

Cation distribution and cooling rates of Cr-substituted Mg-Al spinel from the Olkhon metamorphic complex, Russia

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Abstract: A crystal chemical study was carried out on seven Mg-Al rich and Cr-bearing spinels from a calciphyre of the Olkhon metamorphic complex (western Lake Baikal, Russia) in order to: a) verify the structural effects related to the progressive substitution of Cr³⁺, the main substituent cation in this suite pertaining to the MgAl₂O₄ – MgCr₂O₄ binary join; b) estimate the closure temperature of the exchange reaction involving Mg and Al in tetrahedral (T) and octahedral (M) sites. This will be a first step towards evaluation of the cooling rate of the host rock.

Chemical composition is Mg (Al_{2-p}, Cr_p) O₄ with 0.03 ≤ p ≤ 0.23 afu. With increasing p, the cell edge *a* increases from 8.090 to 8.117 Å, whereas the oxygen positional parameter *u* is almost constant. As *u* is related to the (M-O)/(T-O) ratio, Cr substituting for Al in the M site causes an increase not only of the M-O bond distance, but also that of the tetrahedral T-O. The observed T-O increase is due to Mg ordering into the T site, with increasing Cr content.

Cation distributions were used to estimate the closure temperature of the exchange reaction applying two available models. Both estimates are rather consistent for very low Cr content, but substantial disagreement is observed for Cr-rich samples. The inversion trend of the studied spinel suite extrapolated to Cr = 0, enables us to calculate the closure temperature of the MgAl₂O₄ end-member with the same cooling rate. This suggests that kinetic results from cooling experiments on MgAl₂O₄ may be applied to cation distributions measured in samples along the MgAl₂O₄ – MgCr₂O₄ binary join.

Key-words: spinel, crystal chemistry, intra-crystalline closure temperature, thermodynamic modelling.

Introduction and geological setting

Spinel is a group of compounds interesting both to earth and material sciences. Full descriptions of structural features are found in Hafner (1960) and Hill *et al.* (1979). We briefly recall here that an almost close-packed arrangement of 32 oxygen atoms forms a cubic cell with *a* edge ranging from about 7.9 to 9.4 Å, depending on the size of the cations entering 8 out of the 48 tetrahedral T sites, and 16 out of the 32 octahedral M sites (positions 8*a* and 16*d*, space group *Fd3m*). A large variety of atomic species can enter both sites, but in the most common natural spinels they are mainly divalent and trivalent cations, usually named A and B respectively, so that the general formula of an end-member 2-3 spinel is (A_{1-x} B_x)_T (B_{2-x} A_x)_M O₄, and *x* is the inversion parameter. Only oxygen has one degree of freedom, with coordinates *u,u,u*, those of T and M sites being fixed by symmetry. Cell parameter *a* shows smooth changes with inversion variations which, conversely, strongly affect the coordinate *u*.

Due to its petrologic significance, the distribution of cations among the tetrahedral and octahedral sites is one

of the most frequently investigated features of spinels, being closely dependent on equilibration temperature and cooling rate (Princivalle *et al.*, 1989; Ghiorso & Sack, 1991; Peterson *et al.*, 1991; Millard *et al.*, 1992; Maekawa *et al.*, 1997; Redfern *et al.*, 1999; Andreozzi *et al.*, 2000).

Much work has focused on the temperature and pressure influence on cation distribution in many end-member spinels; the temperature dependence of the cation distribution is known (O'Neill, 1992; O'Neill *et al.*, 1992; Larsson *et al.*, 1994; O'Neill & Dollase, 1994; Harrison *et al.*, 1998; Andreozzi *et al.*, 2000). However, each of these end-member spinel has its own disordering path, so that in a solid solution of normal (*x* ≡ 0) and inverse (*x* ≡ 1) terms it becomes quite difficult to relate equilibration temperature to cation distribution. Several studies face this problem in solid solutions between two end-members (Waerenborgh *et al.*, 1994; Nell *et al.*, 1989; O'Neill & Navrotsky, 1983, 1984; Andreozzi *et al.*, 2001) and in more complex natural compositions. Concerning the latter, on the basis of thermal experiments on natural Fe²⁺-Fe³⁺-Mg-Al spinels, Princivalle *et al.* (1999) illustrated relationships between

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