

Stability of Fe₅O₆ and other Fe²⁺-Fe³⁺-oxides at transition zone conditions

A.B. WOODLAND¹, L. UENVER-THIELE¹, T.
BOFFA BALLARAN²

¹Inst. für Geowissenschaften, Universität Frankfurt,
60438 Frankfurt, Germany

²Bayerisches Geoinstitut, Universität Bayreuth,
95440 Bayreuth, Germany

The recent discovery of Fe₄O₅ and Fe₅O₆ [1, 2, 3, 4] as stable phases at high pressures and temperatures indicates that the Fe-O phase diagram is more complicated than previously thought. These are in addition to the h-Fe₃O₄ phase(s) that appear to be stable at pressures above > 25 GPa.

New multi-anvil experiments using magnetite and metallic Fe as starting materials indicate that the stability field of Fe₅O₆ is significant, spanning the pressure range from at least 10 to 20 GPa at 1200-1300°C. Under these conditions, the assemblages Fe₄O₅ + Fe₅O₆ and Fe₅O₆ + wüstite are stable depending on bulk oxidation state. Under even more oxidizing compositions hematite + Fe₄O₅ is the stable paragenesis. However, considering the rather reduced redox conditions expected in the mantle, assemblages involving Fe₅O₆ should have the most relevance for the Earth. Under the conditions so far explored, Fe₆O₇ was not found to be stable.

Single-crystal X-ray diffraction confirms that Fe₅O₆ belongs to the Cmc₂m space group, making it a member of the CaFe_{2+n}O_{4+n} series, like Fe₄O₅. At ambient conditions, the cell parameters are $a = 2.88 \text{ \AA}$, $b = 9.94 \text{ \AA}$, $c = 15.37 \text{ \AA}$, with small variations depending on the synthesis pressure. This causes the molar volume of Fe₅O₆ to decrease with increasing synthesis pressure, suggesting variable cation distributions may play a role in stabilizing this phase, like that observed for spinel. Unpolarized Raman spectra of Fe₅O₆ and Fe₄O₅ are very similar, with one major broad peak at $\sim 665 \text{ cm}^{-1}$. This peak is only slightly shifted relative to that of magnetite (671 cm^{-1}). However, the additional peaks in the magnetite spectrum should allow it to be distinguished from the other two Fe-oxides.

[1] Lavina et al. (2011) PNAS, 108, 17281-17285. [2] Woodland et al. (2012) Amer Mineral, 97, 1808-1811. [3] Woodland et al. (2015) Goldschmidt Abstracts, 2015 3446. [4] Lavina & Meng (2015) Sci Adv, 2015;1:e1400260.