Diamonds from the lower mantle?

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Natural diamonds, because of their great physical resiliency, can preserve information about their formation, storage and transport conditions for billions of years. Diamond samples therefore provide a unique opportunity to directly study ancient samples of the Earth's deep interior. In order to correctly interpret the information diamonds provide, it is essential to accurately constrain the depth of their origin. This depth provenance is usually identified using coexisting minerals, which are occasionally trapped as inclusions within diamonds during their growth. Comparison of an inclusion's composition and mineralogy with experimental phase equilibria allows the diamond's growth conditions to be estimated. While the majority of diamonds likely originate from depths of 140-220 km in cratonic mantle, a small subset appears to have been exhumed from depths extending to > 800 km, called "superdeep" or "ultradeep" diamonds (Walter et al. 2011; Pearson et al. 2014). Inclusions of magnesiowüstite are among the most commonly described in sub-lithospheric diamonds, and have often been assumed to indicate diamond provenance in the lower mantle because [Mg,Fe]O is not stable at upper mantle conditions in a subsolidus mantle compositions (Trønnes 2009). This is despite the stability field of [Mg,Fe]O extending to ambient pressure conditions and experimental evidence of magnesiowüstite stability in equilibrium with diamond throughout the upper mantle (Brey et al. 2004; Thomson et al. 2016). A new study by Uenver-Thiele et al. (2017) in *American Mineralogist* places important new constraints on the formation and uplift history of inclusions containing magnesioferrite.

Studies of magnesiowüstite inclusions in diamonds from the Juina region of Brazil often report observation of nanometre-sized crystals of magnesioferrite ($[Mg,Fe^{2+}]Fe^{3+}_2O_4$), which supposedly "confirm" the lower mantle origin of these samples. The magnesioferrite precipitates can occur at the interface between the diamond and [Mg,Fe]O inclusion, or as evenly distributed dislocation "necklaces" within the inclusion interior (Harte et al. 1999; Wirth et al. 2014; Palot et al. 2016). Wirth et al. (2014) describe chains of globular $[Mg_{0.5}Fe_{0.5}]Fe_2O_4$ crystals, ~ 75 nm in size, making up 6-11 vol.% of the entire $[Mg_{27}Fe_{71}]O$ inclusion. This suggests the original inclusion had an $Fe^{3+}/\sum Fe$ of 11-14 %, compared with 7 ± 2 % in the recovered magnesiowüstite (McCammon 1997). Wirth et al. (2014) also identified the magnesioferrite is accompanied by small, ~ 10-30 nm, cubic voids, Al-bearing spinel and Ni-Fe metal blebs. Palot et al. (2016) describe isolated 10-20 nm octahedra of $Mg[Fe_{0.75}Cr_{0.17}Al_{0.08}]_2O_4$ throughout a $[Mg_{84}Fe_{16}]O$ host with a recovered $Fe^{3+}/\sum Fe$ content of 1-2 % that also contains ~ 30 ppm H_2O in brucite precipitates. The bulk inclusion composition reported by Palot et al. (~ $[Mg_{72}Fe_{28}]O$ ignoring minor elements) implies the original magnesiowüstite must have had an $Fe^{3+}/\sum Fe$ of approximately 10-12 %. Wirth et al. (2014) and Palot et al. (2016) both observe a topotaxial relationship between magnesioferrite lamellae and the [Mg,Fe]O host, confirming the magnesioferrite must have formed during exsolution from a homogenous magnesiowüstite grain. Using different arguments both studies concluded that the magnesioferrite lamellae are indicative of the lower mantle provenance of these diamonds. Wirth et al. (2014) suggested the highly non-stoichiometric magnesiowüstite inclusion sampled the high-spin-low-spin transition in the in ε-iron stability field, promoting high Fe^{3+} contents. This would place inclusion, and diamond, formation near the very base of the mantle. Alternatively Palot et al. (2016) interpretted the conditions of magnesioferrite exsolution using a phase diagram constructed from atmospheric-pressure experimental data in the MgO-Fe_2O_3, MgO-Al_2O_3 and MgO-Cr_2O_3 systems. This approach suggested that the onset of exsolution occurred at a temperature of ~ 1700 °C, which corresponds to ~ 25 GPa on the mantle adiabat (Palot et al. 2016). Both approaches makes many assumptions and lack experimental verification that magnesioferrite exsolution unambiguously indicates a diamond exhumation from the lower mantle. Indeed, as outlined below, the high ferric iron contents of the inclusions and new phase relations of magnesioferrite (Uenver-Thiele et al. 2017) instead point to a much shallower origin.

