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Crystal chemistry and significance of cation ordering in Mg-Al rich spinels from high-grade hornfels (Predazzo-Monzoni, NE Italy)

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ABSTRACT

Two Mg-Al spinels (FAS1 and FAS2) in high-grade hornfels from the Toal de Mason skarn (Predazzo Monzoni, NE Italy) were investigated by means of single crystal X-ray diffraction and electron microprobe analysis in order to evaluate the last intra-crystalline closure temperature.

The evidence provided by crystal chemical data from the investigated spinels, compared with that for two other spinels from a websterite dyke and a chlorite schist (TS2 and SP78a, respectively) with similar chemical characteristics, yielded a new empirical geothermometer. This allowed estimation of intra-crystalline temperatures as low as *c.* 400°C and indicates that the closure temperature of FAS1 and FAS2 is *c.* 500°C, i.e. 150–200°C lower than the spinel crystallisation temperature.

KEYWORDS: Mg-Al spinel, crystal-chemistry, intra-crystalline temperature.

Introduction and sample description

THE Predazzo-Monzoni area (W Dolomites) was the site of large-scale Early-Middle Triassic intrusive magmatism (240–230 Ma; Borsi *et al.*, 1968; Laurenzi, 1994). The igneous rocks from Monzoni form a NE-SW elongated intrusion (*c.* 4 km^2) trending parallel to the S. Pellegrino valley. They are represented by ultramafic (pyroxenite and dunite), mafic (olivine-gabbro, diorite and monzogabbro) and intermediate (monzonite and monzodiorite) rock-types (Minguzzi *et al.*, 1977; Bocchi *et al.*, 1987). They intruded Permo-Triassic sediments which were affected by high to medium grade contact metamorphism, mainly apparent in the SiO_2-Al_2O_3-bearing limestone of the Bellerophon and Scythian Formations. These hornfels are characterised by diopside (i.e. formerly fassaite; Oberti *et al.*, 1982), forsterite, blue calcite, phlogopite, monticellite, garnet, spinel, wollastonite, anorthite and gehlenite (Minguzzi *et al.*, 1977; Bocchi *et al.*, 1987).

Bocchi *et al.* (1987) pointed out that the skarn mineral assemblages from the Toal de Mason valley, a N–S-trending valley lateral to that of S. Pellegrino, formed at low $P_f = P_T$ pressure (*c.* 0.2–0.5 kbar) and a temperature range of 400 to 700°C, the higher temperature being indicated by the diopside-forsterite-calcite-monticellite isograd.

The spinels investigated in the present work belong to a hornfels collected from the middle sections of the Toal de Mason skarn. Spinel FAS1 (octahedral crystals, 1–3 mm across) is associated with white calcite, dark-green diopside (10 mm along the *c*-axis), monticellite and gehlenite, while the FAS2 spinel (cube-octahedral crystals, 1-5 mm across), is associated with bluish calcite, dark-green diopside (5–10 mm along the c-axis), monticellite (10 mm across), phlogopite plates (10–30 mm across) and sometimes vesuvianite (10 mm across).

Assuming a CO_2/H_2O ratio of *c.* 0.8, the mineral assemblage containing the FAS1 spinel indicates that the equilibration temperature was possibly as high as 700°C. A lower equilibration temperature (e.g. 650°C) is expected for the mineral assemblage containing spinel FAS2, since it is associated with phlogopite, which indicates a lower CO_2/H_2O ratio (Winkler, 1976).

The present paper aims to investigate the crystal-chemistry of the spinels and their intracrystalline equilibration temperature primarily with the view of testing the spinel potential as a geothermometer.

Experimental

Single crystal X-ray diffraction data for two carefully selected euhedral crystals were recorded with an automated KUMA-KM4 (K-geometry) diffractometer, using Mo-$K\alpha$ radiation, monochromatized by a flat graphite crystal. Data collection was made up to 100 degrees of 2θ in the continuous ω-scan mode. Peak-base width was of 2° 2θ and counting times were from 20 to 40 s, according to peak σ. Background was measured for half peak-time. Corrections for absorption were made according to North *et al.* (1968). 24 equivalents of the 12 8 4 reflection (*c.* 90° of 2θ) were accurately centred and used for cell-parameter determination.

