

## Phase relations of Fe-Mg spinels including new high-pressure post-spinel phases and implications for natural samples

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### ABSTRACT

Phase relations of magnesioferrite-magnetite solid solutions ( $\text{Mg,Fe}^{2+}\text{Fe}_3^{3+}\text{O}_4$ ) were investigated at pressures of 9–23 GPa and temperatures of 1200–1600 °C. Our new results indicate that the assemblage  $\text{Mg}_2\text{Fe}_2\text{O}_5 + \text{Fe}_2\text{O}_3$  reconstitutes to a hp- $\text{MgFe}_2\text{O}_4$  phase at 20 GPa and 1300–1500 °C. The stability field of hp- $\text{MgFe}_2\text{O}_4$  begins at ~1300 °C and widens to higher temperature. At lower temperature (1200–1300 °C)  $\text{Mg}_2\text{Fe}_2\text{O}_5 + \text{Fe}_2\text{O}_3$  breaks down to the new phase assemblage  $\text{Mg}_3\text{Fe}_4\text{O}_9 + \text{Fe}_2\text{O}_3$  with its stability field expanding to higher pressures and temperatures at the expense of hp- $\text{MgFe}_2\text{O}_4$ . The  $\text{Mg}_3\text{Fe}_4\text{O}_9$  phase has the same crystal structure that recently reported for  $\text{Fe}_7\text{O}_9$ , and thus represents the Mg-end-member. From powder X-ray diffraction, we find that hp- $\text{MgFe}_2\text{O}_4$  has a structure consistent with an orthorhombic unit cell belonging to the *Pmcn* space group (no. 62). However, it could have undergone a transformation from a different structure during decompression.

Experiments conducted with a  $\text{Mg}_{0.5}\text{Fe}_{0.5}^{2+}\text{Fe}_3^{3+}\text{O}_4$  composition demonstrate that the addition of  $\text{Fe}^{2+}$  significantly changes the topology of the phase relations compared to the  $\text{MgFe}_2\text{O}_4$  end-member system. At 10–11 GPa and 1000–1600 °C,  $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$  breaks down to the assemblage  $\text{MgFeFe}_2\text{O}_5 + \text{Fe}_2\text{O}_3$ , with the phase boundary described by:  $P$  (GPa) =  $2.0 \times 10^{-3} \times T$  (°C) + 8.2. No stability field for the constituent oxides [i.e.,  $(\text{Mg,Fe})\text{O} + \text{Fe}_2\text{O}_3$ ] exists, in contrast to that observed for the  $\text{MgFe}_2\text{O}_4$  end-member. The stability of the assemblage  $\text{MgFe}^{2+}\text{Fe}_3^{3+}\text{O}_5 + \text{Fe}_2\text{O}_3$  is limited at higher pressures and appears to pinch out to higher temperatures. At 15–16 GPa and temperatures up to 1350 °C, this assemblage reconstitutes to form a hp- $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$  phase. However, at higher temperatures a new assemblage of  $(\text{Mg,Fe})_3\text{Fe}_4\text{O}_9 + \text{Fe}_2\text{O}_3$  appears. The occurrence of such compositions suggests that solid solution may be complete across the  $\text{Mg}_3\text{Fe}_4\text{O}_9$ – $\text{Fe}_7\text{O}_9$  binary.

Our results further demonstrate that phase relations even in simple Fe-Mg oxides can become complex at high pressures and temperatures and that phases with various novel stoichiometries (i.e.,  $\text{Mg}_3\text{Fe}_4\text{O}_9$ ) may become stable. In addition, this study has implications for natural samples by helping to place constraints on the range in pressure and temperature at which a given sample formed. For instance, magnetite or magnesioferrite entrapped as inclusions in diamond could have either crystallized directly, or formed from precursor phases at depths that exceed the stability of the spinel-structured phases. Evidence for such high-pressure transformations can potentially be found by investigating micro-textures.

**Keywords:** Magnesioferrite, magnetite, solid solution, deep upper mantle, transition zone, high pressure, inclusion in diamond