GEOLOGY | THE GEOLOGICAL SOCIETY OF AMERICA®

https://doi.org/10.1130/G45235.1

Manuscript received 5 June 2018
Revised manuscript received 11 October 2018
Manuscript accepted 6 November 2018

Published online 30 November 2018

Fe-rich ferropericlase and magnesiowüstite inclusions reflecting diamond formation rather than ambient mantle

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ABSTRACT

At the core of many Earth-scale processes is the question of what the deep mantle is made of. The only direct samples from such extreme depths are diamonds and their inclusions. It is commonly assumed that these inclusions reflect ambient mantle or are syngenetic with diamond, but these assumptions are rarely tested. We have studied inclusion–host growth relationships in two potentially superdeep diamonds from Juina (Brazil) containing nine inclusions of Fe-rich (X_{Fe} ≈0.33 to ≥0.64) ferropericlase-magnesiowüstite (FM) by X-ray diffractometry, X-ray tomography, cathodoluminescence, electron backscatter diffraction, and electron microprobe analysis. The inclusions share a common [112] zone axis with their diamonds and have their major crystallographic axes within 3°–8° of those of their hosts. This suggests a specific crystallographic orientation relationship (COR) resulting from interfacial energy minimization, disturbed by minor post-entrapment rotation around [112] due to plastic deformation. The observed COR and the relationships between inclusions and diamond growth zones imply that FM nucleated during the growth history of the diamond. Therefore, these inclusions may not provide direct information on the ambient mantle prior to diamond formation. Consequently, a "non-pyrolitic" composition of the lower mantle is not required to explain the occurrence of Fe-rich FM inclusions in diamonds. By identifying examples of mineral inclusions that reflect the local environment of diamond formation and not ambient mantle, we provide both a cautionary tale and a means to test diamond-inclusion time relationships for proper application of inclusion studies to whole-mantle questions.

INTRODUCTION

Diamonds found in kimberlites and lamproites are our deepest samples of Earth's interior. Most diamonds come from deep lithospheric roots beneath cratons, but some rare diamonds are believed to have formed at sublithospheric levels, possibly as deep as the core-mantle boundary (see reviews in Stachel et al., 2005; Harte, 2010; Kaminsky, 2012). Ferropericlase-magnesiowüstite [(Mg,Fe)O] (hereafter FM) is the most common mineral contained as inclusions in diamonds of interpreted lower-mantle origin, and its composition has been recently used to estimate oxygen fugacity in the lower mantle (Otsuka et al., 2013; Kaminsky et al., 2015). This is notwithstanding the facts that FM also participates in mineral parageneses straddling the upper mantle–lower mantle boundary (Hutchison et al., 2001), the relative abundance of FM inclusions is higher than predicted by experiments on "pyrolite" at lower-mantle conditions (48%–63% versus 16%–20%; e.g., Irifune, 1994; Fei and Bertka, 1999; Wood, 2000; Kaminsky, 2012), and their composition is more variable and commonly more Fe-rich than expected for FM in the lower mantle [$Fe/(Mg + Fe)_{mol} = X_{Fe}$ = 0.10–0.64 versus 0.10–0.27; e.g., Kesson and Fitz Gerald, 1992; Wood, 2000; Lee et al., 2004]. Fe-rich compositions characterize a significant proportion (~46.5%) of FM inclusions in Brazilian stones (Kaminsky, 2012).

Several hypotheses have been put forward to explain the existence of Fe-rich FM. These hypotheses can be grouped into two categories: (1) the Fe-rich composition is considered to reflect a "non-pyrolitic" composition of the ambient lower mantle, samples of which were captured by the growing diamonds (Harte et al., 1999; Kaminsky, 2012; Ryabchikov and Kaminsky, 2013; Kaminsky and Lin, 2017); or (2) formation of Fe-rich FM *and* diamond is ascribed to reactions involving carbonate melts or minerals in the lower mantle (Liu, 2002; Litvin, 2014) or in the deep upper mantle and transition zone (Thomson et al., 2016). This contrast of views is partly justified by the fact that the traditional criterion used to identify syngenetic inclusions (i.e., a diamond-imposed shape) has proven unreliable (Nestola et al., 2014). Therefore, there is still uncertainty as to whether Fe-rich FM inclusions represent accidentally encapsulated portions of an anomalous ambient mantle or a product of reactions occurring during the growth history of diamond. As diamonds and their mineral inclusions are such important windows on mantle composition and processes, it is critical to test these conflicting hypotheses. This may have profound implications on our interpretation of the mechanisms of formation of sublithospheric diamonds and on the significance of petrological and geochemical data extracted from their inclusions (e.g., Shirey et al., 2013; Thomson et al., 2014, 2016).