At low pressures (< 5 GPa) it is well understood that magnesiowüstite can incorporate significant ferric iron, up to $Fe^{3+}/\sum Fe$ of 70 %, mainly charge balanced by negative cation vacancies (e.g. Hazen and Jeanloz 1984; Dobson et al. 1998). With increasing pressure and decreasing oxygen fugacity the ferric iron capacity of magnesiowüstite decreases, due to a high-pressure phase transition of Fe_3O_4 (Huang and Bassett 1986; McCammon et al. 1998). Since the mantle becomes more reduced with depth, from ~ 1 log unit above the nickel-nickel oxide buffer (NNO+1) at 200 km to 1.5 log units below the iron-wüstite buffer (IW-1.5) at 660 km (Rohrbach and Schmidt 2011), it is expected that ferric iron concentration of [Mg,Fe]O will fall rapidly with increasing formation pressure. Indeed experiments confirm at conditions just within the lower mantle the maximum $Fe^{3+}/\sum Fe$ in $[Mg_{70}Fe_{30}]O$, similar in composition to the inclusion observed by Palot et al. (2016), is < 2% at NNO and < 0.5 % at IW (Otsuka et al. 2013). Similarly $[Mg_{20}Fe_{80}]O$, similar to that observed by Wirth et al. (2014), would have a $Fe^{3+}/\sum Fe$ capacity of ~ 7 - 14 % at IW and NNO respectively. These ferric iron capacities provide an upper bound, because "normal" lower mantle conditions are more reduced and extend to higher pressure than the experimental conditions. Thus, the bulk composition of diamond-hosted inclusions displaying magnesioferrite exsolution appears inconsistent with formation under lower mantle conditions, unless exceptionally oxidsed conditions are present.

In this issue, Uenver-Thiele et al. (2017) experimentally determined the high-pressure phase relations of magnesioferrite ($MgFe_2O_4$) using the multi anvil apparatus. Prior to this study it was believed that $MgFe_2O_4$ had a relatively simple phase diagram, with the ambient cubic spinel structure (*Fd-3m*) stable until an isochemical phase transition to orthorhombic $CaMn_2O_4$ structure (*Pbcm*), HP- $MgFe_2O_4$, at ~ 17 GPa and temperatures above 1700 °C, or breakdown to MgO + Fe_2O_3 at lower temperatures (Levy et al. 2004). This chemography makes the interpretations of Wirth et al. (2014) and Palot et al. (2016) feasible. However, the experiments of Uenver-Thiele et al. (2017) have revealed a very different phase diagram, where the spinel-structured $MgFe_2O_4$ decomposes at ~ 10 GPa. It forms a phase assemblage of MgO + Fe_2O_3 at temperatures below 1200 °C or Fe_2O_3 + an unrecoverable phase of $Mg_5Fe_2O_8$-$Mg_4Fe_2O_7$ stoichiometry at higher temperatures. At pressures beyond ~ 13 GPa the unrecoverable phase(s) are replaced by orthorhombic, $CaFe_3O_5$ structured (*Cmcm*), $Mg_2Fe_2O_5$ (Boffa Ballaran et al. 2015). HP-$MgFe_2O_4$ was not observed at any conditions up to 18 GPa and 1300 °C in this study. Further high-pressure experiments are required in order to determine the structure(s) of the unrecoverable phase(s) using *in-situ* methods, the full extent of the $Mg_2Fe_2O_5$ stability field and whether HP-$MgFe_2O_4$ becomes stable at higher pressures as suggested by previous studies (Andrault and Bolfan-Casanova 2001; Levy et al. 2004).

The phase relations determined by Uenver-Thiele et al. (2017), coupled with the low ferric iron capacity of magnesiowüstite in the lower mantle, have very significant consequences for the interpretation diamond formation pressures. Firstly, magnesioferrite is not stable at lower mantle conditions where the diamond inclusions (Wirth et al. 2014; Palot et al. 2016) were believed to have formed. Secondly, if the magnesioferrite did exsolve from (Mg,Fe)O as HP-$MgFe_2O_4$ in the lower mantle, it could not have directly inverted to the spinel structure, due to the large stability field of $Mg_2Fe_2O_5$ + Fe_2O_3 as previously suggested. The presence of an additional minor phase between the magnesioferrite platelets (Wirth et al. 2014) does suggest the magnesioferrite results from inversion of lamellae of alternative stoichiometry. This idea that magnesioferrite resulted from the conversion of $Mg_2Fe_2O_5$ + Fe_2O_3 into magnesioferrite at ~ 300 km depth requires further investigation. However, the phase relations determined by Uenver-Thiele et al. (2017) demonstrate that magnesioferrite exsolution from magnesiowüstite is not an indicator of formation in the lower mantle. Instead, it suggests a maximum depth for exsolution of ~ 10 GPa. While the conditions of original inclusion entrapment of the samples described previously (Wirth et al. 2014; Palot et al. 2016) remain uncertain without further studies, the high ferric iron contents and magnesioferrite phase relations are consistent with formation in the upper mantle or transition zone, possibly from oxidized slab materials. The study of Uenver-Thiele et al. (2017) highlights the potentially rich and unexplored chemography and importance of post-spinel phase relations for understanding the Earth’s fundamental geochemical and geodynamic cycles.

