

Ringwoodite and zirconia inclusions indicate downward travel of super-deep diamonds

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ABSTRACT

Natural diamonds and their inclusions provide unique glimpses of mantle processes from as deep as ~800 km and dating back to 3.5 G.y. Once formed, diamonds are commonly interpreted to travel upward, either slowly within mantle upwelling or rapidly within explosive, carbonate-rich magmas erupting at the surface. Although global tectonics induce subduction of material from shallow depths into the deep mantle, mineralogical evidence for downward movement of diamonds has never been reported. We report the finding of an unusual composite inclusion consisting of ringwoodite (second finding to date), tetragonal zirconia and coesite within an alluvial super-deep diamond from the Central African Republic. We interpret zirconia + coesite and ringwoodite as prograde transformation products after zircon or reidite, ZrSiO_4 , and olivine or wadsleyite, respectively. This inclusion assemblage can be explained if the diamond travelled downward after entrapping olivine/wadsleyite + zircon/reidite, dragged down by a subducting slab, before being delivered to the surface. This indicates that the commonly assumed view that diamonds form at and capture material from a specific mantle level and then travel upward is probably too simplistic.

INTRODUCTION

Investigating the most inaccessible parts of the Earth's mantle is a challenging task. Most of our knowledge of deep mantle composition and processes is based on indirect evidence from laboratory experiments, numerical models and seismic tomography (Stacey and Davis, 2008). Xenoliths (i.e., mantle rocks transported to the surface by eruptions of, e.g., kimberlitic magmas) provide critical geochemical data from depths down to >300 km (Haggerty, 2017). Diamonds, which are also found in kimberlites, can incorporate material (as mineral and fluid inclusions) from the environment in which they form. Although extremely rare, sub-lithospheric diamonds

from below ~300 km depths, known as super-deep diamonds, offer the unique possibility to directly investigate regions of the mantle down to 800 km depths (Shirey et al., 2013). Mineral inclusions in these diamonds commonly show evidence of retrograde transformations, such as unmixing (Walter et al., 2011) or inversion to lower pressure phases (Stachel et al., 2000). These transformations record the ascent of diamonds through the mantle, consistent with models of diamond transport in mantle upwellings and uprising magmas.

Geochemical data on carbon and nitrogen isotopes suggest that the majority of super-deep diamonds precipitated during reactions of melts released by subducting slabs with the surrounding mantle (e.g., Thomson et al., 2016). Therefore, a scenario wherein super-deep diamonds first travel downwards, following slab-imposed dynamics, before being caught into uprising mantle plumes seems plausible. However, no mineralogical evidence of prograde transformations recording diamond descent within downwelling mantle has been found until now. It remains unknown whether the lack of preservation of prograde reactions is due to complete mineralogical resetting, to sample bias, or to diamonds only moving upward after their formation.

We studied a 1.3-carat (Fig. 1), type IaAB (Fig. S1 in the Supplemental Material¹), colorless alluvial diamond, from the Central African Republic. Micro-Raman spectroscopy enabled identification of a tiny (~10 μm) composite inclusion of ringwoodite ($\gamma\text{-Mg}_2\text{SiO}_4$), tetragonal zirconia (ZrO_2) and coesite (SiO_2), which represents the first mineralogical evidence of the downward movement of diamonds. This finding opens new possibilities for the interpretation of information provided by super-deep diamonds.

METHODS

Carbon isotope ($\delta^{13}\text{C}_{\text{VPDB}}$), N content, and N isotope ($\delta^{15}\text{N}_{\text{Air}}$) spot analysis on the diamond were performed *in-situ*, using a CAMECA 1280 (HR) Large Geometry Secondary Ion Mass Spectrometer (LG-SIMS). Micro-Raman analyses were performed using a Thermo Scientific DXR Micro-Raman spectrometer equipped with 10x and 50x-long working distance (LWD) objectives. A single Fourier Transform Infrared (FTIR) analysis was performed with a Thermo Scientific Nicolet Centaurus FT-IR microscope. See the Supplemental Material for details of the methods.

