

Structural systematics of Mg-Fe²⁺-bearing spinels and spinelloids

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Spinel and structurally related spinelloids have been synthesised in the geologically relevant system M_2SiO_4 - $MFe^{3+}_2O_4$, where $M = Mg$ and Fe^{2+} at 1100-1200°C and 3 to 16 GPa. Starting materials were mixtures of Fe_3O_4 and pre-synthesised olivine solid solutions. Unit-cell parameters were determined by Rietveld refinement of powder diffraction patterns containing Si as an internal standard.

Spinel exhibits a range in composition, which requires consideration of four endmembers: ringwoodite, Fe-ringwoodite, magnetite and magnesioferrite. As expected, the cell parameter decreases with increasing M_2SiO_4 content. A least squares fit to the dataset ($n=53$) suggests ideal or near ideal behaviour in this quaternary system. The derived molar volume for $MgFe_2O_4$ ($V^\circ = 44.51(12) \text{ cm}^3$) implies a degree of inversion of $x = 0.78$ [1], although this was not explicitly accounted for in the fit.

Spinelloid II exhibits only a limited compositional range with $nMg \leq 0.26$ c.p.f.u. Molar volumes decrease with increasing Mg content. Single-crystal refinements indicate that Mg preferentially resides on the M3 site, which is the octahedral site containing the bridging oxygen of the T_3O_{10} tetrahedral group.

Compared with Mg-free [2] spinelloid III, the incorporation of Mg causes a systematic reduction in volume. A weighted least squares fit yields $V^\circ_{Fe_3O_4} = 45.04(6) \text{ cm}^3$, $V^\circ_{Fe_2SiO_4} = 42.89(10) \text{ cm}^3$ and $V^\circ_{Mg_2SiO_4} = 40.9(4) \text{ cm}^3$, assuming ideal mixing (non-ideality is not statistically significant). Mg prefers the M2 site, which is attached to the bridging oxygen of the T_2O_7 group.

The volume behaviour of spinelloid V is similar to the other spinelloids, except that the volume reduction from Mg addition is not so clearly defined. This could be due to changing ordering of i) Fe^{3+} and Si on the TO_4 and T_2O_7 sites, and/or ii) Mg, Fe^{2+} and Fe^{3+} across the octahedral sites. A weighted least squares fit yields $V^\circ_{Fe_3O_4} = 44.96(4) \text{ cm}^3$, $V^\circ_{Fe_2SiO_4} = 42.53(8) \text{ cm}^3$ and $V^\circ_{Mg_2SiO_4} = 40.3(3) \text{ cm}^3$ for the theoretical endmembers, assuming ideal mixing.

[1] O'Neill *et al.* (1992) *Am Min* **77**, 725-40, [2] Woodland, Angel (2000) *Contrib Mineral Petrol* **139**, 734-47.

F, Cl and S contents of olivine-hosted melt inclusions from picritic dike rocks, Etendeka, NW Namibia

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Volatile contents and their evolution during magma differentiation are important to understand for better assessment of their role during volcanic eruptions and for estimation of atmospheric loading. Furthermore volatiles have shown potential to be used to put constraints on different mantle sources. Here we present for the first time F, Cl and S concentrations of olivine-hosted melt inclusions analyzed by SIMS from picritic dikes from the southern Etendeka region, NW Namibia.

The analyzed host olivines are Mg-rich ($F_{O_{84,93}}$) and their re-homogenized (and post-entrapment corrected) melt inclusions contain between 10 and 18 wt.% MgO and show SiO_2 contents of 45-52 wt.% and thus range from basalt to komatiite in composition.

F concentrations in the analyzed melt inclusions vary from 200 to 450 ppm, Cl varies from 5 to 40 ppm and S from 10 to 1100 ppm. F and S concentrations increase with decreasing forsterite content of the host olivine, whilst Cl does not. F/Cl ratios are variable and range from 4 to 45, with the highest values presumably being influenced by degassing prior to melt inclusion entrapment and/or post entrapment leaking. Most F/Cl ratios and low Cl/K ratios (≤ 0.3) indicate a depleted mantle source for these picritic dikes [1-3], which is consistent with earlier Sr and Nd isotope work of [4]. We plan to compare the volatile contents of the melt inclusions with that of the corresponding whole rocks (analyzed by pyrohydrolysis) in order to further constrain the significance of potential degassing processes.

[1] Stroncik & Haase (2004), *Geology* **32**, 945-948. [2] Michael & Cornell (1998), *Journal of Geophysical Research* **103**, 18, 325-18, 356. [3] Pyle & Mather (2009), *Chemical Geology* **263**, 110-121. [4] Thompson *et al* (2001), *Journal of Petrology* **42**, 2049-2081.