Crystal chemistry of a suite of natural Cr-bearing spinels with $0.15 \leqslant Cr \leqslant 1.07$

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With 2 figures and 5 tables in the text

Abstract: Eight $Mg–Al–Cr–Fe$ spinels with increasing Cr content from Mt. Leura, Newer Volcanics of Victoria, Australia have been investigated. They represent a suite of spinel lherzolite nodules that suffered an increasing melting process. An accurate analysis was performed to confirm the Fd3m symmetry. Since the available cation radii are rather inaccurate for spinel structure, a new set of bond distances relative to Mg, Al, Fe^{2+}, Fe^{3+} in both tetrahedral (T) and octahedral (M) coordination has been derived from recent single crystal x-ray data on $MgAl_2O_4$ and $FeFe_2O_4$. A set of equations including these distances has been used to obtain the cation distribution, the main features of which are: a) Cr^{3+} substitutes in M both Al^{3+} and Mg^{2+}: the consequent overcharge of the oxygen is balanced through an exchange $Fe^{2+} – Al^{3+}$ in the T site; b) Fe^{2+} is ordered in the T site, and the small amount of Fe^{3+} seems to prefer the M site; c) the higher the Cr^{3+} content, the higher is the ordering of Mg^{2+} in the T site and of Al^{3+} in the M site.

In spite of the strong changes of the bulk chemistry, the ratio $(T–O)/(M–O)$ is virtually constant in the eight crystals. A comparison with previous data shows that natural spinels with similar bulk chemistry but different genetic environments, can show different cation distributions.

K e y   w o r d s : Spinel, crystal chemistry, lherzolite nodules; Mt. Leura, Victoria Australia.

Introduction

The aim of this work is to give a contribution to the knowledge of natural oxide spinels in order to understand better their crystal chemistry, which up to now has been studied mainly by synthetic binary compounds (HILL et al., 1979; YAMANAKA et al., 1983; GRIMES et al., 1983; WECHSLER et al., 1984; HILL, 1984). Only few authors performed accurate structure refinements of natural spinels (e.g. BASSO et al., 1984; FLEET, 1981 and 1982; STOUT & BAYLISS, 1975; ESSENE & PEACOR, 1983).

The spinel structure is usually described in the Fd3m space group, but a few arguments contradicting that symmetry have been recently made; they are summarized in TAKEUCHI et al. (1983). According to GRIMES et al. (1983) the symmetry of the sites occupied by the Cr^{3+} ions should be 3m (which is inconsistent with the space group Fd3m), with a consequent deviation from the conventional symmetry to an extent that depends on the Cr^{3+} content. The suite under investigation, reaching high Cr^{3+} contents, is therefore well suitable in order to test the existence of this deviation in natural spinels.

Experimental

The crystals were obtained from a suite of spinel lherzolite nodules associated with the Newer Volcanics of Victoria, Australia (IRVING, 1974; FREY & GREEN, 1974; ELLIS, 1976). Detailed petrological and crystallographic studies on the associated Ca-rich pyroxenes (DAL NEGRO et al., 1984) indicate that the selected lherzolite nodules may be considered mantle materials which suffered small to substantial degrees of partial melting. The melting process(es) would be responsible for a decrease in clinopyroxene content from 27 to 9 % volume and for an increase in the $MgCr_2O_4$ component in the coexisting spinel from 18 to 57 mol%. The analyzed crystals were selected under a petrographic microscope from rock sections about 100 μm thick obtained from the same specimens described by DAL NEGRO et al. (1984). Some crystals were carefully examined with the oscillating crystal technique for possible presence of F forbidden reflections reported by BASSO et al. (1984). However, none were observed, nor were any observed of those reported by GRIMES et al. (1983). The x-ray intensities were measured by a SIEMENS AED II four circle automated diffractometer up to 40−45 degrees of theta, using Mo monochromatized radiation, and omega scan mode. Three to six equivalent reflections were measured; the absorption correction was performed by the empirical method proposed by NORTH et al. (1968). The lattice constant was calculated by least-squares refinement of 22 accurately adjusted reflections. The same crystals used for x-ray data collection were mounted on glass slides and polished for electron microprobe analysis by means of an energy dispersive microprobe (ETEC-AUTOSCAN SEM and ORTEC EEDS spectrometer) operated at 15 kV, 10^{-10} A. A MAGIC program (COLBY, 1972) in the ORTEC MAGIC IV M version was used to convert x-ray counts into weight % of the corresponding oxides. Three to six analyses were obtained from each crystal, showing a good chemical homogeneity. The analytical results are considered accurate to within 2−5 % for major elements, and better than 10 % for minor elements. The analyses of the spinels are given in Table 1. MgO, Al_2O_3, Cr_2O_3 and FeO are the most abundant components; Fe_2O_3, calculated from the total iron as FeO to yield 3 cations on the formula A B_2O_4, is always less than 3 %, and other oxides (TiO_2, NiO, SiO_2) are present in very small amounts.