The structural refinement, performed with the SHELX-93 program (Sheldrick, 1993), was carried out in the F*d*3*m* space group (with origin at –3m), since no evidence of different symmetry appeared and without chemical constraints. Refined parameters were: scale factor, secondary extinction coefficient (Ext), oxygen coordinate (x), tetrahedral (T) and octahedral (M) site occupancies, and displacement parameters (U). Two scattering curves, Mg *vs*. Fe in the T site and Al *vs*. Fe the in M site were used with the constraints of full occupancy and equal displacement parameters for the two species. The best values of all statistical descriptors in all the sin θ/λ shells were obtained with full ionised curves for cations, and a partial ionisation for oxygen ($O^{1.4-}$). Correlation between the parameters greater than 0.70 were not observed.

Table 1 shows site occupancies and oxygen positional parameters obtained from six refinements for each crystal, using different shells of reciprocal space (Kroll *et al.*, 1997) with no less than 99 reflections. For the three refinements with high angle truncation, occupancies are the same within one standard deviation. On the other hand, the latter increases up to 10 σ for the three refinements with low-angle truncation. In our experience, this is due to the presence of a few

TABLE 1. Refinements data of FAS1 and FAS2, using high and low angle truncation. Estimated standard deviations in parentheses

Upper limit Angle 2θ	M occ.	T occ.	x	N. Refl.	GooF	Rw %	R1 % (4σ)	Scale factor	Ext-coeff. G*10⁴
FAS1									
100°	0.976(3)	0.884(5)	0.26315(4)	156	1.209	4.12	1.90	0.217(1)	0.029(2)
90°	0.976(3)	0.884(4)	0.26308(3)	126	1.078	2.66	1.48	0.2085(1)	0.025(2)
80°	0.975(3)	0.884(5)	0.26305(3)	99	1.232	2.28	1.45	0.2074(1)	0.024(2)
FAS2									
100°	0.974(5)	0.888(2)	0.26314(6)	151	1.139	5.64	2.45	0.3104(4)	0.030(1)
90°	0.972(4)	0.887(2)	0.26309(5)	123	1.141	3.97	1.94	0.3040(3)	0.027(2)
80°	0.971(4)	0.887(2)	0.26309(5)	97	1.227	3.66	1.79	0.3030(3)	0.028(2)

Lower limit Angle 2θ	M occ.	T occ.	x	N. Refl.	GooF	Rw %	R1 % (4σ)	Scale factor	Ext-coeff. G*10⁴
FAS1									
20°	0.992(3)	0.901(5)	0.26314(4)	152	1.222	3.98	1.90	0.2144(1)	0.030(2)
30°	0.993(3)	0.899(5)	0.26314(4)	146	1.231	4.04	2.07	0.2143(1)	0.027(3)
40°	0.995(3)	0.903(5)	0.26313(4)	146	1.169	4.07	1.81	0.2162(1)	0.028(3)
FAS2									
20°	0.978(5)	0.897(7)	0.26315(6)	147	1.192	5.21	2.30	0.3122(4)	0.010(2)
30°	0.986(5)	0.892(7)	0.26313(6)	141	1.138	4.90	2.16	0.3189(4)	0.027(4)
40°	0.999(5)	0.904(7)	0.26311(6)	141	1.125	4.94	2.06	0.3243(4)	0.023(4)

extremely strong reflections at low angle, whose exclusion can lead to inaccurate occupancy values. Consequently, we retained the averaged values of the high-angle truncated refinements (Table 2). Only isotropic displacement parameters are reported, being the out of diagonal terms of the same magnitude as their σ.

The same crystals used for X-ray single-crystal data collection were also used for microanalysis, performed by means of a CAMECA-CAMEBAX microprobe operating at 15 kV and 15 nA sample current, using the WDS method. A PAP-CAMECA program was used to convert X-ray counts into weight percentages of the corresponding oxides. Synthetic oxide standards were used. Results are considered accurate to within 1–2% for major and 5% for minor elements. At least 10 point analyses were obtained from each crystal. The Fe^{3+} was calculated on the basis of three cations for four oxygens.

