# The behaviour of Mn in amphiboles: Mn in synthetic fluor-edenite and synthetic fluor-pargasite

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**Abstract:** The crystal structures of two synthetic C2/m amphiboles, manganoan fluor-edenite Na<sub>1.06</sub>(Ca<sub>1.41</sub>Na<sub>0.12</sub>Mn<sub>0.47</sub>)(Mg<sub>4.44</sub>Mn<sub>0.41</sub>1Al<sub>0.15</sub>)(Si<sub>6.91</sub>Al<sub>1.09</sub>)O<sub>22</sub>F<sub>2</sub>, a = 9.829(4), b = 18.024(9), c = 5.284(2) Å,  $\beta = 104.66(2)^{\circ}$ , and manganoan fluor-pargasite (Na<sub>0.96</sub>Ca<sub>0.13</sub>)(Ca<sub>1.51</sub>Mn<sub>0.49</sub>) (Mg<sub>3.47</sub>Mn<sub>0.73</sub>Al<sub>0.80</sub>)(Si<sub>5.95</sub>Al<sub>2.05</sub>)O<sub>22</sub>F<sub>2</sub>, a = 9.812(4), b = 17.926(6), c = 5.308(3) Å,  $\beta = 105.10(3)^{\circ}$ , have been refined to *R* indices of 2.0 % and 1.4 %, respectively, using MoK $\alpha$  X-ray data. Site-scattering refinement and electron-microprobe data both indicate that there is a large amount (~ 0.50 *apfu*) of Mn<sup>2+</sup> at the *M*(4) site in each synthetic amphibole. C-group Mn<sup>2+</sup> shows the ordering pattern *M*(2) >> *M*(3) in these amphiboles as in many natural sodic-calcic and alkali amphiboles. This behaviour is significantly different from that of Fe<sup>2+</sup> which shows the ordering pattern *M*(1) ≤ *M*(3) in Mn-poor calcic, sodic-calcic and alkali amphiboles. The presence of significant Ca at the A site in F-rich pargasite is also confirmed.

Key-words: amphibole, crystal-structure refinement, manganese, synthesis.

# Introduction

Manganese can be a significant component in all of the major groups of amphiboles, and yet its behaviour is not very well known, particularly when it is in the divalent state. As  $Mn^{2+}$  shows a strong geochemical coherence with Fe<sup>2+</sup>, the problem of adequately characterizing the distribution of  $Mn^{2+}$  in the amphibole structure is rather intractable because of the similarity in X- ray scattering factors of Mn and Fe. The small size of most amphibole crystals with appropriate compositions precludes the use of neutron diffraction to distinguish between Mn and Fe. The fact that the Mössbauer spectra of most complex natural amphiboles cannot adequately be resolved prevents combined crystal-structure refinement and Mössbauer spectroscopy from being used to resolve the distribution of Mg, Fe and Mn over the octahedrally coordinated sites in

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amphiboles. Site-scattering refinement coupled with crystal-chemical analysis (Ungaretti, 1980; Hawthorne, 1983) can resolve this problem in principle, but can be defeated in some cases by the complexity of natural amphibole compositions. This problem can usually be overcome by making some 'reasonable assumptions' about the ordering behaviour of one or more cation species. In such cases, the accuracy of the result depends on the accuracy of these reasonable assumptions, and a general knowledge of the ordering behaviour of major ionic species in amphiboles is important in assessing the accuracy of the resultant site-populations. Consequently, we have focused our attention on amphiboles in which Mn<sup>2+</sup> is the principal transition metal. Oberti & Ghose (1993) and Oberti et al. (1993) characterized the ordering behaviour of Mn<sup>2+</sup> in alkali and sodic-calcic amphiboles, respectively. Here, we examine the behaviour of Mn<sup>2+</sup> in synthetic calcic amphiboles manganoan fluor-edenite (MFE) and manganoan fluor-pargasite (MFP).

## Experimental

## Synthesis

The intention of the syntheses was to grow crystals large enough for single-crystal structure refinement by slowly cooling from a stochiometric melt, a technique which generally works well for congruently-melting compounds.