Table 1. Microprobe analyses. Total iron determined as FeO. e^- (a) and e^- (b) = total number of electrons calculated from the microprobe analyses and the site occupancies, respectively. The cation distribution (per 4 oxygens) results from the minimization process described in the text, that takes into account both the microprobe and x-ray refinement data. $K_D = Mg(M) \cdot Al(T)/Mg(T) \cdot Al(M)$.
SR = sum of the squares of the 8 normalized residuals after the minimization process.

	LE 20	LE 4	LE 5	LE 15	LE 7	LE 11	LE 13	LE 8
MgO	20.8	19.9	20.2	20.1	18.9	17.9	15.1	15.3
Al_2O_3	60.7	59.6	58.6	56.0	51.7	36.2	26.7	24.8
FeO	11.2	11.7	11.6	11.5	12.9	12.7	15.7	14.1
Cr_2O_3	7.3	8.0	8.8	11.4	15.4	32.1	41.2	44.8
NiO	0.4	0.4	0.4	0.5	0.4	0.3	0.3	0.2
TiO_2	0.2	0.2	0.2	0.3	0.3	0.2	0.3	0.2
SiO_2	0.1	0.1	0.1	0.1	0.2	0.4	0.4	0.5
Sum	100.7	99.9	99.9	99.9	99.8	99.8	99.7	99.9
Mg/Mg+Fe	0.79	0.76	0.76	0.78	0.74	0.74	0.66	0.67
Cr/R^{3+}	0.07	0.08	0.09	0.12	0.16	0.36	0.49	0.54
e^-: a)	43.2	43.6	43.8	44.4	45.9	50.5	54.7	54.9
b)	43.3	43.2	43.6	44.4	45.7	50.7	53.6	54.9
T site:								
Mg	0.580	0.582	0.601	0.591	0.568	0.632	0.609	0.619
Al	0.200	0.203	0.198	0.184	0.159	0.084	0.043	0.048
Fe^{2+}	0.212	0.210	0.196	0.220	0.253	0.258	0.323	0.306
Fe^{3+}	0.006	0.002	0.002	0.002	0.015	0.015	0.013	0.012
Si	0.002	0.003	0.003	0.003	0.005	0.011	0.012	0.015
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
M site:								
Al	1.615	1.605	1.583	1.532	1.462	1.121	0.896	0.829
Cr	0.146	0.162	0.179	0.235	0.324	0.719	0.970	1.063
Mg	0.207	0.182	0.175	0.189	0.182	0.121	0.064	0.064
Fe^{2+}	0.003	0.030	0.029	0.004	0.004	0.000	0.017	0.064
Fe^{3+}	0.017	0.009	0.022	0.024	0.014	0.028	0.039	0.006
Ni	0.008	0.008	0.008	0.010	0.008	0.007	0.007	0.005
Ti	0.004	0.004	0.004	0.006	0.006	0.004	0.006	0.004
Sum	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
$SR \cdot 10^5$	.053	.180	.046	.099	.048	.180	.350	.050
K_D	.044	.040	.036	.039	.035	.014	.005	.006

Crystal structure refinement

Symmetry

As previously mentioned, we did not detect reflections forbidden by the space group Fd3m. Anyway, since GRIMES et al. (1983) emphasize that the refinement symmetry F$\bar{4}$3m produced some significant improvements in fit of the Fd3m allowed reflections, we performed the refinements in both space groups. Special attention was payed to the Cr^{3+}-high specimens; these were refined also in the space groups suggested by HAFNER (1962) for superstructure arrangements without increase in the lattice constant, and with 1:1 and 1:3

ratios between octahedrally coordinated cations. These ratios are sufficiently well represented by specimens 11, 13, 8. The refinements were initially performed with the strategy adopted by GRIMES et al. (1983) in order to derive simultaneously a low number of parameters. But this led to absolutely unacceptable values of the site occupancies (up to 35% difference in the total number of electrons, compared with the microprobe results). Consequently all parameters were allowed to change simultaneously; in this way the results converged to the same values, within two standard deviations, in spite of the different space groups used. Moreover, the increased number of parameters in the lower symmetries never led to significant improvements of the R factor.