The investigated spinels are characterised by high contents of Mg and Al. Fe^{2+} and Fe^{3+} sum up to about 0.25 atoms per formula unit (a.f.u.): their substitution for Mg and Al is responsible for the cell edge values (8.107 Å for FAS1 and 8.106 Å for FAS2), higher than that of 'spinel ss' (8.096 Å; Grimes *et al.*, 1983). Other cations are virtually negligible (<0.01 a.f.u.). The resulting number of electrons matches very well those obtained from site occupancies: 40.34 *vs.* 40.24, and 40.34 *vs.* 40.28 for FAS1 and FAS2, respectively.

Cation distribution between tetrahedral (T) and octahedral (M) sites was calculated by minimising the following function which takes into account structural and chemical data (Carbonin *et al.*, 1996):

$$F(X_i) = \Sigma_j \left((O_j - C_j(X_i)/\sigma_j\right)^2 \qquad (1)$$

where O_j is the observed quantity (a, x, e(T), e(M), and the atomic proportions from microprobe analysis), and σ_j its standard deviation. C_j is the same quantity, calculated from the eight variable parameters, that is the cation fractions of Mg, Fe^{2+}, Fe^{3+}, Al in T and M sites. Minor elements were assigned on the basis of their site preference: Mn to T, and Ti to M. Full occupancy of both sites and charge balance were required. The set of 'ideal' bond distances proposed by Della Giusta *et al.* (1996) were used to calculate T-O and M-O, and hence the calculated a and x values (Hill *et al.*, 1979). Fe^{2+} is essentially ordered in the T site; Mg and Al are ordered preferentially in T and M sites respectively, while Fe^{3+} is almost equally distributed.

Table 2 shows the cell parameters, the mean structural and chemical data and site partitioning of the two spinels here investigated, as well as those of the TS2 spinel (Della Giusta *et al.*, 1996) and SP78a spinel (Lucchesi and Della Giusta, 1997), from a websterite dyke and a chlorite schist, respectively.

Geothermometry

The Mg-Al distribution between T and M sites of natural spinels depends on the thermal history of the host rock: if cooling is very slow, Mg and Al cations strongly order in T and M sites, respectively, while fast quench, as in volcanic ejecta, preserves disordered distributions (Princivalle *et al.*, 1989; Della Giusta *et al.*, 1996; Lucchesi and Della Giusta, 1997).

The dependence of the cation distribution on temperature has been investigated by several authors. This dependence is rather complex even in simple spinels. O'Neill and Navrotsky (1983, 1984) proposed a quadratic approximation of temperature *vs.* inversion which is reasonable for magnetite, magnesioferrite and hercynite, but in other end-members the dependence is of higher degree (Della Giusta and Ottonello, 1993). Nell and Wood (1991) proposed a thermodynamic model for complex spinels (Mg, Fe^{2+})(Fe^{3+}, Al, Cr)$_2$O$_4$, which allows calculation of the cation distribution at a given temperature. Applying this model, no solution exists for the cation distribution in FAS1 and FAS2. This is not surprising, since all the quoted models rest on cation distributions measured at high temperature (i.e. higher than 650°C), and no experimental data lower than 650°C are available for the composition of interest. Anyway, all the models suggest a monotonic decrease of $Al(T)/Al_{tot}$ with temperature decrease.

Della Giusta *et al.* (1996) carried out heating experiments on spinels from a websterite dyke (sample TS2), and measured the increase of Mg-Al disordering between T and M sites with temperature. Disordering caused a strong decrease of the x-oxygen parameter, from 0.2637 to 0.2618. The above authors fitted the data of their heating experiments (650–1150°C, 1 atm.) with an empirical equation which relates the equilibrium (quenching) temperature of spinels to both bulk composition and Al distribution between the T and M sites:

$$T(°C) = C1 - C2 \cdot B + C3 \cdot B^2 \qquad (2)$$

TABLE 2. Results of the crystal structure refinements, electron microprobe compositions and cation distribution between T and M sites for FAS1, FAS2 and TS2 (Della Giusta *et al.*, 1996), and SP78a (Lucchesi and Della Giusta, 1997). B = isotropic equivalent of the anisotropic temperature factor of the tetrahedral (T) site, the octahedral (M) site and the oxygen (O) atom. Mg(T) and Al(M) = occupancies obtained deriving Mg *vs.* Fe^{2+} in T and Al vs. Fe^{2+} in M. Numbers in parentheses are the standard deviations and refer to the last digit. Total iron determined as FeO. *T*°C calculated by using the proposed thermometer (this paper)

