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On the stability of Mg-Fe oxide spinels and their post-spinel phases

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High-P “post-spinel” oxide phases have received attention as potential indicators of formation conditions of inclusions in diamond and shock events in extraterrestrial materials. This requires knowledge of P-T stabilities of these phases, including the influence of major element substitutions. Along with literature data, our recent studies permit an assessment of phase stabilities in Mg-Fe^{2+}-Fe^{3+}-Cr-Al oxides at conditions extending to the base of the transition zone (~24 GPa).

In these compositions a spinel-structured phase breaks down to i) its constituent oxides or ii) an assemblage containing a $(Mg,Fe)_2(B)_2O_5$ or related post-spinel phase, where B=Fe^{3+},Cr^{3+},Al. Thus, there is no direct transformation between a spinel-structured phase and a high-P O_4-polymorph, which appears at even higher pressures. Spinel-breakdown occurs at different P depending on composition: ~7 GPa(Fe^{2+}-Al), ~8-10 GPa(Mg,Fe^{2+}-Fe^{3+}), ~ 13-15 GPa(Mg,Fe^{2+}-Cr) and ~15-16 GPa(Mg-Al).

In the Fe^{2+}-Fe^{3+}-O-system, numerous phases with different stoichiometries and structures are stable: Fe_4O_5, Fe_5O_6, Fe_7O_9, Fe_9O_{11}, hp-Fe_3O_4. Having different Fe^{3+}/Fe^{2+}, their relative stabilities are also $fO2$-dependent. There are notable differences in behavior between Fe^{2+}- and Mg-bearing compositions. While Fe^{2+}-Mg solid solution is complete in $(Fe^{2+},Mg)_2Fe^{3+}{}_2O_5$, $(Fe^{2+},Mg)_3Fe^{3+}{}_4O_9$ and hp-$(Fe^{2+},Mg)Fe^{3+}{}_2O_4$, Mg incorporation in Fe_9O_{11} is limited, with even less substitution in Fe_5O_6.

Cr is readily incorporated into $(Fe^{2+},Mg)_2Fe^{3+}{}_2O_5$, forming a complete solid solution in spite of the Fe^{3+}- and Cr-endmembers having somewhat different crystal structures. Aside from hp-$(Fe^{2+},Mg)Cr_2O_4$, no other stoichiometries with Cr have been reported. The behavior of Al in these high-P oxide phases is more varied. While no further phases besides hematite+ corundum have been found in the Fe^{2+}-Al-system and Al incorporation in Fe_4O_5, Fe_7O_9 and hp-Fe_3O_4 is very limited, there appears to be complete $Mg_2(Fe^{3+},Al)_2O_5$solid solution and significant Al incorporation in $Mg_3(Fe^{3+},Al)_4O_9$ and hp-$Mg(Fe^{3+},Al)_2O_4$.

Considering these systematics, Fe_4O_5 appears the most flexible in forming solid solutions with other 2+ and 3+ cations and is thus more likely to occur as an accessory phase in the deep upper mantle and transition zone, where it is stabilized by Fe^{3+}. An exception is localized Fe-rich domains, where the stable phase stoichiometry is dictated by the redox conditions. At higher P, a phase with hp-O_4 stoichiometry is expected to be stabilized.