RESULTS AND DISCUSSION

Geochemistry of investigated diamond

The C isotopic composition of the diamond ($\delta^{13}\text{C}_{\text{VPDB}}$ [VPDB – Vienna Pee Dee belemnite] ranging from -2.8‰ to -1.65‰) is homogeneous (standard deviation = 0.27‰) and shows a ^{13}C enriched signature with respect to average mantle ($\delta^{13}\text{C}_{\text{VPDB}} = -5 \pm 2$ ‰, Javoy et al., 1986). Measurements of N content returned low values (≤ 44 ppm, see Table S1). Because the N concentration is low, *in-situ* determination of the N isotopic composition is associated with large uncertainties (see the Supplemental Material and Fig. S2 therein). However, for N contents greater than the detection limit of our instrument (24 ppm), all $\delta^{15}\text{N}_{\text{Air}}$ values point to ^{15}N -enriched compositions ($\delta^{15}\text{N}_{\text{Air}} = -0.49$ ‰ to +6.2 ‰) and are significantly higher than that of the average mantle ($\delta^{15}\text{N}_{\text{Air}} = -5 \pm 3$ ‰, Javoy et al., 1986, see Fig. S3). These isotopic compositions are consistent with an origin from fluids or melts derived from slab materials rich in carbonates ($\delta^{13}\text{C}_{\text{VPDB}}$ of ~ 0 ‰) and clays ($\delta^{15}\text{N}_{\text{Air}}$ of $\sim +16$ ‰) similar to those observed in sedimentary covers (Palot et al., 2017). The low N content and the C and N isotopes are in agreement with previously reported data for super-deep diamonds worldwide, in particular those formed in the

deeper portions of the upper mantle or the transition zone (Tappert et al., 2009; Palot et al., 2012, 2014, 2017).

Diamond super-deep origin

The diamond encloses numerous inclusions measuring up to a few tens of microns (Fig. 1). Micro-Raman spectroscopy identified most of the dark-colored inclusions with irregular shape as graphite due to the characteristic Raman peak at $\sim 1578\text{-}1593\text{ cm}^{-1}$. Three inclusions of hydrous silicic fluid were also recognized from broad peaks at $616\text{-}674\text{ cm}^{-1}$ and $755\text{-}821\text{ cm}^{-1}$ (Fig. S4), which are interpreted as trapped diamond-parent fluid (cf. Nimis et al., 2016, Supplemental Material). Such fluid inclusions have never been reported in super-deep diamonds. Their occurrence supports a hydrous environment of formation, possibly related to a subduction environment, as also suggested by the isotopic data. Finally, a composite inclusion measuring $\sim 10\text{ }\mu\text{m}$ across is observed, in which ringwoodite ($\gamma\text{-Mg}_2\text{SiO}_4$), tetragonal zirconia (ZrO_2), and coesite (SiO_2) are all in contact with one other (Fig. 1). Two Raman peaks at ~ 797 and 832 cm^{-1} corresponding to the asymmetric (T_{2g}) and symmetric (A_{1g}) stretching vibrations of SiO_4 tetrahedra in ringwoodite (Kleppe et al., 2002), respectively, were clearly observed (Fig. 2). Vibrational modes of zirconia are measured at $\sim 170, 258, 330$ and 648 cm^{-1} (Ghosh et al., 2006), while the peak at 537 cm^{-1} is attributed to coesite (Smith et al., 2018). The higher wavenumber of the coesite peak measured inside the diamond with respect to the reference vibrational mode position at ambient conditions ($\sim 521\text{ cm}^{-1}$) is indicative of a high residual pressure.