Dry mixtures of nominal fluor-amphibole stoichiometry were prepared from commercial reagent-grade oxides and other materials (NaF, CaF<sub>2</sub>, CaCO<sub>3</sub>, MnCO<sub>3</sub>, MgO, y-Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> glass) according to the nominal compositions specified in the following. After weighing out components, mixtures were blended by hand for 5 minutes and ground in a powered alumina mortar under alcohol for 1 hour. Mixtures were dried and decarbonated overnight at 1000°C. Fluoramphibole charges consisted of 20 to 40 mg of mix, sealed by welding into flattened 4 x 23 mm Pt tubes. The experiments were done at 1 atm, starting at 1200°C and cooled to 770°C at a cooling rate of 1.2°C/h for 15 days. As these were intended as reconnaissance experiments, no attempt was made to control oxygen fugacity; however, octahedral-site geometries clearly show that oxidation to Mn<sup>3+</sup> did not occur. Further experimental details are given by Raudsepp *et al.* (1991).

Crystal MFP (pink to reddish, roughly 0.18 x 0.16 x 0.10 mm in size) comes from sample FMg3MnPA-A2 (nominal composition NaCa<sub>2</sub>Mg<sub>3</sub>MnAlSi<sub>6</sub>Al<sub>2</sub>O<sub>22</sub>F<sub>2</sub>); the run product contains about 50 % phlogopite, 40 % amphibole, the remainder being clinopyroxene and cristobalite.

Crystal MFE (pink, roughly 0.23 x 0.16 x 0.10 mm in size) comes from sample FMg3MnKA-A1 (nominal composition NaCaNaMg3MnAlSi7 AlO<sub>22</sub>F<sub>2</sub>); the run product contains 70 % amphibole, the remainder being clinopyroxene and plagioclase. The deviations from the expected stoichiometry are discussed in the following.

#### X-ray data collection

Crystals were mounted on a Philips PW-1100 four-circle diffractometer and examined with graphite-monochromatized MoK $\alpha$  X-radiation; crystal quality was assessed via the profile and width of Bragg diffraction peaks. Unit-cell dimensions were calculated from least-squares refinement of the *d* values obtained from 50 rows of the reciprocal lattice by measuring the centroid of gravity of each reflection and of the corre-

Table 1. Miscellaneous crystallographic information for synthetic manganoan fluor-edenite (MFE) and synthetic manganoan fluor-pargasite (MFP).

	MFE	MFP		MFE	MFP			
Space group	C2/m	C2/m						
a (Å)	9.829(4)	9.812(4)	Total Ref.	1375	1371			
ь (Å)	18.024(9)	17.926(6)	$[ (obs) > 5\sigma( )]$	757	965			
c (Å)	5.284(2)	5.308(3)						
β(°)	104.66(2)	105.10(3)	Final R(all)	5.5%	2.8%			
V (Å <sup>3</sup> )	905.6	901.4	Final R(obs)	2.0%	1.4%			
$R = \Sigma( F_0  -  F_c ) / \Sigma  F_0 $								

Table 2. Final positional parameters and equivalent isotropic displacement parameters  $(Å^2)$  for MFE and MFP\*.

	x	У	z	B <sub>eq.</sub>
0(1)	0.11109	0.08493	0.21840	0.66
	0.10757	0.08763	0.21490	0.83
O(2)	0.12030	0.17079	0.72608	0.78
	0.11940	0.17303	0.73483	0.81
O(3)	0.10460	0	0.71264	0.89
	0.10486	0	0.71233	0.98
O(4)	0.36555	0.24881	0.78522	1.09
	0.36929	0.25143	0.78655	1.07
O(5)	0.34975	0.13632	0.10108	1.10
	0.35293	0.14081	0.11259	1.06
O(6)	0.34669	0.11598	0.59908	1.10
	0.34603	0.11656	0.60869	1.20
0(7)	0.34495	0	0.27958	0.99
	0.34403	0	0.27491	1.06
T(1)	0.28276	0.08428	0.29818	0.49
	0.28308	0.08548	0.30233	0.47
T(2)	0.29062	0.17140	0.80456	0.59
	0.29281	0.17301	0.81272	0.57
<b>M</b> (1)	0	0.08881	1/2	0.57
	0	0.09012	1/2	0.63
M(2)	0	0.17688	0	0.66
	0	0.17613	0	0.52
M(3)	0	0	0	0.59
	0	0	0	0.58
<i>M</i> (4)	0	0.27573	1/2	1.16
	0	0.27900	1/2	0.86
M(4')	0	0.25212	1/2	0.73
	0	0.26570	1/2	1.03
А	0	1/2	0	2.51
	0	1/2	0	2.18
A(m)	0.0441	1/2	0.1024	2.33
	0.0442	1/2	0.0997	2.37
A(2)	0	0.4734	0	2.54
	0	0.47227	0	2.66