Sample	FAS1	FAS2	TS2	SP78a
a_0	8.1072 (1)	8.1057 (1)	8.1104 (4)	8.1003 (3)
x	0.26312 (3)	0.26312 (5)	0.2636 (1)	0.2633 (3)
B (T)	0.45 (1)	0.41 (1)	0.69 (2)	0.47 (1)
B (M)	0.38 (1)	0.35 (1)	0.58 (2)	0.43 (1)
B (O)	0.54 (1)	0.49 (1)	0.69 (2)	0.56 (1)
Mg (T)	0.884 (5)	0.887 (7)	0.767 (4)	0.985 (3)
Al (M)	0.976 (3)	0.972 (4)	0.971 (3)	0.984 (3)
T-O	1.931 (1)	1.939 (1)	1.947 (1)	1.940 (4)
M-O	1.927 (1)	1.926 (1)	1.924 (1)	1.923 (2)
MgO	25.20 (6)	25.29 (9)	20.58	28.04
Al_2O_3	65.6 (3)	65.78 (3)	65.33	67.47
FeO	8.3 (2)	8.4 (3)	13.43	3.85
Cr_2O_3			0.33	0.00
TiO_2	0.07 (2)	0.07 (1)	0.04	0.00
SiO_2			0.00	0.00
MnO	0.12 (3)	0.12 (5)	0.11	0.14
NiO			0.00	0.00
ZnO			0.11	0.14
Sum	99. 29	99.66	99.93	99.67
T Site:				
Mg	0.774 (8)	0.781 (9)	0.653	0.871
Al	0.116 (3)	0.113 (3)	0.122	0.113
Fe^{2+}	0.061 (8)	0.058 (9)	0.221	0.000
Fe^{3+}	0.046 (5)	0.045 (4)	0.000	0.010
Si			0.000	0.000
Mn	0.003 (1)	0.003 (1)	0.002	0.003
Zn			0.002	0.006
Sum.	1.000	1.000	1.000	1.000
M Site:				
Al	1.788 (15)	1.791 (16)	1.813	1.811
Cr			0.007	0.000
Mg	0.149 (4)	0.143 (5)	0.118	0.121
Fe^{2+}	0.013 (3)	0.014 (4)	0.003	0.000
Fe^{3+}	0.049 (8)	0.051 (8)	0.058	0.067
Ti	0.001	0.001	0.001	0.000
Ni			0.000	0.000
Sum.	2.000	2.000	2.000	2.000
B	0.074 (2)	0.073 (2)	.086 (2)	.063 (2)
T°C	494 ±25	484 ±25	588 ±30	419 ±20

Where:

$$B = Al(T)/Al_{tot} + C4 \cdot (1 - Mg(T) - Al(T)) + C5 \cdot (2 - Al(M) - Mg(M)) \quad (3)$$

and C1 to C5 are the fitting coefficients. Note that the second term of Eqn. 3 takes into account the compositional influence of ($Fe^{2+} + Fe^{3+} + Si + Mn + Zn$) in the T site, and the third term ($Cr + Fe^{2+} + Fe^{3+} + Ti + Ni$) in the M site. Omitting these two terms, i.e. using only the K_D relative to Mg-Al distribution, it is impossible to obtain a reasonable fit of the experimental data.

Equation 2 holds only within the range of experiments and cannot yield solutions at temperatures below 650°C, due to the presence of the quadratic term. The latter temperature is the lowest at which the reordering was appreciable after three months at heating, experimentally performed by Della Giusta *et al.* (1996) and corresponds to a B value of 0.093 (Eqn. 3). Values lower than this are shown by natural spinels as TS2 (0.087; Della Giusta *et al.*, 1996), FAS1 and FAS2 (0.075 and 0.073, respectively, present work), and SP78a (0.063; Lucchesi and Della Giusta, 1997).