The occurrence of ringwoodite, the high-pressure polymorph of olivine that is stable at depths between 525 and 660 km, represents only the second terrestrial finding of ringwoodite after that of Pearson et al. (2014) and the first in an African diamond. The presence of ringwoodite unequivocally confirms the sub-lithospheric nature of the specimen and indicates

that, at some point, the diamond resided in the lower part of the transition zone. The presence of tetragonal ZrO₂, a high-temperature, high-pressure polymorph of zirconia that is stable between ~1170-2370 °C (Yoshimura, 1988) and up to 20 GPa (Haines et al., 1997), is also remarkable, as a ZrO₂ phase has been previously detected only by electron microprobe analysis on two polished super-deep diamonds from Juina (Thomson et al., 2014). However, the mineral structure of these zirconia inclusions (monoclinic vs tetragonal) has never been documented. Finally, whereas coesite has been previously recognized in several super-deep diamonds (Smith et al., 2018; Zedgenizov et al. 2019), it has never been reported in contact with zirconia or high-pressure olivine polymorphs within the same diamond.

Evidence of diamond's downward movement

Although zircon is a common accessory mineral in crustal rocks (Hoskin and Schaltegger, 2003), its occurrence in diamonds is extremely rare and limited to few lithospheric samples (Kinny and Meyer, 1994). This is probably because zircon does not normally crystallize in the mantle as its lithologies are undersaturated in Zr and Si. However, zircons are found in orogenic peridotites (Zhao et al., 2019), altered mantle xenoliths (Konzett et al., 1998; Liu et al., 2010) and ophiolites (Robinson et al., 2015), suggesting that local Zr enrichment, e.g., related to metasomatic events, can stabilize this mineral in mantle rocks.

The composite inclusion of ringwoodite, tetragonal zirconia and coesite indicates that the investigated diamond sampled one of these enriched mantle lithologies. Zircon (or reidite, the high-pressure polymorph of zircon that is stable at depths >270-330 km, Tange and Takahashi, 2004) was possibly a product of the same metasomatic event that precipitated the diamond, involving a slab-derived fluid/melt interacting with peridotites in the supra-subduction mantle (Zhao et al., 2019). Alternatively, stable and resistant zircon may have originated in a shallow

environment and survived a long downward movement within the subducting slab or the immediately overlying dragged mantle before being enclosed by the diamond.

Considering the association with ringwoodite, the coexistence of high-temperature, high-pressure ZrO_2 and SiO_2 can be interpreted as the result of the breakdown of zircon (ZrSiO_4) or reidite. Within the Earth's mantle, reidite transforms into orthorhombic zirconia (cotunnite structure) + stishovite (SiO_2) at conditions corresponding to a depth of ~ 550 km along a subduction geotherm or 610 km along a normal mantle geotherm (Tange and Takahashi, 2004; Van Westrenen et al., 2004). These conditions also correspond to depths where ringwoodite is stable. However, in our composite inclusion, we did not directly observe stishovite and orthorhombic zirconia, but we did observe coesite and tetragonal zirconia. These polymorphs likely represent the products of stishovite and orthorhombic zirconia back-transformation during the ascent of the diamond toward the surface.

Experiments have demonstrated that ringwoodite and stishovite can form together in suitable chemical systems (Bolfan-Casanova et al., 2000). However, the bulk compositions of these systems are either very simplified ($\text{MgO-SiO}_2\text{-H}_2\text{O}$) or significantly SiO_2 -enriched with respect to mantle peridotites, in particular when they interact with slab-derived carbonatite melts (Thomson et al., 2016), i.e., the typical systems in which super-deep diamonds are formed. Therefore, ringwoodite and stishovite are not expected to form stable mineral associations in mantle rocks. In particular, experiments that reproduced deep diamond-forming conditions (Thomson et al., 2016) never produced diamond-ringwoodite-stishovite mineral assemblages. This excludes entrapment of ringwoodite and stishovite as inclusions during precipitation of the diamond in the lower part of the transition zone. Instead, the observed inclusion assemblage is consistent with the entrapment of olivine (or wadsleyite) and zircon (or reidite) by their host at