 $^{\star}$  MFE and MFP are the upper and lower sets of parameters, respectively

sponding antireflection in the  $\theta$  range between -30 and +30°. Intensity data were collected for the monoclinic equivalent pairs (*hkl* and *hkl*) in the  $\theta$  range 2 <  $\theta$  < 30°. Intensities were then corrected for absorption, Lorentz and polarization effects, averaged and reduced to structure factors. Reflections with I  $\geq$  5 $\sigma$ (I) were considered as observed during structure refinement.

## Structure refinement

Structure-refinement procedures were as described in Oberti *et al.* (1992) following the model of Ungaretti (1980). Refinement information and final R values are given in Table 1. Atomic positions and isotropic displacement factors are given in Table 2, refined scattering

powers in Table 3, and selected interatomic distances and angles in Table 4; structure factors may be obtained from the authors (or through the E.J.M. Editorial Office, Paris).

#### **Electron-microprobe analysis**

Following collection of the X-ray intensity data, the same crystals were mounted in epoxy, polished, carbon-coated and analyzed with a fully automated Cameca SX-50 electron microprobe according to the procedure of Raudsepp *et al.* (1991). Ten points were analyzed and the average compositions are given in Table 5 together with the unit formula calculated on the basis of 22 oxygen atoms and assuming 2 F atoms.

# **Comparison of SREF and EMPA results**

The scattering powers at the cation sites were refined unconstrained, and the resulting occupancy values provide the number of electrons at each site, calculated for neutral atoms. Summing over all sites corresponding to the A-, B- and C-group cations of the standard chemical formula gives the values for these three groups. The formula unit calculated from the electron-microprobe analysis provides an independent evaluation of the equivalent electron content of the A-, B- and C-groups, and a comparison of these two sets of values is given in Table 3. The numbers of electrons obtained by both methods are generally in very close agreement: the overall difference is less than 2 %. The higher (positive) difference observed for the C-group cations in

Table 3. Refined site-scattering values (electrons per formula unit) and equivalent electrons (EMP) from the unit formulae of Table 5.

	MFE	MEP
<i>M</i> (1)	26.30	27.96
M(2)	29.80	30.74
M(3)	12.78	13.47
$\Sigma[M(1), M(2), M(3)]$	68.88	72.17
EMP [M(1),M(2),M(3)]	65.59	70.36
$\mathcal{M}(4) + \mathcal{M}(4')$	40.57	42.16
EMP M(4)	41.29	42.44
A	10.74	12.11
EMP A	11.00	12.12
Σ SREF	120.19	126.45
Σ ΕΜΡ	117.88	124.92

	MFE	MFP		MFE	MFP
7(1)-0(1)	1.632	1.663	M(2)-O(1) x2	2.152	2.075
7(1)-0(5)	1.657	1.682	M(2)-O(2) x2	2.091	2.053
7(1)-0(6)	1.656	1.677	M(2)-O(4) x2	2.017	1.964
<i>T</i> (1)-O(7)	1.650	1.665	<m(2)-o></m(2)-o>	2.087	2.031
< 7(1)-0>	1.649	1.672			
			M(3)-O(1) x4	2.057	2.063
T(2)-O(2)	1.620	1.643	M(3)-O(3) x2	2.038	2.051
T(2)-O(4)	1.593	1.616	< <i>M</i> (3)-O>	2.050	2.059
7(2)-0(5)	1.653	1.651			
7(2)-O(6)	1.668	1.663	M(4)-O(2) x2	2.385	2.403
< T(2)-0>	1.633	1.643	M(4)-O(4) x2	2.285	2.296
			M(4)-O(5) x2	2.750	2.614
M(1)-O(1) x2	2.058	2.059	M(4)-O(6) ×2	2.599	2.564
M(1)-O(2) x2	2.072	2.091	< <i>M</i> (4)~0>	2.505	2.469
M(1)-O(3) x2	2.073	2.082			
< <i>M</i> (1)-O>	2.068	2.077	A-0(5) x4	2.984	3.043
			A-0(6) x4	3.084	3.054
0(5)-0(6)-0(5)	164.2	161.2	A-0{7) x4	2.376	2.374
7(1)-O(5)-7(2)	135.4	133.2	<a-0></a-0>	2.902	2.914
$T{1}-O{6}-T{2}$	136.4	137.3			
T{1}-O(7)-T(1)	134.1	133.9			

Table 4. Selected interatomic distances (Å) and angles (°) for MFE and MFP.

