Stability of Fe$_5$O$_6$ and its relation to other Fe-Mg-oxides at high pressures and temperatures

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ABSTRACT

The stability of Fe$_5$O$_6$ has been experimentally determined under pressure-temperature conditions relevant for the Earth’s deeper upper mantle down to the upper portion of the lower mantle (to 28 GPa). In addition, we investigated the incorporation of Mg into Fe$_5$O$_6$ and its systematics, which allows us to discuss the relevance of this phase for the mantle. Experiments were performed from 8–28 GPa and 900–1600 °C. Additional oxide phases may appear if the bulk composition does not maintain the Fe$_3^+$Fe$_2^+$O$_6$ stoichiometry during the experiment, including coexisting Fe$_4$O$_5$ or Fe$_9$O$_{11}$. Unfortunately, the similarities in Raman spectra between several high-pressure Fe-oxide phases make this method unsuitable for distinguishing which phase is present in a given sample. The stability field for Fe$_5$O$_6$ extends from ~9 to at least 28 GPa but is truncated at lower temperatures by the assemblage Fe$_4$O$_5$ + wüstite. Refined thermodynamic properties for Fe$_5$O$_6$ are presented. The range of redox stability of Fe$_5$O$_6$ appears to be more limited than that of Fe$_4$O$_5$.

Solid solution along the Fe$_5$O$_6$-Mg$_3$Fe$_2$O$_6$ binary is quite limited, reaching a maximum Mg content of ~0.82 cations per formula unit (i.e., $X_{Mg}$Fe$_3$O$_6$ ≈ 0.27) at 1400 °C and 10 GPa. The observed sharp decrease in molar volume of the O$_6$-phase with Mg content could be a possible explanation for the limited range of solid solution. A phase diagram has been constructed for a composition of approximately Mg$_{0.5}$Fe$_{2.5}$Fe$_{2.5}$O$_6$ stoichiometry. This small amount of Mg causes a significant change in the relations between the O$_6$-structured phase and the assemblage O$_5$-structured phase + (Mg,Fe)O. Several experiments were performed to test whether the O$_5$-phase can coexist with mantle silicates like wadsleyite and ringwoodite. In all cases, the run products contained (Mg,Fe)$_2$Fe$_2$O$_5$ rather than the O$_6$-phase, further underlining the limited ability of Fe$_5$O$_6$ to accommodate enough Mg to be stable in a mantle assemblage.

The large stability field of Fe$_5$O$_6$ implies that this phase could likely occur in locally Fe-rich environments, like those sampled by some “deep” diamonds. However, the limited solubility of Mg in the O$_5$-phase leads us to conclude that the O$_5$-phase should be of much more relevance as an accessory phase in a peridotitic mantle assemblage.

Keywords: Fe-oxide, Fe-Mg-oxide, Fe$_5$O$_6$, Fe$_4$O$_5$, high pressure, high temperature, phase stability, inclusion in diamond, wüstite, magnetite

INTRODUCTION

The recent high-pressure synthesis of several new mixed-valence Fe-oxide phases with different stoichiometries indicates that phase relations in the Fe-O system at conditions corresponding to the deeper mantle can be quite complicated. Along with the well-known minerals hematite, magnetite, and wüstite, the orthorhombic-structured phases Fe$_3^+$Fe$_2^+$O$_5$ and Fe$_3^+$Fe$_2^+$O$_8$ (Lavina et al. 2011; Woodland et al. 2012, 2015; Lavina and Meng 2015), and the monoclinic-structured phases Fe$_3^+$Fe$_2^+$O$_5$ and Fe$_2^+$Fe$_2^+$O$_8$ (Simmyo et al. 2016; Ishii et al. 2018) have been synthesized at pressures in excess of ~10 GPa. All four of these oxides lie compositionally between wüstite and magnetite, with each phase having its own Fe$^+$/ΣFe. Of course, the Fe$^+$/ΣFe of each phase can be modified through the formation of solid solutions with other cations like Mg, Cr, and Al (e.g., Uenver-Thiele et al. 2018).

The relevance of these Fe-oxides for the mineralogy of the Earth’s interior rests upon the extent of their stability in terms of pressure, temperature, and oxidation state. Nearly pure magnetite has been reported as a rare inclusion in diamond (e.g., Stachel et al. 1998; Jacob et al. 2016), but a precursor phase may have originally formed at depth rather than magnetite itself (Uenver-Thiele et al. 2017b). Currently, very little information is available on the phase relations involving these four Fe-oxides. The maximum pressure stability of magnetite and its breakdown to Fe$_4$O$_5$ + hematite was described by Woodland et al. (2012). Myhill et al. (2016) reported on the minimum pressure stability of Fe$_4$O$_5$ and provided a thermodynamic framework for estimating the stabilities of Fe$_5$O$_6$ and Fe$_4$O$_5$. A recent in situ diamond-anvil