shallower depths, followed by phase transformation of olivine/wadsleyite to ringwoodite and breakdown of zircon/reidite to $\text{ZrO}_2 + \text{SiO}_2$ in response to an increase in pressure. The breakdown products could thus coexist with ringwoodite and be protected from subsequent reactions. Ringwoodite and stishovite would be stable at $T < 1375^\circ\text{C}$, while at higher temperatures they would transform to akimotoite or majorite (see Fig. 3). In our case, this transformation did not occur, which suggests that this diamond was carried to the surface by rapidly ascending kimberlite magmas, as was suggested for the previously reported ringwoodite occurrence in diamond (Pearson et al., 2014).

Combining the petrological considerations with the low N content of the diamond, which is typical of subduction-related, super-deep diamonds that formed at ≥ 300 km, a minimum depth of formation of ~ 300 km also can be envisaged also for the investigated diamond. For a first approximation, the maximum possible depth is constrained by the stability of reidite, i.e., ~ 550 or 610 km for a subduction or mantle geotherm, respectively (Tange and Takahashi, 2004, Fig. 4). However, unless the diamond behaved plastically, the true reidite breakdown depth could have been even greater. In fact, the inclusion volume reduction, due to the reidite transformation, could have acted as a pressure buffer, considering the high incompressibility of diamond.

Because the exact depth at which the diamond was formed is unknown, it is not possible to determine the original mineral assemblage entrapped by the diamond (i.e. olivine vs. wadsleyite vs. ringwoodite + zircon vs. reidite). Regardless, the occurrence of dissociated SiO_2 and ZrO_2 suggests that the diamond traveled toward greater depths after formation, allowing its inclusion assemblage to cross the ~ 550 or 610 km (or slightly greater) depth at which reidite decomposes (Fig. 4). In principle, isobaric cooling of an inclusion starting from conditions close to the reidite breakdown curve, e.g., due to intrusion of ‘cold’ slab-derived melts, could also lead

to reidite decomposition (Tange and Takahashi, 2004). Nonetheless, a purely isobaric scenario seems unrealistic, as coupling of the mantle with the subducting slab would most likely drag the diamond downward in any case.

The unique phase assemblage observed in this diamond indicates the downward movement of a super-deep diamond in the mantle, possibly following subducting slab dynamics, to depths reaching the lower part of the transition zone. Even though the extent of this downward movement cannot be constrained, it may have occurred over hundreds of kilometers. Considering the possibility that the original entrapped zircon had a shallower origin, our finding suggests that diamond may act as a long-route vessel for the recycling of crustal material to extreme depths within the Earth. We suggest that a comprehensive understanding of super-deep diamonds and the information contained in their inclusions may include the possibility of prograde downward movement before upwelling and final eruption.

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FIGURE CAPTIONS

Figure 1. The investigated diamond (from the Central African Republic) under incident light showing polished faces. Inset shows the composite mineral inclusion containing ringwoodite, tetragonal zirconia and coesite.



Figure 2. Raman spectrum of ringwoodite, tetragonal zirconia and coesite composite inclusion within the diamond from the Central African Republic (top). Spectra of synthetic tetragonal zirconia reported in Ghosh et al., 2006 and those of ringwoodite and coesite from the RRUFF database (<https://rruff.info/>; ID: R090003 and ID: R070565, respectively) are also shown. The shift of the Raman peak of coesite (arrow) is consistent with a high remnant pressure (Zedgenizov et al., 2019).