\* standard deviations are  $\leq 1$  in the last digit

MFE (5 %) couples with negative differences for the A- and B-group cations; this pattern has been taken into account during the calculation of the site populations reported in Table 6.

Table 5. Results of electron-microprobe analysis of MFE and MFP.

	MFE	MFP
SiO <sub>2</sub>	wt% 48.37	40.32
Al <sub>2</sub> O <sub>3</sub>	7.35	16.39
MgO	20.83	15.77
MnO	7.37	9.96
CaO	9.20	10.36
Na <sub>2</sub> O	4.27	3.37
F	4.87	4.53
O≂F	2.05	1.91
Sum	100.21	98.79
Si	6.909	5.947
AI	1.091	2.053
Sum	8.000	8.000
AI	0.146	0.796
Mn	0.892	1.224
Mg	4.435	3.468
Sum	5.473	5.488
Mn	0.473	0.488
Ca	1.408	1.637
Na	0.119	0.000
Sum	2.000	2.125
Ca	-	0.125
Na	1.064	0.964
Sum	1.064	1.089
F	2.000	2.000

## Comparison with the nominal compositions

As shown by both EMPA and SREF, there are significant deviations from the stoichiometry of the starting mixtures. For crystal MFP, the low Ca content is a consequence of the strong preference of  $Mn^{2+}$  for the B-sites, as it will be discussed later; <sup>C</sup>Al is also lower than expected. On the other hand, crystal MFE is definitely off-composition, so as to be classified as edenite instead of the expected katophorite. In particular, the very low <sup>C</sup>Al content is paralleled by the very low <sup>B</sup>Na content. These deviations have most probably to be ascribed to crystal-chemical constraints due to the difference in the ionic radii between Al and Mn<sup>2+</sup> in 8-fold coordination, respectively

#### Site populations

Combination of the results of the site-scattering refinement and electron-microprobe analysis allows site populations to be derived (Table 6) according to Hawthorne *et al.* (1995). Boschmann *et al.* (1994) refined the structure of synthetic fluor-edenite, and Oberti *et al.* (1995c) refined the structure of synthetic fluor-pargasite; these data provide useful comparisons with the results of the present work.

Table 6. Site populations (apfu) in MFE and MFP.

····	MFE	MFP
7(1)	1.04 Al + 2.96 Si	1.90 Al + 2.10 Si
T{2}	4.00 Si	0.09 Al + 3.91 Si
<i>M</i> (1)	1.85 Mg + 0.15 Mn	1.68 Mg + 0.32 Mn
M(2)	0.18 Al + 1.52 Mg + 0.30 Mn	0.86 Al + 0.76 Mg + 0.38 Mn
M(3)	0.98 Mg + 0.02 Mn	0.94 Mg + 0.06 Mn
<i>M</i> (4)	0.44 Mn + 1.42 Ca + 0.14 Na	0.48 Mn + 1.52 Ca
A	1.00 Na	0.13 Ca + 0.87 Na

## A-group sites

In crystal MFE, both site-scattering refinement and electron-microprobe analysis indicate complete occupancy of the A site by Na. The pattern of electron density in the A cavity is shown in Fig. 1; the Na is split approximately equally between the A(2) and A(m) sites, as was found for fluor-edenite by Boschmann *et al.* (1994).

In crystal MFP, the *nominal* content of the A site is 1.0 Na. However, site-scattering refinement gives a value of 12.11 epfu at this site. indicating that a stronger X-ray scatterer than Na must also occur at the A site. The unit formula calculated from the electron-microprobe analysis indicates an excess of Ca over that required to fill the M(4) site after assignment of excess Cgroup cations to B-group sites. If the slight excess of Na (by EMPA) is ignored, the electron contents of the A site by SREF and by EMPA are nearly identical (Table 3). Thus there is a significant amount of Ca (0.10 apfu) at the A site in MFP. The results for both MFE and MFP exactly parallel the results of Boschmann et al. (1994) and Oberti et al. (1995c) on synthetic fluoredenite and synthetic fluor-pargasite, respectively: the synthetic edenite crystals have the A site occupied just by Na, whereas the synthetic pargasite crystals have significant Ca at the A site.