Concluding, we could not find arguments against the symmetry Fd3m. The crystal structure refinements were carried out using the crystallographic programs STRUCSY (copyright STOE, West Germany). The derived parameters were: scale factor, secondary extinction coefficient, oxygen positional parameter, anisotropic thermal factors, and the occupancies of Mg vs Fe in the tetrahedral T site, and Al vs Cr in the octahedral M site. No chemical constraint was applied to the site occupancies.

Scattering curves

Scattering curves relative to neutral and fully ionized atoms have been indifferently used by the authors who performed crystal structure refinements of the spinels. The choice, indeed, turned out to be rather important, since the use of different curves led to relevant differences of the site occupancies, mainly in the M site, corresponding to changes of the total number of electrons up to 5%. A detailed analysis of the reflections in the low sin ϑ/λ-range showed that this change reduces to about 1% omitting the rather weak reflection 222. The reason is evident from Table 2, where the contributions to

Table 2. Structure factors F(222) and F(113) with the contributions from the independent sites. Only F(222) undergoes strong changes when neutral (N) instead of fully ionized (I) scattering curves are used.

		F(222)	M	Ox	F(113)	T	M	Ox
LE 4	N	−7.6	+155.5	−163.1	−134.3	−62.2	−79.1	+6.9
	I	−24.4	+152.4	−176.8	−132.1	−62.5	−77.1	+7.5
LE 7	N	+4.5	+167.9	−163.4	−144.2	−65.8	−85.4	+7.5
	I	−14.2	+163.1	−177.3	−141.0	−66.1	−82.6	+7.7
LE 8	N	+63.8	+229.1	−165.3	−178.6	−69.0	−116.6	+7.1
	I	+36.4	+216.1	−179.7	−171.1	−69.3	−109.6	+7.7

the structure factor F(222) are reported for three different compositions. It must be outlined that 222 is the reflection with the maximum contribution by the oxygen atom. Due to its low sin ϑ/λ value this contribution is very sensitive to the ionization level of the oxygen atom, and causes strong variations in

Table 3. Results of the crystal structure refinements. The crystals are listed in order of increasing Cr content (see Table 1).
B = isotropic equivalent of the anisotropic temperature factor of the tetrahedral site (coordinates 1/8, 1/8, 1/8), the octahedral site (1/2, 1/2, 1/2), and the oxygen atom. – Mg (T), Al (M) = occupancies obtained deriving Mg vs Fe and Al vs Cr respectively. – R = unweighted residual factor. – N = number of reflections with $I/\sigma(I) > 3$ used in the structure refinement.
Numbers in parentheses are the standard deviations and refer to the last digit. The specimen labels refer to the same nodules investigated by DAL NEGRO et al. (1984), and PRINCIVALLE & SECCO (1985).

	LE 20	LE 4	LE 5	LE 15	LE 7	LE 11	LE 13	LE 8
a (Å)	8.1230(5)	8.1286(3)	8.1297(4)	8.1403(3)	8.1522(4)	8.2001(5)	8.2410(4)	8.2470(3)
u	0.2623(2)	0.2622(1)	0.2622(1)	0.2623(2)	0.2624(2)	0.2625(1)	0.2626(2)	0.2623(2)
B (T)	0.41	0.41	0.31	0.30	0.41	0.30	0.35	0.37
B (M)	0.34	0.35	0.26	0.25	0.32	0.21	0.26	0.29
B (O)	0.48	0.51	0.41	0.39	0.48	0.34	0.39	0.41
Mg (T)	0.77(2)	0.78(1)	0.79(1)	0.76(2)	0.72(2)	0.71(2)	0.67(3)	0.67(2)
Al (M)	0.91(3)	0.91(2)	0.88(2)	0.86(3)	0.83(3)	0.61(3)	0.50(4)	0.44(5)
T–O	1.932(2)	1.932(1)	1.932(1)	1.936(2)	1.940(2)	1.953(1)	1.964(2)	1.961(2)
M–O	1.936(2)	1.938(1)	1.938(1)	1.940(2)	1.942(2)	1.953(1)	1.962(2)	1.966(2)
R	0.026	0.016	0.018	0.027	0.025	0.019	0.040	0.021
ext	2.3E–4	2.4E–5	3.7E–5	5.0E–5	3.6E–5	8.3E–6	9.1E–6	7.3E–6
N	87	97	88	119	93	107	138	97

