This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
(DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am-2017-6061

Diamonds from the lower mantle?

A.R. Thomson

Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, UK.

Natural diamonds and the mineral inclusions they trapped during growth provide a unique opportunity to directly study material exhumed from great depths in the Earth. 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. These "superdeep" or "ultradeep" diamonds are distinguished by mineral inclusions, or reverted inclusions, of high-pressure phases (Walter et al. 2011; Pearson et al. 2014) and provide an unparalleled opportunity to study deep mantle processes. In order to understand the information these samples provide it is critically important that the depth of their formation is accurately constrained. Inclusions of magnesiowüstite are among the mostly commonly described in sub-lithospheric diamonds and observation of these inclusions are often assumed to indicate diamond provenance in the lower mantle. 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.

Detailed studies of magnesiowüstite inclusions in diamonds from the Juina region of Brazil report they often contain nanometre-sized crystals of magnesioferrite ($[Mg,Fe^{2+}]Fe^{3+}{}_2O_4$). These precipitates occur at the interface between the diamond and 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 an original $Fe^{3+}/\sum Fe$ for the inclusion of 11-14 %, compared with 7 ± 2 % in the recovered magnesiowüstite (McCammon 1997). 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. Using the reported bulk inclusion composition (~ $[Mg_{72}Fe_{28}]O$ ignoring minor elements) implies the original magnesiowüstite must have had an $Fe^{3+}/\sum Fe$ of approximately 10-12 %. In both studies the magnesioferrite lamellae have a topotaxial relationship with the [Mg,Fe]O host, confirming they 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

Always consult and cite the final, published document. See http:/www.minsocam.org or GeoscienceWorld

diamonds. However, both their high ferric iron contents and new evidence from the phase relations of magnesioferrite (Uenver-Thiele et al. 2017) might instead point to a 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). Thus, at conditions just within the lower mantle the maximum $Fe^{3+}/\sum Fe$ in $[Mg_{70}Fe_{30}]O$, similar to that observed by Palot et al. (2016), is < 2% at the nickel-nickel oxide buffer (NNO) and < 0.5 % at the iron-wüstite buffer (IW) (Otsuka et al. 2013). Similarly, a magnesiowüstite with $[Mg_{20}Fe_{80}]O$, similar to that observed by Wirth et al. (2014), would have a $Fe^{3+}/\sum Fe$ capacity of ~ 7 - 14 % at the IW and NNO buffers respectively. Further increasing pressure or decreasing temperature lowers the ferric iron solubility. Thus, the magnesioferrite exsolution observed in diamond-hosted inclusions, presumably driven by high ferric iron, appears inconsistent with the compositions of magnesiowüstite expected in the lower mantle.

In this issue, Uenver-Thiele et al. (2017), have 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). Instead, the experiments of Uenver-Thiele et al. (2017) have revealed a very different phase diagram, observing 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 pressure. Firstly, magnesioferrite is not stable at lower mantle

Always consult and cite the final, published document. See http:/www.minsocam.org or GeoscienceWorld

This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
(DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am-2017-6061

conditions where the diamond inclusions (Wirth et al. 2014; Palot et al. 2016) are 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 suggested by Palot et al. (2016). The presence of an additional minor phase between the magnesioferrite platelets (Wirth et al. 2014) does suggest inversion from exsolution lamellae of alternative stoichiometry, and the conversion of $Mg_2Fe_2O_5$ + Fe_2O_3 into magnesioferrite at ~ 300 km depth would appear to be consistent with these observations. The conditions of original inclusion entrapment remain uncertain, however, high ferric iron contents and magnesioferrite phase relations are more consistent with formation in the upper mantle or transition zone. 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

Always consult and cite the final, published document. See http:/www.minsocam.org or GeoscienceWorld

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.

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.

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.

Always consult and cite the final, published document. See http:/www.minsocam.org or GeoscienceWorld