Here we investigate the growth relationships of nine Fe-rich (X_{Fe} = 0.33 to ≥0.64) FM inclusions in two diamonds from the notable alluvial deposits of tributaries of the Rio Aripuanã, Juina district, Brazil (e.g., Hutchison et al., 2004; see detailed provenance data in the GSA Data Repository[1]).

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[1]GSA Data Repository item 2019006, sample location and analytical methods, and microcomputed X-ray tomography of diamond BZ270 (Video DR1), is available online at http://www.geosociety.org/datarepository/2019/ or on request from editing@geosociety.org.

CITATION: Nimis, P., et al., 2018, Fe-rich ferropericlase and magnesiowüstite inclusions reflecting diamond formation rather than ambient mantle: Geology, v. 47, p. 27–30, https://doi.org/10.1130/G45235.1

We will show that our Fe-rich FM formed by direct segregation from a fluid or melt or from fluid- or melt-assisted dissolution-precipitation during the growth history of their diamond hosts. Hence, the entrapped FM inclusions should not be considered as representative samples of the ambient mantle in which the diamond-forming processes took place.

SAMPLE MATERIAL AND ANALYTICAL METHODS

The diamonds studied in the present work (BZ270 and JUc4) appeared as irregular, brown-colored stones with maximum dimensions of 7 and 3 mm, respectively. Sample preparation and analyses were conducted in such a way as to preserve as much of the samples as possible for future investigations. The stones were polished on two opposite sides to obtain small windows that allowed visual recognition of most of their inclusions. The FM inclusions showed a faceted to subround shape, in some cases with concave angles, and maximum dimensions of a few tens of microns to 500 µm (Figs. 1A and 1B). The largest inclusions in diamond BZ270 exhibited stepped surfaces on some of the faces (Fig. 1B). Decompression cracks were observed around most of the inclusions. Microcomputed X-ray tomography (µ-CT) of diamond BZ270 showed the presence of numerous additional inclusions, which have a size up to a few microns and are distributed along a set of interconnected {111} diamond planes (Fig. 1C; Video DR1 in the Data Repository).

Previous investigation by X-ray diffraction topography showed that both samples are affected by plastic deformation (Agrosì et al., 2017). BZ270 is more strongly deformed and consists of an aggregate of different "grains", which are misoriented by at least a few seconds of arc, whereas JUc4 appears to be a single grain. Micro–Fourier-transform infrared spectroscopy (µFTIR) (Agrosì et al., 2017) showed that BZ270 was predominantly type IIa diamond (i.e., nitrogen below detection of ~10 ppm; Fig. 1D). The µFTIR of a portion of JUc4 suggested the presence of a more N-rich core (270 ppm N, 100% IaB, no platelets) and decreasing N content toward the rim (~40 ppm, 100% IaB, no platelets) (Fig. 1E).

Both samples were studied by single-crystal X-ray diffraction (XRD) to determine the approximate chemical compositions of the FM inclusions and their crystallographic orientation relationships (CORs) with the diamonds. Diamond BZ270 was then further polished to expose some of the large and small inclusions and investigated by cathodoluminescence (CL) and electron backscatter diffraction (EBSD). Electron microprobe analysis (EMPA) was performed on the exposed inclusions (Table DR1 in the Data Repository). Additional details on analytical methods are given in the Data Repository.