## **B**-group sites

There are two sites that can accommodate the *B*-group cations, the M(4) site which can be occupied by Ca and Na, and the M(4') site which can be occupied by Mn<sup>2+</sup>, Fe<sup>2+</sup> and Mg [*cf.* Oberti *et al.* (1993) for more details]. For both MFE and MFP, site-scattering refinement showed significant occupancy of the M(4') site, indicating significant amounts of Mn and

possibly Mg at this site. This is in accord with the results of electron-microprobe analysis (Table 5) which indicates a significant amount of excess C-group cations (approximately 0.45 apfu) that must be assigned to the *B*-group. Assuming that this excess amount of C-group cations is actually Mn<sup>2+</sup>, there is almost exact agreement between the SREF and EMPA values of the scattering at the M(4) + M(4') sites (Table 3). The occupancy of M(4') by a considerable amount of Mn<sup>2+</sup> is immediately apparent from the SREF value for MFP as the refined M(4) + M(4') scattering (42.16 *epfu*) exceeds that from 2.0 apfu of Ca (= 40.0 epfu). The same feature is not as apparent for MFE. Although significant Mn occurs at M(4'), there is also sufficient Na to maintain the total M(4) + M(4') scattering close to 40 epfu (Table 3).

## C-group sites

There are three atomic species, Mg, Al and Mn, that occur at the M(1), M(2) and M(3) sites. On the basis of the observed site-scattering (Table 3), the unit formulae (Table 5) and the mean bond-lengths (Table 4), the site populations were assigned as shown in Table 6, such that they fit equally well to the site-scattering, overall electroneutrality requirement, mean bond-length and chemical composition data, using the mean bond-lengths in synthetic fluor-pargasite (Oberti *et al.*,



Fig. 1. Diff<u>e</u>rence Fourier map through the (A2/m) site parallel to (201) for synthetic manganoan fluor-edenite. The contour interval is  $1 e/Å^3$  and the broken line is the zero contour; the tick marks at the top of the figure denote 1 Å.

[ · · ·	M(1)			M(2)			M(3)			O(3)		Ref.		
	Mg	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Mg	AI	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Mg	Fe <sup>2+</sup>	Mn <sup>2+</sup>	ОН	F	
MR1	1.90	0.10	-	1.34	0.08	0.46	0.12	-	0.98	0.02	-	1.67	0.33	(1)
MR2	1.92	0.08	-	1.36	0.04	0.46	0.14		0.98	0.02	~	1.66	0.34	(1)
MR3	1.90	0.10	-	1.38	0.04	0.46	0.12	-	0.98	0.02	-	1.70	0.30	(1)
MR4	1.86	0.14	-	1.08	0.06	0.82	0.04	-	0.98	0.02	-	1.65	0.35	(1)
OG*	1.84	-	0.16	1.12		0.22	-	0.66	0.88	-	0.06	1.60	0.40	(2)
MFE	1.85	-	0.15	1.52	0.18	0.30	-	-	0.98	-	0.02	-	2.00	(3)
MFP	1.68		0.32	0.76	0.86	0.38	-	-	0.94	~~	0.06	-	2.00	(3)

Table 7. Selected site-populations (apfu) in Mn-rich amphiboles.

References: (1) Oberti et al. (1993): (2) Oberti & Ghose (1993): (3) this study. \* M(3) site-population includes 0.06 Li.

1995c) and synthetic fluor-edenite (Boschmann *et al.*, 1994) as the ideal values for complete Mg occupancy of the M(1,2,3) sites.

## **T**-group sites

The mean interatomic distances (Table 4) and unit formulae (Table 6) indicate significant Al at the tetrahedral sites. In MFE, the <T(1)-O> and <T(2)-O> distances are conformable with no more than 1.06 Al *apfu* at T(1) and complete occupancy of T(2) by Si, respectively (Table 6). In MFP, the <T(2)-O> distance indicates significant Al occupancy of T(2); this is in accord with the <T(1)-O> distance (Table 4) which indicates no more than 1.90 Al *apfu* at the T(1) site (Oberti *et al.*, 1995b). Similar partial disorder of <sup>[4]</sup>Al over T(1) and T(2) also occurs in synthetic fluorpargasite (Oberti *et al.*, 1995c).