The above considerations suggested a revision of Eqn. 2. A satisfactory fit of the experimental data of Della Giusta *et al.* (1996) was obtained with the linear equation:

$$T(°C) = 6640 \cdot B \quad (4)$$

The new coefficients C4 and C5 of Eqn. 3 were 0.101 and 0.041, respectively. The experimental temperatures were reproduced to within 20°C(1σ), with a maximum difference of 64°C (Fig. 1) which refers to a quench from 1150°C, subject to considerable uncertainty because of the tendency for reordering during cooling (O'Neill and Navrotsky, 1983). The use of this empirical relationship is presently supported by two considerations:

(*a*) in natural Mg-Al rich spinels the main end-members are spinel$_{ss}$ and hercynite. For both, thermodynamic models suggest a decrease of $Al(T)/Al_{tot}$ with decreasing temperature;

(*b*) for the chlorite schist containing the SP78a spinel (Table 2) petrology suggests a temperature in the range 350–450°C; Eqn. 3 applied to this sample gave an intracrystalline temperature of 419±20°C (Fig. 1).

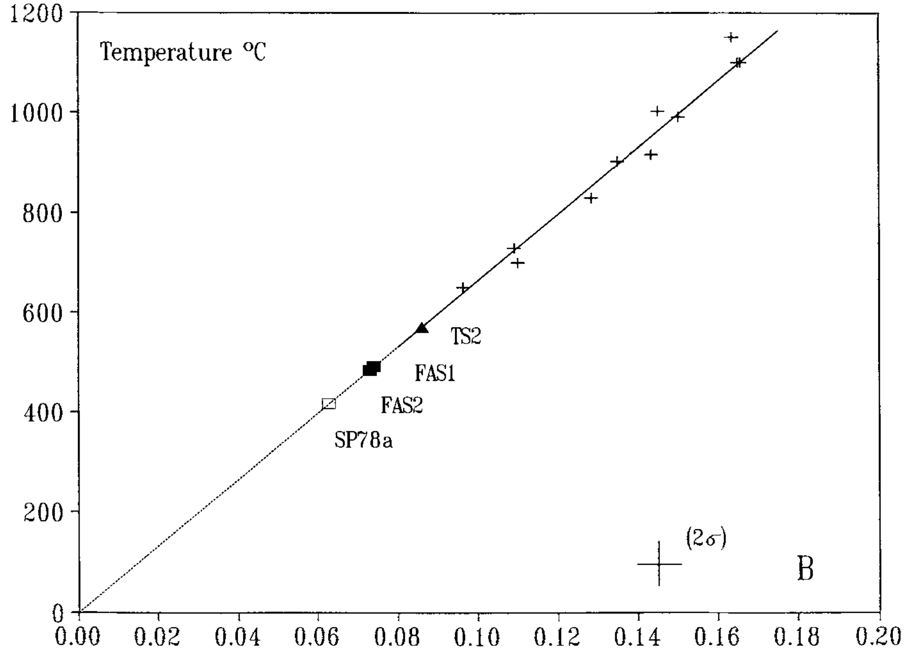

FIG. 1. B value *vs.* temperature for the heating data of TS2 spinel (crosses; Della Giusta *et al.*, 1996). The linear correlation coefficient for the solid straight line is 0.9856. The dotted line represents the low-temperature extension of the straight-line through the experimental data.

The calculated intracrystalline temperatures of spinels FAS1 and FAS2 were 494±25 and 484±25°C, respectively, i.e. 100–150°C below those (650–700°C) of their crystallisation, as estimated from silicate-carbonate mineral assemblages. This temperature differences implies Mg-Al reordering during rock cooling.

Equation 4 needs to be tested against other known petrological environments, but requires heating experiments at temperatures lower than 650°C. These heating experiments are necessary to calculate the disordering rate constants, which would allow use of the Mg-Al distributions of spinels as a geospeedometer.

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