F(222) since the corresponding variations of the contribution by the M site are not equally relevant. The remaining low sin ϑ/λ-reflections receive weak oxygen-contributions, similar to that reported in Table 2 for 113, and hence their structure factors are less sensitive to the ionization level. An incorrect choice of the scattering curves causes clearly relevant changes of the ratio Al/Cr in the M site to minimize the contribution of 222 to the R factor. As a result, this reflection can be used to determine the most suitable ionization level that in all our specimens corresponds to scattering curves of 50 % ionized atoms, in according with the model proposed by URUSOV (1983). The results of the structure refinements are summarized in Table 3. Almost all crystals showed strong effects of secondary extinction, so in the last stage of the refinement a few strong reflections with Fo < Fc were omitted. No residual peaks appeared in the difference Fourier syntheses. The x-ray data turned out to agree quite well with the microprobe analyses: the mean difference in the total number of electrons calculated from the results of these two methods is 0.3 e⁻, with a maximum value of 1.1 e⁻ for LE 13 (Table 1). Several crystals from LE 13 nodule were tested and turned out to be of poor quality for x-ray diffraction; their R-factors stopped at about 4 %, while all the other specimens reached values less than 2.5 % (Table 3).

Cation distribution

Taking into account the results of both the chemical and crystallographic data, the cation distribution in the T and M sites can be obtained by means of

the simultaneous minimization of the squares of the following normalized residuals:

1. $(\Sigma\, A_i \cdot Z_i - ET)/ET$
2. $(\Sigma\, 0.5 \cdot B_i \cdot Z_i - EM)/EM$
3. $(\Sigma\, A_i \cdot D_i - [T-O])/(T-O)$
4. $(\Sigma\, 0.5 \cdot B_i \cdot D_i - [M-O])/(M-O)$
5. $\Sigma\, ([Ox_i\ calc - Ox_i\ obs]/Ox_i\ obs)/n$
6. $\Sigma\, (A_i - 1)$
7. $\Sigma\, (B_i - 2)/2$
8. $(\Sigma\, A_i \cdot V_i + \Sigma\, B_i \cdot V_i - 8)/8$

where A_i and B_i are the atomic fractions of the elements assigned to the T and M sites, respectively; Z_i and V_i the atomic number and valence of the elements; ET and EM the number of electrons assigned to T and M sites, as determined from the site occupancies; D_i the pure cation-oxygen bonds; (T-O) and (M-O) the measured bond distances; Ox_i obs the oxides from Table 1, Ox_i calc the oxides computed from the atomic fractions A_i and B_i during the minimization process; n is the number of the analyzed oxides.

Equations 1 and 2 take into account the T and M site populations determined by the x-ray refinement; equations 3 and 4 are essential to discriminate between cations with very similar scattering powers. It is assumed that each atomic species and its cation-oxygen bond length contribute linearly to the observed (T-O) and (M-O) distances. In equation 5 the oxides calculated during the minimization process from the atomic fractions A_i and B_i – which are the only variable parameters – are fitted against the microprobe data. The last three equations take into account the stoichiometry and the neutrality of the formula. The resulting atomic fractions A_i and B_i obviously depend on the pure cation-oxygen bonds D_i used. Beside the classical values by SHANNON (1976), a new set of distances has been optimized for spinels by O'NEILL & NAVROTSKY (1983), but both of them turned out rather inaccurate when tested against the recent data on spinel and magnetite published by YAMANAKA et al. (1983), GRIMES et al. (1983), FLEET (1982 and 1983). Table 4 reports the differences between the observed a_o and x values, and those calculated with the two sets of distances. The (T-O) and (M-O) values for the data collected at high temperatures by YAMANAKA et al. (1983) were corrected for thermal expansion according to the empirical relation by HAZEN & PREWITT (1977):

$$\alpha = C\,(0.75 - Zc/n)\ 10^{-6}\,°C$$

where C = 32.9, Zc = charge of the site, n = coordination number. The data of columns 1 to 6, Table 4, represent the best fit obtained deriving only the inversion parameter i to minimize the squares of the normalized residuals Δa_o and Δx for all the data concerning $MgAl_2O_4$ (rows 1 to 10). Clearly the a_o values calculated with both sets of distances are much higher than the values measured at room temperature (rows 1 to 3); moreover Δa_o suffers a strong decrease with the temperature of the data collection, suggesting an underestimate