## Ordering

#### **B**-group sites

The ideal compositions of F-edenite and Fpargasite have the *B*-group sites completely occupied by Ca. However, site-scattering refinement and electron-microprobe analysis show that both these amphiboles have nearly 0.50 *apfu* of Mn at the M(4') site. We found this result to be somewhat surprising. It is well established that Mn<sup>2+</sup> strongly favours the *B*-group sites in ferromagnesian amphiboles (Papike *et al.*, 1969; Ghose & Hexiong, 1989) and both chemical and structural work (Ghose *et al.*, 1973; Oberti & Ghose, 1993; Schau et al., 1993) have shown over 0.5 apfu of Mn<sup>2+</sup> at the M(4') site in alkali amphiboles. Oberti et al. (1993) have shown that manganoan richterite (i.e, a sodic-calcic amphibole) has Mn<sup>2+</sup> strongly ordered at *B*-group sites, with M4' site population of up to  $0.35 \text{ Mn}^{2+} apfu$ . Several hundred calcic amphiboles have been refined at the CSCS over the past fifteen years, and only minor Mn<sup>2+</sup> at the B-group sites has been found. Those data are in accord with a trend of decreasing Mn<sup>2+</sup> with decreasing Na content at the B-group sites in alkali and sodic-calcic amphiboles, and led us to suspect that synthetic calcic amphiboles would have only a small amount of  $Mn^{2+}$  at M(4'). This is certainly not the case for both synthetic amphiboles examined here. The  $Mn^{2+}$  site-populations of *B*-group sites exceed those of the natural manganoan richterite crystals of Oberti et al. (1993) and approach that of a Mn<sup>2+</sup>-rich alkali amphibole described by Oberti & Ghose (1993). Presumably it is geochemical factors, rather than crystal-chemical factors, that inhibit the crystallization of natural calcic amphiboles with large amounts of Mn2+ at the B-group sites, as it is rare to find Mn- and Ca-rich environments with Mn >> Fe.

#### C-group sites

The work of Oberti *et al.* (1993), Oberti & Ghose (1993) and this study provide significant information as to the behaviour of  $Mn^{2+}$  when it is a C-group cation. The site populations of the C-group cations for the amphiboles from these studies are summarized in Table 7. In all these amphiboles,  $Mn^{2+}$  preferentially occupies the M(2) site relative to the M(1) and M(3) sites. This

ordering pattern occurs irrespective of the anionic composition at O(3), as both the hydroxy-richterites of Oberti et al. (1993) and the synthetic fluor-amphiboles of this study show Mn<sup>2+</sup> strongly ordered at the M(2) site. Regarding the distribution between M(1) and M(3), in the manganese-rich alkali amphibole of Oberti & Ghose (1993) and the fluor-amphiboles of this work, Mn<sup>2+</sup> clearly shows preferential ordering at the M(1) site (Table 7). This behaviour is significantly different from the ordering behaviour of Fe<sup>2+</sup> in Mn-poor calcic, sodic-calcic and alkali amphiboles in which Fe<sup>2+</sup> shows a strong preference for M(3) relative to M(1) (e.g., Hawthorne et al., 1993, Fig. 3). Thus, the ordering pattern of Mn<sup>2+</sup> over the C sites in non-ferromagnesian, Li-free amphiboles is:  $M(2) \gg M(1) \gg M(3)$ . In Li-bearing amphiboles, Mn<sup>2+</sup> tends to order at M(3); this is probably due to the entrance of the (large) Li<sup>+</sup> at M(3), which is paralleled by the entrance of additional (small) high-charged cations at M(2) in order to achieve local chargebalance (Hawthorne et al., 1996a).

## A-group sites

As already discussed, MFE has no Ca at the A site whereas MFP has a significant amount of Ca at the A site. This is in accord with the occurrence of Ca at the A site in some pargasites from marbles. Hawthorne et al. (1996b) report a new amphibole end-member, fluor-cannilloite [ideally CaCa<sub>2</sub>(Mg<sub>4</sub>Al)(Si<sub>5</sub>Al<sub>3</sub>)O<sub>22</sub>F<sub>2</sub>], in which the A site is completely occupied by Ca. The holotype specimen actually has 0.52 Ca apfu at the A site. Re-examination of several other pargasite analyses from the same locality (Pargas, Finland) shows the systematic presence of small amounts of Ca at the A site in every sample of pargasite from this locality (Hawthorne et al., 1996b). This cumulative evidence indicates that the common assumption that Ca occupies only the M(4) site in amphiboles is not correct. However, the chemical and paragenetic evidence does suggest some sort of chemical constraints for the presence of Ca at the A site. The marble at Pargas contains significant amounts of fluorite, and we have identified the presence of A-site Ca in synthetic fluor-amphiboles. Furthermore, careful work on F-free pargasites (Oberti et al., 1995a) has shown that there is no Ca at the A site in these amphiboles. All this evidence suggests that the presence of F at the O(3) site promotes the

occurrence of Ca at the A site in pargasitic amphiboles.

