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Mg incorporation in Fe_5O_6 and its relevance as a possible mantle phase

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Recent studies on the simple Fe-O system demonstrate that the list of possible high-pressure phases has to be expanded by adding new oxide phases such as Fe_4O_5, Fe_5O_6, Fe_7O_9, Fe_9O_{11} [1,2,3,4,5]. These new stoichiometries highlight that our understanding of such a simple binary system was far too limited. Fe_4O_5 and Fe_5O_6 has been proven to be stable over a wide range of pressure and temperature corresponding to those of the Earth's deep upper mantle and transition zone. Based on their ability to incorporate Fe^{3+} as well as Fe^{2+}, the stability of these mixed-valenced Fe-oxides are related to the prevailing oxygen fugacity in the Earth's interior.

Since M_4O_5 stoichiometries become stable as post-spinel phases and can coexist with Si-bearing phases [6,7,8], this stoichiometry needs to be considered as a potential constituent of the mantle assemblage. However, based on the fact that Fe_4O_5 has a higher Fe^{3+}/Fe_{tot} (=0.5) than Fe_5O_6 with Fe^{3+}/Fe_{tot} =0.4, the latter phase might be more relevant for the expected redox conditions in the Earth. Since Fe_5O_6 and Fe_4O_5 share the same orthorombic *Cmcm* space group and Fe_4O_5 forms a complete solid solution along the $Fe_2Fe_2O_5$-$Mg_2Fe_2O_5$ binary join [8], the same behavior might be also expected for Fe_5O_6. But, the ability of Fe_5O_6 to form Mg^{2+}-Fe^{2+} solid solutions (i.e. Fe_5O_6-$Mg_3Fe_2O_6$) remains essentially unknown, which is why the aim of this experimental study is to investigate (i) the solubility of Mg in the Fe_5O_6 structure and (ii) its phase relations at relevant mantle conditions.

Experiments were carried out at 8-20 GPa and temperatures 1000-1600°C using the multi-anvil apparatus. Starting materials were stoichiometric mixtures of MgO, Fe^0 and Fe_3O_4 components. Run products were analysed by electron microprobe, powder XRD and in some cases by TEM.

Preliminary results indicate that a solid solution along the Fe_5O_6-$Mg_3Fe_2O_6$ binary is incomplete; the $Mg_3Fe_2O_6$ is not stable. The phase diagram for $Mg_{0.5}Fe_{2.5}Fe_2O_6$ indicates that the phase relations strongly deviate from that of the Fe^{2+}-endmember composition. The low-pressure stability of Fe_5O_6 is limited down to ∼9 GPa over a wide temperature range (900-1400°C), where the assemblage M_3O_4 + (Mg,Fe)O becomes stable. The stability field of Fe_5O_6 pinches out with increasing pressure, but is still stable at 28 GPa (at 1500°C). In contrast, in the Mg-bearing compositions an intervening M_4O_5 + (Mg,Fe)O assemblage is stable between 9-18 GPa. With increasing pressure, $Mg_{0.5}Fe_{2.5}Fe_2O_6$ becomes stable relative to the assemblage $(Mg,Fe)_2Fe_2O_5$ + (Mg,Fe)O and seems to be limited to ∼20 GPa. $Mg_{0.5}Fe_{2.5}Fe_2O_6$ can coexist with (Mg,Fe)O and/or M_9O_{11}.

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