Table 4. Agreement in $\Delta a_o = a_o$ calc $- a_o$ obs and $\Delta x = x$ calc $- x$ obs according to the set of bond distances used. The relations used are:

a_o calc $= [5(T-O) + \sqrt{33(M-O)^2 - 8(T-O)^2}]\, 8/11\sqrt{3}$

x calc $= (R^2/4 - 2/3 + \sqrt{11\, R^2/48 - 1/18})/(2R^2 - 2)$

$R = (M-O)/(T-O)$

Rows 1 to 10 refer to $MgAl_2O_4$: 1 GRIMES et al. (1983); 2 to 10 YAMANAKA et al. (1983), data collected at temperatures from 25 to 1660 °C; 3 quenched from 1200 °C. Rows 11 and 12 refer to natural magnetites by FLEET (1981 and 1982). * indicates a minimization process terminated without convergence.

	SHANNON			O'NEILL			This paper		
	Δa_0	Δx	i	Δa_0	Δx	i	Δa_0	Δx	i
1	.0050	−.0003	.12	.0081	−.0003	.12	−.0004	−.0003	.18
2	.0102	.0000	.14	.0133	.0000	.21	.0013	.0000	.20
3	.0118	.0000	.21	.0136	.0000	.27	.0014	.0000	.25
4	.0068	.0000	.15	.0097	.0000	.21	.0002	.0000	.20
5	.0031	.0000	.12	.0066	.0000	.18	.0004	.0000	.17
6	.0034	.0000	.12	.0067	.0000	.19	.0031	.0000	.17
7	.0049	.0000	.18	.0070	.0000	.24	.0055	.0000	.22
8	−.0052	.0000	.21	.0038	.0000	.26	.0026	−.0001	.24
9	−.0073	−.0003	.22	−.0065	−.0002	.27	.0031	−.0001	.25
10	−.0106	−.0003	.24	−.0103	−.0002	.29	.0032	−.0004	.26
11	.0646	−.0023	1.0*	.0038	−.0017	1.0*	−.0010	−.0002	.90
12	.0657	−.0021	1.0*	.0049	−.0015	1.0*	−.0010	−.0001	.92

of the thermal expansion. The minimization process was then repeated deriving the inversion parameter, the bond distances of Mg^{IV}, Mg^{VI}, Al^{IV} and Al^{VI}, and the fitting parameter C of the thermal expansion correction. The Δa_o values almost halved, but a definitely better agreement was obtained allowing the C parameter to take independent values for the T and M coordinations. Table 4, columns 7 to 9, reports the final data; the fitting parameter C assumed the values 31.7 and 41.7 for T and M coordinations, respectively. It is interesting to note that the inversion parameter i relative to rows 3 and 9, which refer to the same crystal quenched from 1200 °C, and measured at 1230 °C, are always equal. This means that the cation distribution in spinel is easily quenchable. The same calculations were performed for the two magnetites investigated by FLEET (1981 and 1982). The best fit for magnetite 2741 was obtained with equal amounts of Mg in T and M sites (total Mg = 0.04 atoms). The Mg^{IV} and Mg^{VI} bond distances were taken from the previous results on $MgAl_2O_4$. Table 5 compares these new distances with the former ones. These distances were inserted in the previously described equations; as far as Cr^{3+}, Ni^{2+}, Ti^{4+} and Si^{4+} are concerned, we retained the distances by O'NEILL & NAVROTSKY (1983). Moreover, on the basis of their very strong site-preference energies (URUSOV, 1983; O'NEILL & NAVROTSKY, 1984; WECHSLER et al., 1984) Cr^{3+} has been assigned only to the M site, and Si^{4+} only to the T site; Ni^{2+} and Ti^{4+} have been assigned only to the M site, taking into account the inversion parameters of the relative binary spinels reported by HILL et al. (1979).

Table 5. The bond distances used in the present paper (C) compared to those given by
SHANNON (1976) and O'NEILL & NAVROTSKY (1983) in columns (A) and (B), respectively.