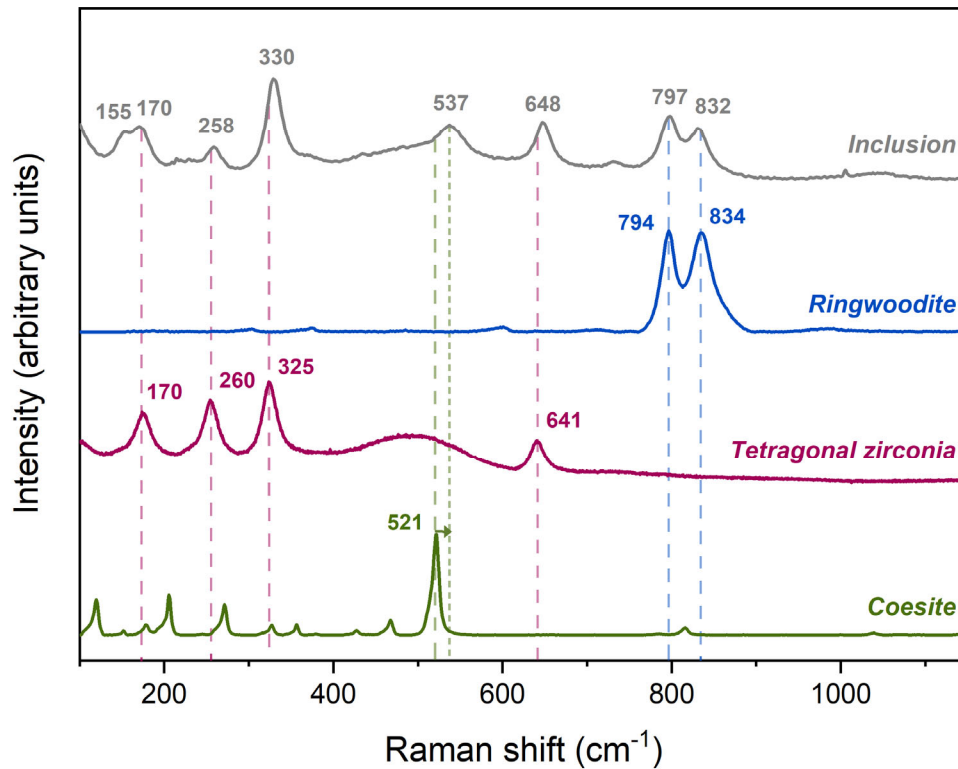


Figure 3. Pressure-temperature (P - T) stability diagram of the MgSiO_3 system (modified after Gasparik, 2003). Reaction boundaries between wadsleyite + stishovite (St) and ringwoodite + stishovite, ringwoodite + stishovite and akimotoite, wadsleyite + stishovite and akimotoite reported in black are from Ono et al., (2017) and references therein. Reaction curves for the transformations of zircon in reidite and reidite in $\text{ZrO}_2 + \text{SiO}_2$ (Tange and Takahashi, 2004) are also reported (dashed lines) along with the P - T path of the typical mantle (Katsura et al., 2010) and subduction geotherms (Syracuse et al., 2010). Note that ringwoodite and stishovite can coexist at high pressures of up to 1150 °C and 1375 °C, according to Gasparik (2003) and Ono et al. (2017), respectively.