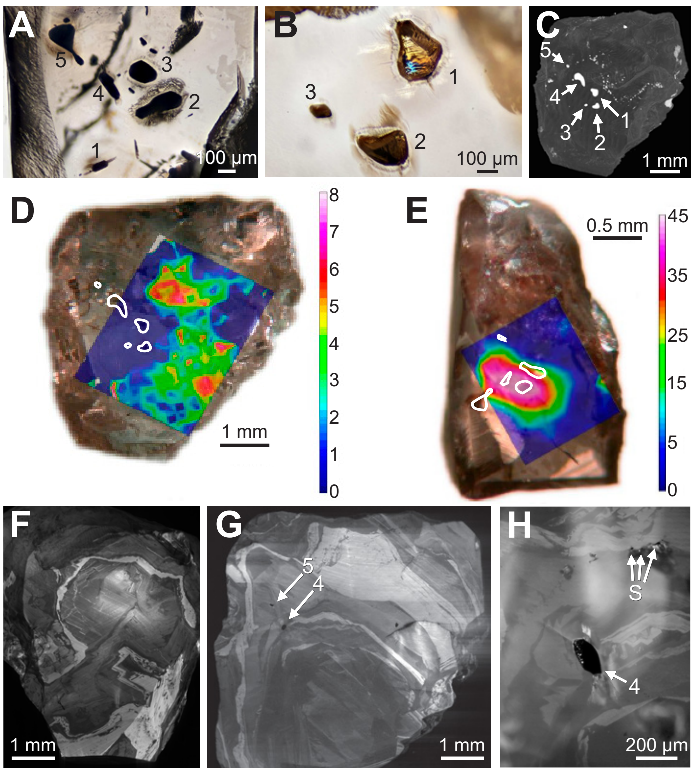

Figure 1. A,B: Microphotographs of ferropericlase-magnesiowüstite (FM) inclusions in polished diamonds JUc4 (A; transmitted light) and BZ270 (B; transmitted plus incident light) from alluvial deposits of tributaries of Rio Aripuanã, Juina district, Brazil. C: Microcomputed X-ray tomography (µ-CT) image of diamond BZ270, showing cluster of FM inclusions (numbered) and trail of tiny inclusions. D: Fourier-transform infrared spectroscopy (FTIR) map of diamond BZ270; color scale, from blue (zero intensity) to red to whitish (max intensity), is qualitative, and given the low values, is not necessarily related to nitrogen concentration; white outlines indicate projection of FM inclusions (modified after Agrosì et al., 2017). E: Same as in D for diamond JUc4, but here the color scale has been confirmed to correlate to nitrogen concentration (modified after Agrosì et al., 2017). F: Cathodoluminescence (CL) image of diamond BZ270 after limited polishing. G,H: CL images of reverse side of diamond BZ270 after different degrees of polishing, with exposed FM and sulfide (S) inclusions. Numbers in A–C, G, and H are as in Table 1.

RESULTS

The analyzed FM inclusions have their major crystallographic axes within 3°–8° of those of the host diamonds (Fig. 2; Table DR2). Despite this minor misorientation, the angular mismatch between the [112] axes of the inclusions and those of the diamonds is remarkably small (<2°), i.e., within the uncertainty of the measurements (cf. Nestola et al., 2014), and the inclusions appear to be mutually rotated around the [112] axis of their host (Fig. 2).

The CL images of sample BZ270 show a complex growth-resorption pattern, disturbed by plastic deformation (Figs. 1F–1H), as commonly observed in sublithospheric diamonds (Shirey et al., 2013). EBSD data are consistent with the activation of {111}<011> slip systems (Fig. DR3), a mechanism observed in several natural and experimentally deformed

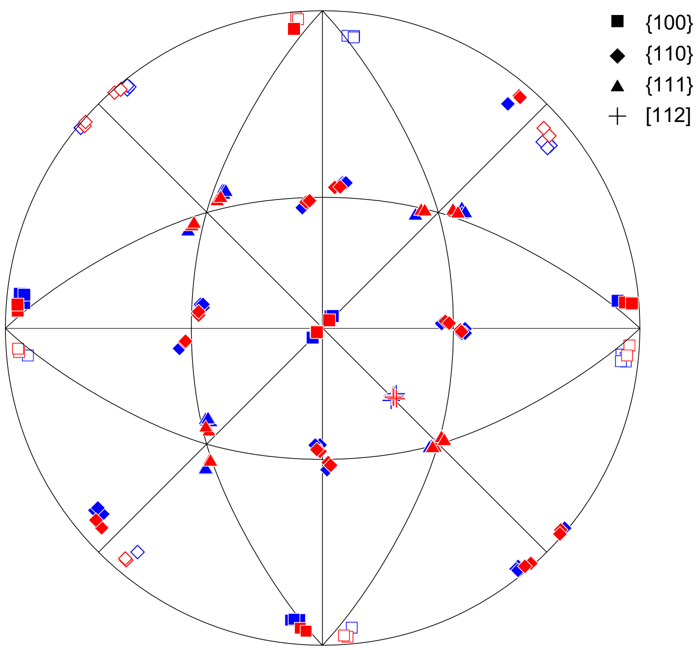

Figure 2. Crystallographic orientations of ferropericlase-magnesiowüstite inclusions relative to their diamond hosts, plotted using OrientXplot software (Angel et al., 2015). Open symbols plot in lower hemisphere. Blue symbols are diamond BZ270; red symbols are diamond JUc4.

