Stability of Fe₅O₆ and its relation to other Fe-Mg-oxides at high pressures and temperatures

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ABSTRACT

The stability of Fe_5O_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_5O_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 $Fe_3^{2+}Fe_3^{4+}O_6$ stoichiometry during the experiment, including coexisting Fe_4O_5 or Fe_9O_{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_5O_6 extends from ~9 to at least 28 GPa but is truncated at lower temperatures by the assemblage $Fe_4O_5 +$ wüstite. Refined thermodynamic properties for Fe_5O_6 are presented. The range of redox stability of Fe_5O_6 appears to be more limited than that of Fe_4O_5 .

Solid solution along the Fe_5O_6 -Mg₃Fe₂O₆ binary is quite limited, reaching a maximum Mg content of ~0.82 cations per formula unit (i.e., $X_{Mg_3Fe_2O_6} \approx 0.27$) at 1400 °C and 10 GPa. The observed sharp decrease in molar volume of the O₆-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 $Mg_{0.5}Fe_{2.5}^{2+}Fe_2^{2+}O_6$ stoichiometry. This small amount of Mg causes a significant change in the relations between the O₆-structured phase and the assemblage O₅-structured phase + (Mg,Fe)O. Several experiments were performed to test whether the O₆-phase can coexist with mantle silicates like wadsleyite and ringwoodite. In all cases, the run products contained (Mg,Fe)₂Fe₂O₅ rather than the O₆-phase, further underlining the limited ability of Fe₅O₆ to accommodate enough Mg to be stable in a mantle assemblage.

The large stability field of Fe_5O_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_6 -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_5O_6 , Fe_4O_5 , high pressure, high temperature, phase stability, inclusion in diamond, wüstite, magnetite