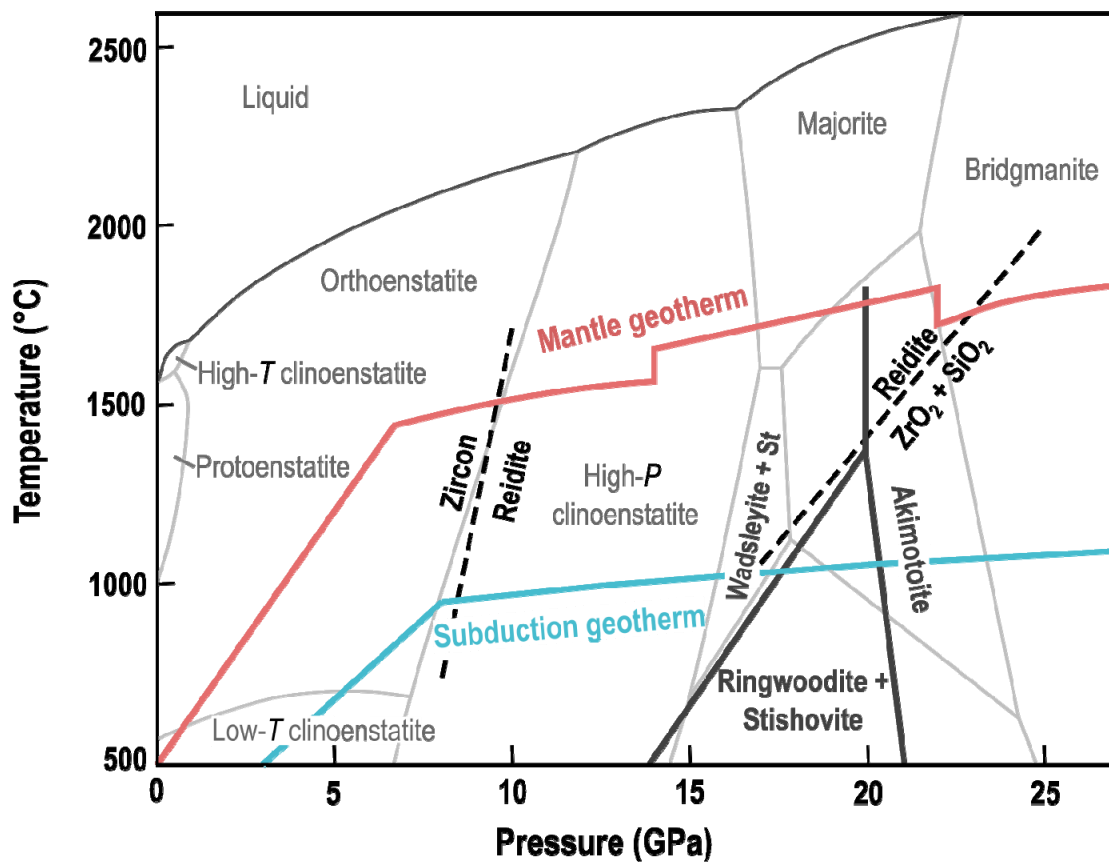


Figure 4. Cartoon showing the possible, simplified path of the investigated diamond (from Central African Republic), containing a composite inclusion of ringwoodite, tetragonal zirconia and coesite within the Earth's mantle. Graphite (G) and diamond (D) reaction curve (black dashed line) is from Day (2012). Zircon $\rightarrow$ reidite and reidite $\rightarrow$ $\text{ZrO}_2 + \text{SiO}_2$ reaction boundaries following subduction (blue dashed lines) and mantle (light blue dashed lines) geotherms are from Tange and Takahashi (2004). Black and grey straight lines indicate olivine $\rightarrow$ wadsleyite (410 km), wadsleyite $\rightarrow$ ringwoodite (525 km) and ringwoodite $\rightarrow$ ferropericlase + bridgmanite (660 km) transformations (Frost, 2008). Red and grey polygons represent zircons and diamonds, respectively. 1) Given the C- and N- isotopic compositions, the super-deep diamond precipitated from slab-derived fluid/melt, sampling an enriched peridotite containing zircons. This can occur at any depth from $\sim$ 300 km (the minimum depth at which super-deep diamonds presumably crystallize) to 550-610 km (where reidite dissociates into $\text{ZrO}_2 + \text{SiO}_2$), and an arbitrary depth was chosen here. 2) The diamond traveled downward within a subducting slab, and resided for a certain time in the lower part of the transition zone, where the composite inclusion equilibrated ringwoodite + tetragonal zirconia (former orthorhombic zirconia) + coesite (former stishovite). 3) The diamond was delivered to the surface by a mantle plume or the kimberlitic magma.