diamonds (Howell et al., 2012). Domains characterized by slightly different lattice orientations (difference of up to 3.5°) are observed, which show no special relationship with the distribution of the inclusions (Fig. DR3). Polishing of diamond BZ270 allowed us to uncover two of the FM inclusions and three of the aligned, micron-sized inclusions. The FM inclusions sit on distinct diamond growth zones (Fig. 1G). The analyzed micron-sized inclusions have a composition corresponding to Ni-poor pyrrhotite (Table DR1), within the compositional range reported for other Juina diamonds (Hutchison, 1997), and are located at the boundary between two more external CL growth bands (Fig. 1H).

The compositions of the FM inclusions indicate an X_{Fe} range of ~0.33 to ≥0.64 (Table 1). Because high-quality XRD and EMPA data could be obtained only on some of the inclusions, some X_{Fe} data have large uncertainties, but are sufficient to establish a relatively Fe-rich composition for all studied inclusions. Data for sample JUc4 suggest a progressive X_{Fe} increase in inclusions sitting outside the N-rich diamond core. The moderate NiO (0.4 wt%) and very low Na_2O (<0.06 wt%) contents measured on exposed inclusions 4 and 5 in diamond BZ270 (Table DR1) are in line with those reported for FM inclusions of similar X_{Fe} in diamonds worldwide (Thomson et al., 2016).

TABLE 1. COMPOSITIONAL DATA FOR FERROPERICLASE-MAGNESIOWÜSTITE INCLUSIONS

Diamond	Inclusion	X_{Fe} (site occ.)*	X_{Fe} (*a* edge)†	X_{Fe} (EMPA)§
BZ270	1	0.31 (2)	≥0.34 (2)	–
	2	0.31 (2)	≥0.35 (2)	–
	3	–	≥0.35 (5)	–
	4	–	0.34 (2)	0.346 (3)
	5	0.36 (2)	0.35 (2)	0.338 (0)
JUc4	2	–	≥0.57 (5)	–
	3	–	≥0.44 (5)	–
	4	–	≥0.43 (6)	–
	5	–	≥0.64 (3)	–

Note: Numbers in parentheses are 1σ uncertainties on the last digit. Dashes indicate no data. See the Data Repository (see text footnote 1) for details on evaluation of chemical compositions. Inclusion 1 in diamond JUc4 was not analyzed.

*Based on site occupancies (occ.) after crystal structure refinement.

†Based on equation $X_{Fe} = 8.441 \cdot a$ (Å) – 35.553, valid for stoichiometric ferropericlase-magnesiowüstite at room pressure; minimum values for unexposed inclusions analyzed in situ, which may be under residual pressure.

§Based on electron microprobe analysis (EMPA) of exposed inclusions (Table DR1 in the Data Repository).

DISCUSSION AND CONCLUSIONS

Data for multiple inclusions in two stones indicate a non-random COR between FM and diamond (Fig. 2; Table DR2). The nearly parallel orientation of the FM's and diamond's crystal lattices suggests an original specific COR (cf. Griffiths et al., 2016). Post-entrapment plastic deformation in the diamond along {111}<011> slip systems (Fig. DR3), with consequent slight rotation of the inclusions around the normal [112] axis (Fig. 2), may well account for the small observed angular mismatch. Consistently, this particular type of rotational COR was not observed in inclusions from less-deformed lithospheric diamonds (Nestola et al., 2014; Milani et al., 2016).