		A	B	C
$(Mg-O)$	T	1.95	1.965	1.960
$(Mg-O)$	M	2.10	2.095	2.090
$(Al-O)$	T	1.77	1.77	1.770
$(Al-O)$	M	1.915	1.910	1.908
$(Fe^{2+}-O)$	T	2.010	1.995	2.010
$(Fe^{2+}-O)$	M	2.160	2.120	2.120
$(Fe^{3+}-O)$	T	1.870	1.865	1.872
$(Fe^{3+}-O)$	M	2.025	2.025	2.009

Random values were initially assigned to all the atomic fractions. The calcula-
tions were performed with MINUIT, a CERN library computer program by
JAMES & ROSS (1975). The results are reported in Table 1, together with SR, the
sum of the normalized square residuals at the end of the minimization cycles.
SR always reached values less than 4×10^{-6}, and the eight residuals randomly
assumed positive or negative values, suggesting a comparable reliability of all
the data entering the cation distribution determination.

Discussion

The eight specimens represent successive stages of a process of partial melting
suffered by a spinel lherzolite; a comparative analysis of their cation distribu-
tions can consequently highlight the crystal chemical response of the spinel
structure during the evolution from an originally Mg–Al rich term towards
Mg-chromites. The changes occurring in the cation distribution over the two
distinct crystallographic sites are reported in Fig. 1 as a function of Cr/R^{3+},
where $R^{3+} = Cr^{3+} + Fe^{3+} + Al^{3+} + Ti^{4+}$. It is to be noted that the increase of
Cr^{3+} in the M site is accompanied not only by a depletion in Al^{3+}, but also in
Mg^{2+}. The consequent overcharge of the unique independent oxygen is bal-
anced by the decrease in Al^{3+} also in the T site, where an equal amount of Fe^{2+}
substitutes for Al^{3+}. The only cation which remains virtually constant is
$Mg^{2+}(T)$, with an average value of 0.59 atoms per formula unit. $Mg^{2+}(M)$ de-
creases by about 75 % while $Al^{3+}(M)$ decreases only by ca. 50 % from sample
20 to sample 8. This means that, with increasing of Cr^{3+}, there is a tendency of
Al^{3+} to be ordered in the M site and Mg^{2+} in the T site. Increasing melting has,
therefore, the effect of lowering the degree of $Mg^{2+}–Al^{3+}$-inversion in the
spinel structure of the residual assemblage. The highest inversion values are
present in the spinels of the undepleted nodules, with up to ca. ¼ of Mg^{2+} in
the "wrong" octahedral site. In Fig. 2 the distribution coefficient K_D relative to
Mg–Al has been plotted vs Cr/R^{3+} and the trend of the ordering shows that
this phenomenon takes place quite rapidly at low range of Cr/R^{3+} values
(< 0.20). The ordering process that follows the increase in Cr^{3+} content, that is
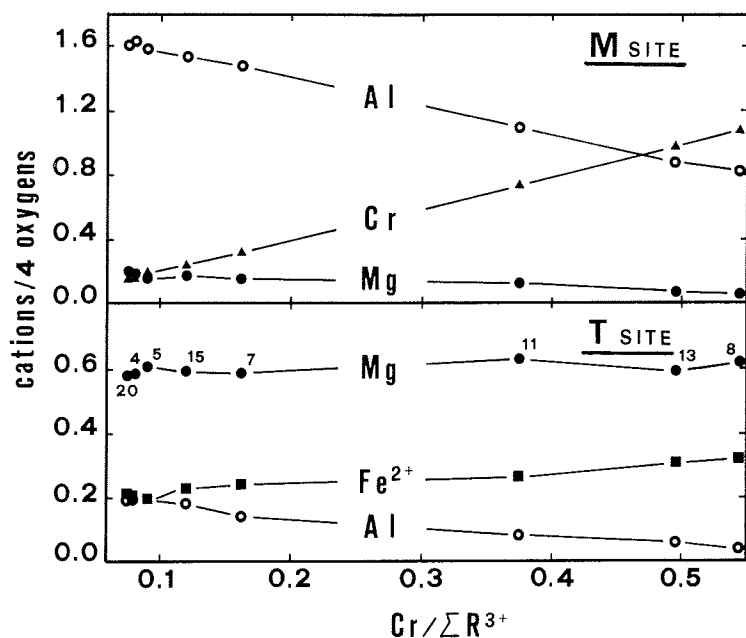the tendency of Mg^{2+} to occupy the T site and Al^{3+} the M site, is in agreement