References

Andrault, D., and Bolfan-Casanova, N. (2001) High-pressure phase transformations in the $MgFe_2O_4$ and Fe_2O_3-$MgSiO_3$ systems. Physics and Chemistry of Minerals, 28, 211–217.

Boffa Ballaran, T., Uenver-Thiele, L., and Woodland, A.B. (2015) Complete substitution of Fe^{2+} by Mg in Fe_4O_5: The crystal structure of the $Mg_2Fe_2O_5$ end-member. American Mineralogist, 100, 628–632.

Brey, G.P., Bulatov, V., Girnis, A., Harris, J.W., and Stachel, T. (2004) Ferropericlase—a lower mantle phase in the upper mantle. Lithos, 77, 655–663.

Dobson, D.P., Cohen, N.S., Pankhurst, Q.A., and Brodholt, J.P. (1998) A convenient method for measuring ferric iron in magnesiowustite (MgO-Fe_{1-x}) O). American Mineralogist, 83, 794–798.

Harte, B., Harris, J.W., Hutchison, M.T., Watt, G.R., and Wilding, M.C. (1999) Lower mantle mineral associations in diamonds from São Luiz, Brazil. (Y. Fei, C.M. Bertka, & B.O. Mysen, Eds.)Field Observations and High Pressure Experimentation A tribute to Francis R. Joe Boyd The Geochemical Society, Houston, 125–153.

Hazen, R.M., and Jeanloz, R. (1984) Wüstite ($Fe_{1-x}O$): A review of its defect structure and physical properties. Reviews of Geophysics, 22, 37–46.

Huang, E., and Bassett, W.A. (1986) Rapid determination of Fe_3O_4 phase diagram by synchrotron radiation. Journal of Geophysical Research, 91, 4697.

Levy, D., Diella, V., Dapiaggi, M., Sani, A., Gemmi, M., and Pavese, A. (2004) Equation of state, structural behaviour and phase diagram of synthetic $MgFe_2O4$, as a function of pressure and temperature. Physics and Chemistry of Minerals, 31, 122–129.

McCammon, C. (1997) Ferric iron content of mineral inclusions in diamonds from São Luiz: A view into the lower mantle. Science, 278, 434–436.

McCammon, C., Peyronneau, J., and Poirier, J.-P. (1998) Low ferric iron content of (Mg,Fe)O at high pressures and temperatures. Geophysical Research Letters, 25, 1589–1592.

Otsuka, K., Longo, M., McCammon, C.A., and Karato, S.-I. (2013) Ferric iron content of ferropericlase as a function of composition, oxygen fugacity, temperature and pressure: Implications for redox conditions during diamond formation in the lower mantle. Earth and Planetary Science Letters, 7–16.

Palot, M., Jacobsen, S.D., Townsend, J.P., Nestola, F., Marquardt, K., Miyajima, N., Harris, J.W., Stachel, T., McCammon, C.A., and Pearson, D.G. (2016) Evidence for H_2O-bearing fluids in the lower mantle from diamond inclusion. Lithos, 237–243.

Pearson, D.G., Brenker, F.E., Nestola, F., McNeill, J., Nasdala, L., Hutchison, M.T., Matveev, S., Mather, K., Silversmit, G., Schmitz, S., and others (2014) Hydrous mantle transition zone indicated by ringwoodite included within diamond. Nature, 507, 221–224.

Rohrbach, A., and Schmidt, M.W. (2011) Redox freezing and melting in the Earth’s deep mantle resulting from carbon–iron redox coupling. Nature, 472, 209–212.

Thomson, A.R., Walter, M.J., Kohn, S.C., and Brooker, R.A. (2016) Slab melting as a barrier to deep carbon subduction. Nature, 529, 76–79.

Trønnes, R.G. (2009) Structure, mineralogy and dynamics of the lowermost mantle. Mineralogy and Petrology, 99, 243–261.

Uenver-Thiele, L., Woodland, A.B., Boffa Ballaran, T., Miyajima, N., and Frost, D.J. (2017) Phase relations of $MgFe_2O_4$ at conditions of the deep upper mantle and transition zone. American Mineralogist.

Walter, M.J., Kohn, S.C., Araujo, D., Bulanova, G.P., Smith, C.B., Gaillou, E., Wang, J., Steele, A., and Shirey, S.B. (2011) Deep mantle cycling of oceanic crust: Evidence from diamonds and their mineral inclusions. Science, 334, 54–57.

Wirth, R., Dobrzhinetskaya, L., Harte, B., Schreiber, A., and Green, H.W. (2014) High-Fe (Mg, Fe)O inclusion in diamond apparently from the lowermost mantle. Earth and Planetary Science Letters, 404, 365–375.