A specific COR may result from interface energy minimization (1) on precipitation from a fluid or melt, during mutual growth or when one of the two minerals provides a substrate for nucleation of the other (e.g., Mutaftschiev, 2001), (2) on static recrystallization, when the small effect of interface energies is not swamped in magnitude by that of imposed stress (Wheeler et al., 2001), or (3) on fluid- or melt-assisted recrystallization, when dissolution-precipitation and epitaxial nucleation of new grains occur (Putnis and Austrheim, 2010). Scenario 2 is highly unlikely in our case, given the high-stress environment in which our diamonds have formed. Scenario 3 is most likely accompanied by chemical resetting and in fact, with increasing solid-fluid disequilibrium, may grade into scenario 1. Note that the distinction between "fluid" and "melt" tends to vanish with increasing pressure and may not exist under sublithospheric conditions (Luth, 2014). Mechanical interactions between euhedral crystals can also potentially lead to non-random COR (Wheeler et al., 2001). However, in this case only one inclusion crystallographic direction, normal to the contact face, is fixed to the host. Therefore, a statistical rotational relationship (cf. Griffiths et al., 2016) rather than a strongly clustered orientation would be expected. Note that {112} faces are not found in periclase-group minerals and are uncommon in diamond (Goldschmidt, 1916; Gaines et al., 1997); therefore, they are unlikely to have played any role in determining the minor rotational component in the observed COR (Fig. 2).

The distribution of the FM inclusions relative to diamond growth zones (Figs. 1G and 1H) and N zoning (Figs. 1D and 1E) indicates that at least some of them are sitting well away from the diamond growth centers and, thus, cannot have acted as seeds for diamond nucleation (cf. the "central inclusions" of Bulanova [1995] and Bulanova et al. [1998]). Moreover, none of the FM inclusions are located on healed cracks or subgrain boundaries (Figs. 1G and 1H; Fig. DR3), which excludes that the inclusions were formed or modified after diamond formation. Therefore, either diamond and FM precipitated from the same parent medium, i.e., they are syngenetic, or FM nucleated epitaxially on diamond and was later incorporated during a further episode of diamond growth. Whatever the nucleation mechanism (dissolution-precipitation or precipitation as a new mineral), our Fe-rich FM inclusions may not represent accidentally encapsulated portions of the ambient mantle, but rather the product of reactions occurring during the growth history of diamond. A similar conclusion can be drawn for the tiny pyrrhotite inclusions in diamond BZ270, sitting at the boundary between two diamond growth zones (Figs. 1C and 1H). Their low-Cr, low-Ni composition (Table DR1) suggests an "eclogitic" or melt-rich environment.

FM compositions in diamond JUc4 (X_{Fe} = 0.43 to ≥0.64) show no overlap with the range for FM in association with former bridgmanite (X_{Fe} = 0.10–0.36, median = 0.17, n = 19; Hutchison, 1997; Stachel et al., 2000; Davies et al., 2004; Hayman et al., 2005; Tappert et al., 2009; Zedgenizov et al., 2014), and FM compositions in diamond BZ270 are tightly clustered at its Fe-rich end. This suggests that the processes recorded in our diamonds may not be typical of the lower mantle. Indeed, experiments by Thomson et al. (2016) suggest that precipitation of variously Fe-enriched FM and diamond may occur by reaction of slab-derived carbonatite melt with mantle rocks, at varying melt/rock ratios, in the deep upper mantle and transition zone. This scenario is fully compatible with our observations and provides a plausible mechanism for formation of our FM-bearing diamonds at depths shallower than the lower mantle under increasing melt/rock ratio.

Our interpretation of Fe-rich FM inclusions as a product of reactions occurring during the growth history of diamond may potentially apply to other FM inclusions for which evidence of pre-diamond formation is lacking. Therefore, using FM inclusions to provide direct information on the composition of the ambient mantle and, particularly, of the lower mantle is unwarranted. Specifically, a "non-pyrolitic" composition of the lower mantle is not required to explain the occurrence of Fe-rich FM inclusions in diamonds. By identifying examples of mineral inclusions that reflect local growth conditions rather than ambient mantle, we emphasize the importance of, and provide a means for testing, host-inclusion time relationships in strongly deformed diamonds.

ACKNOWLEDGMENTS

Material for the present study was supplied by Hutchison. This research was supported by the Alfred P. Sloan Foundation's Deep Carbon Observatory (DMGC-project), European Research Council Starting Grant INDIMEDEA to Nestola (agreement 307322), grants CPDA 122324/12 and FACCPRAT12 (University of Padua), and National Project PONa3_00369 "SISTEMA" (University of Bari).

Constructive reviews by F. Kaminsky and two anonymous reviewers helped us improve the manuscript.

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