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## References

- Boschmann, K., Burns, P.C., Hawthorne, F.C., Raudsepp, M., Turnock, A.C. (1994): A-site disorder in synthetic fluor-edenite, a crystal structure study. *Can. Mineral.*, **32**, 21-30.
- Ghose, S. & Hexiong, Y. (1989): Mn-Mg distribution in a C2/m manganoan cummingtonite: Crystalchemical considerations. Am. Mineral., 74, 1091-1096.
- Ghose, S., Forbes, W.C. & Phakey, P.P. (1973): Unmixing of an alkali amphibole (tirodite) into magnesio-richterite and magnesio-riebeckite. *Indian J. Earth Sci.*, 1, 37-42.
- Hawthorne, F.C. (1983): The crystal chemistry of the amphiboles. *Can. Mineral.*, **21**, 173-480.
- Hawthorne, F.C., Ungaretti, L., Oberti, R., Bottazzi, P., Czamanske, G. (1993): Li: An important component in igneous alkali amphiboles. *Am. Mineral.*, 78, 733-745.
- Hawthorne, F.C., Ungaretti, L., Oberti, R., (1995): Site populations in minerals: terminology and presentation of results of crystal-structure refinement. *Can. Mineral.*, 33, 907-911.
- Hawthorne, F.C., Ungaretti, L., Ottolini, L., Foord, E.F. (1996a): Lithium-bearing fluor-arfvedsonite from Hurricane Mountain, New Hampshire: a crystalchemical study. *Can. Mineral.*, in press.
- Hawthorne, F.C., Ungaretti, L., Grice, J.D. (1996b): A new hyper-calcic amphibole with Ca at the A site: Fluor-cannilloite from Pargas, Finland. Am. Mineral., 81, 995-1002.
- Oberti, R. & Ghose, S. (1993): Crystal chemistry of a complex Mn-bearing alkali amphibole ("tirodite") on the verge of exsolution. *Eur. J. Mineral.*, **5**, 1153-1160.
- Oberti, R., Hawthorne, F.C., Ungaretti, L., Cannillo, E. (1992): The behaviour of Ti in amphiboles: <sup>[4]</sup>Ti<sup>4+</sup> in richterite. *Eur. J. Mineral.*, **3**, 425-439.
- —, —, —, (1993): The behaviour of Mn in amphiboles: Mn in richterite. Eur. J. Mineral., 5, 43-51.
- —, —, —, (1995a): <sup>[6]</sup>Al disorder in amphiboles from mantle peridotites. *Can. Mineral.*, **33**, 867-878.

- —, —, —, (1995b): Temperature-dependent Al order-disorder in the tetrahedral double-chain of *C2/m* amphiboles. *Eur. J. Mineral.*, **7**, 1049-1063.
- Oberti, R., Sardone, N., Hawthorne, F.C, Raudsepp, M., Turnock, A.C. (1995c): Synthesis and crystalstructure refinement of synthetic fluor-pargasite. *Can. Mineral.*, **33**, 25-31.
- Papike, J.J., Ross, M., Clark, J.R. (1969): Crystalchemical characterization of clinoamphiboles based on five new structure refinements. *Mineral. Soc. Am. Spec. Pap.*, 2, 117-136.
- Raudsepp, M., Turnock, A.C., Hawthorne F.C. (1991): Amphibole synthesis at low pressure: what grows and what doesn't. *Eur. J. Mineral.*, 3, 983-1004.

- Schau, Y.-H., Peacor, D.R., Ghose, S., Phakey, P.P. (1993): Submicroscopic exsolution from Mn-bearing alkali amphiboles from Tirodi, Maharashtra, India. Am. Mineral., 78, 96-106.
- Ungaretti, L. (1980): Recent developments in X-ray single crystal diffractometry applied to the crystalchemical study of amphiboles. *God. Jugosl. Cent. Kristallogr.*, 15, 29-65.

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