Fig. 1. Cation distribution over the T and M sites as a function of Cr/R^{3+}. Due to their very small amounts (see Table 1) the $Fe^{3+}(M)$, $Fe^{3+}(T)$ and $Fe^{2+}(M)$ contents are not plotted here.

with the theories on the octahedral site-preference energy, which is much higher for Cr^{3+} than for Al^{3+} and Mg^{2+}, respectively (URUSOV, 1983). On the other hand, there is a systematic ordering of Fe^{2+} in the T site and a moderate preference of the small amount of Fe^{3+} for the M site. This is consistent with the results of OSBORNE et al. (1981), who found no evidence for either $Fe^{3+}(T)$ or $Fe^{2+}(M)$ in synthetic chromites and Cr-bearing spinels. We must outline that several of the $Fe^{2+}(M)$ and $Fe^{3+}(T)$ non-zero values in our results are believed to be of the same magnitude as that of their error.

It is interesting that the described ordering process maintains the ratio (T−O)/(M−O) at a constant value near to 1, that is the positional parameter x of the oxygen atom is almost constant in spite of the relevant changes of the bulk chemistry.

The ordering trend previously described is also exhibited by the Mg−Al−Fe−Cr spinels from the Balmuccia peridotite (BASSO et al., 1984) whose Cr content ranges from 0.01 to 0.22 a.f.u. However, with respect to the presently investigated spinels with a similar Cr content, their K_D values are never greater than 0.01, corresponding to a much higher Mg−Al ordering (Fig. 2).
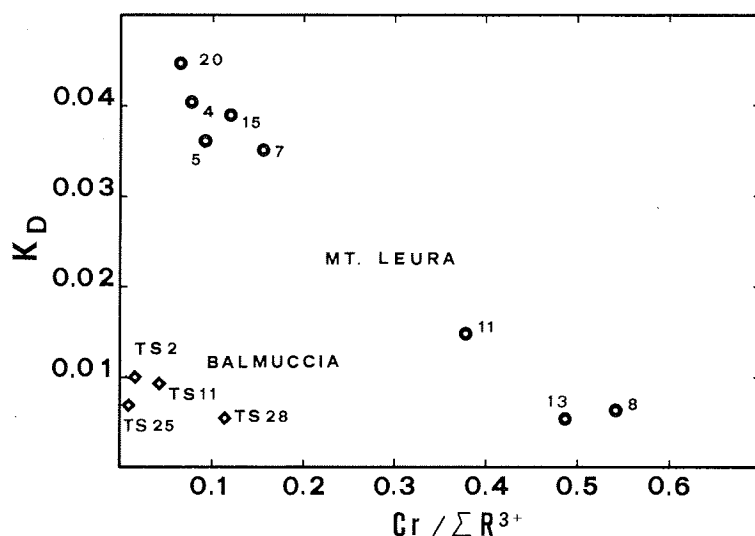
Fig. 2. Variation of the $Mg^{2+}-Al^{3+}$ ordering as a function of Cr/R^{3+}. K_D = $Mg(M) \cdot Al(T)/Mg(T) \cdot Al(M)$. The spinels from Mt. Leura, Newer Volcanics of Victoria, parallel the Balmuccia peridotite spinel trend at higher K_D values. The cation distribution of the Balmuccia spinels has been recalculated using the method described in this paper.

Concluding remarks

1. The conventional symmetry Fd3m is confirmed in this suite of natural spinels. An incorrect ionization level of the scattering curves can lead to wrong site occupancies, mainly in the M site, when the reflections with low sin ϑ/λ, including 222, are used in the structure refinement. When the 222-reflection is strong enough to be measured and is not affected by Renninger effect, it can be used to choose the correct scattering curves.

2. A new set of bond distances relative to spinels has been optimized using recent data on $MgAl_2O_4$ and $FeFe_2O_4$. The fitting of the high temperature data by YAMA-NAKA et al. (1983) led also to new values of the fitting parameter in the empirical equation of the thermal expansion coefficient given by HAZEN & PREWITT (1977).

3. The possibility of quenching different cation distributions evidenced by the experimental results of YAMANAKA et al. (1983) on synthetic spinel, is also shown by natural crystals. This is evident comparing the difference of K_D between specimens of very similar bulk chemistry, but different genetic environment, like TS 28 and LE 15 (Fig. 2).

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