (1995) and Kiflawi and Bruley (2000) observed nitrogen-bearing "voidites" (that are identical to our nanoinclusions) within or very close to dislocation loops left after destruction of platelets in platelet-bearing diamonds that were heated to 2650-2750°C. Using the kinetics of their experiments and the activation energy for the migration of B centers that is equal or larger than that for the formation of B centers, we constrained the rate of
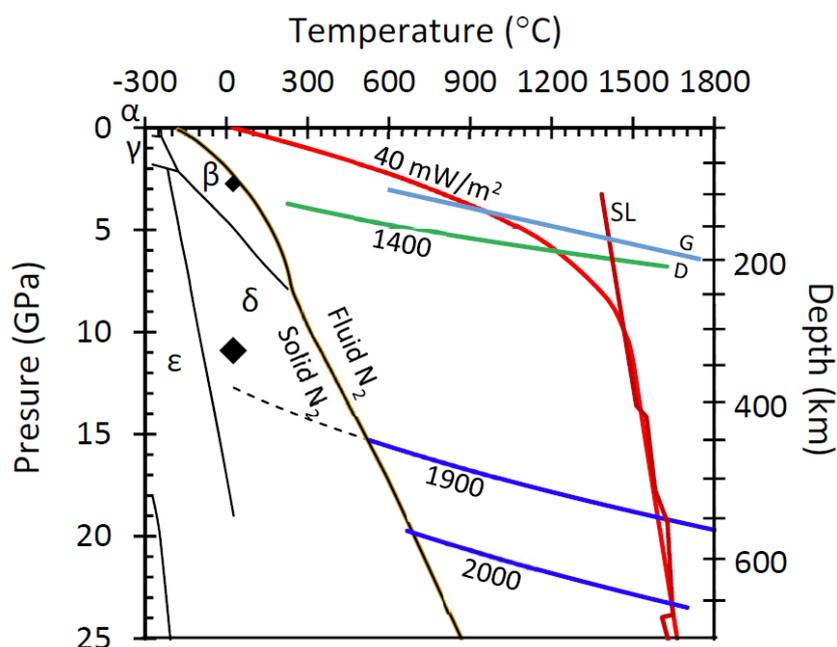
Fig. 3. Phase diagram for molecular nitrogen, the PT conditions of the inclusions and the mantle geotherm. α, β, γ, δ and ε: the stability fields of the various phases of molecular N_2. Large black diamond – the pressure measured using Raman spectroscopy (10.9 GPa at room T). The small black diamond – The PT conditions for the tetragonal phase measured using TEM. Red and brown lines – the geotherm (adiabat from Stixrude and Lithgow-Bertelloni, 2007). Blue and green lines – isochores for 2000, 1900 and 1400 kg/m^3. The density at room T and 10.9 GPa is 1900 kg/m^3. Since the diamond expands during ascent, the initial density maust have been higher, intemediate between 1900 and 2000 kg/m^3, intersecting the geotherm at 22 GPa, 1640°C.

growth of the nano- and microinclusions. The high concentrations of nitrogen and the need for a short growth period (of the order of a few million years) advocates growth in a subducting environment.

We favor a scenario where the diamonds formed deep in the transition zone in a down-flowing mantle current associated with subduction. The nitrogen aggregated to form B centers, platelets were degraded and most of the dislocation loops disappeared or served as site for the microinclusions. At the high temperatures at the base of the transition zone, nitrogen exsolved to form the microinclusions and then the nanoinclusions. The diamonds were then trapped and transported up in a plume or a melt. Growth of the inclusions ceased quickly as temperatures decreased during ascent. The diamonds traveled to the base of the lithosphere, and were later transported to the surface by a kimberlitic melt. Cooling at the surface led to solidification of the nitrogen that remained under high pressure, the highest pressure ever measured in any mineral inclusion.

References

Kagi H, Zedgenizov DA, Ohfuji H, Ishibashi H (2016) Micro-and nano-inclusions in a superdeep diamond from São Luiz, Brazil. Geochem Internat, 54:834-838.

Kiflawi I, Bruley J, Luyten W, van Tendeloo G (1998) 'Natural' and 'man-made' platelets in type-Ia diamonds. Phil Mag B, 78:299-314.

Luyten W, van Tendeloo GV, Fallon PJ, Woods GS (1994) Electron microscopy and energy-loss spectroscopy of voidites in pure type IaB diamonds. Phil Mag A 69:767-778.

Rudloff-Grund J, Brenker FE, Marquardt K, et al. (2016) Nitrogen nanoinclusions in milky diamonds from Juina area, Mato Grosso State, Brazil. Lithos, 265:57-67.

Schneider H, Häfner W, Wokaun A, Olijnyk H (1992) Room temperature Raman scattering studies of external and internal modes of solid nitrogen at pressures of 8-54 GPa. J Chem Phys 96:8046-8053.

Stixrude L and Lithgow-Bertelloni C (2007) Influence of phase transformations on lateral heterogeneity and dynamics in Earth's mantle. Earth Planet Sci Lett 263:45-55.