

## CRYSTAL STRUCTURE AND MÖSSBAUER SPECTROSCOPY OF TSCHERMAKITE FROM THE RUBY LOCALITY AT FISKENAESSET, GREENLAND

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### ABSTRACT

The crystal structure of tschermakite from Fiskenaeset, Greenland,  $(K_{0.05}Na_{0.38})_{\Sigma 0.43}(Ca_{1.80}Na_{0.05}Fe^{2+}_{0.15})_{\Sigma 2.00}(Mg_{3.65}Fe^{2+}_{0.18}Mn_{0.03}Fe^{3+}_{0.09}Al_{0.81}Cr_{0.19}Ti_{0.05})_{\Sigma 5.00}(Si_{6.43}Al_{1.57})_{\Sigma 8.00}O_{22}[(OH)_{1.95}F_{0.04}Cl_{0.01}]_{\Sigma 2.00}$ ,  $a$  9.8059(5),  $b$  17.9721(8),  $c$  5.3012(2) Å,  $\beta$  105.063(1)°,  $V$  902.15 Å<sup>3</sup>, space group  $C2/m$ ,  $Z = 2$ , has been refined to an  $R_1$  index of 3.2% using MoK $\alpha$  single-crystal X-ray diffraction. The ratio  $Fe^{3+}/Fe_{tot}$  was determined by Mössbauer spectroscopy. The unit formula (calculated from the results of electron-microprobe analysis), the refined site-scattering values, observed average bond-lengths, and Mössbauer spectroscopy were used to assign site populations. Tetrahedrally coordinated Al occurs at both the  $T(1)$  and  $T(2)$  sites, but is strongly ordered at  $T(1)$ , and  $^{61}Al$  occurs at both the  $M(2)$  and  $M(3)$  sites, but is strongly ordered at  $M(2)$ . Magnesium shows the site preference  $M(1) = M(2) > M(3)$ , and higher-valence transition metals (Ti,  $Fe^{3+}$  and  $Cr^{3+}$ ) are ordered at  $M(2)$ . The formula calculated from the electron-microprobe analysis showed an excess of C-group cations of 0.15 *apfu*, exactly in accord with the amount of  $Fe^{2+}$  at  $M(4)$  indicated by Mössbauer spectroscopy. At the A site, Na was split between the  $A(2)$  and  $A(m)$  sites, and K was assigned to the  $A(m)$  site. We derived the short-range arrangements involving the  $M(4)$ , O(3) and A sites, and calculated their relative fractions. As with other complicated monoclinic amphiboles, short-range order is common and dictated by the valence-sum rule of localized bond-valence theory.

**Keywords:** tschermakite, amphibole, crystal structure, Mössbauer spectroscopy, short-range order, Fiskenaeset, Greenland.

### SOMMAIRE

Nous avons affiné la structure cristalline de la tschermakite provenant de Fiskenaeset, au Groënland,  $(K_{0.05}Na_{0.38})_{\Sigma 0.43}(Ca_{1.80}Na_{0.05}Fe^{2+}_{0.15})_{\Sigma 2.00}(Mg_{3.65}Fe^{2+}_{0.18}Mn_{0.03}Fe^{3+}_{0.09}Al_{0.81}Cr_{0.19}Ti_{0.05})_{\Sigma 5.00}(Si_{6.43}Al_{1.57})_{\Sigma 8.00}O_{22}[(OH)_{1.95}F_{0.04}Cl_{0.01}]_{\Sigma 2.00}$ ,  $a$  9.8059(5),  $b$  17.9721(8),  $c$  5.3012(2) Å,  $\beta$  105.063(1)°,  $V$  902.15 Å<sup>3</sup>, groupe spatial  $C2/m$ ,  $Z = 2$ , jusqu'à un résidu  $R_1$  de 3.2% au moyen de la diffraction X d'un monocristal, étudiée avec rayonnement MoK $\alpha$ . Le rapport  $Fe^{3+}/Fe_{tot}$  a été établi par spectroscopie de Mössbauer. La formule unitaire, calculée à partir des résultats d'analyses avec une microsonde électronique, les valeurs affinées de la dispersion d'électrons aux divers sites, les longueurs de liaisons observées, et la spectroscopie de Mössbauer, a servi pour établir le bilan de populations des sites. L'aluminium tétra-coordonné se trouve à deux sites,  $T(1)$  et  $T(2)$ , mais surtout à  $T(1)$ , et  $^{61}Al$  se trouve aux sites  $M(2)$  et  $M(3)$ , mais il est fortement ordonné à  $M(2)$ . Le magnésium occupe les sites selon la préférence  $M(1) = M(2) > M(3)$ , et les métaux de transition à valence plus élevée (Ti,  $Fe^{3+}$  et  $Cr^{3+}$ ) sont concentrés au site  $M(2)$ . La formule calculée à partir des données acquises avec la microsonde électronique montre un excédent de cations du groupe C de 0.15 *apfu*, ce qui correspond exactement à la proportion de  $Fe^{2+}$  au site  $M(4)$  selon la spectroscopie de Mössbauer. Au site A, le Na est partagé entre les sites  $A(2)$  et  $A(m)$ , et le K est assigné au site  $A(m)$ . Nous avons dérivé les arrangements à courte échelle impliquant les sites  $M(4)$ , O(3) et A sites, et nous en avons calculé les fractions relatives. Tout comme dans les autres amphiboles monocliniques compliquées, une mise en ordre à courte échelle s'avère importante et semble régie par la règle de la somme des valence de liaison selon la théorie des valences de liaisons localisées.

(Traduit par la Rédaction)

**Mots-clés:** tschermakite, amphibole, structure cristalline, spectroscopie de Mössbauer, mise en ordre à courte échelle, Fiskenaeset, Groënland.

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## INTRODUCTION

Tschermakite is a monoclinic calcic amphibole with the  $C2/m$  structure and an end-member formula  $\square\text{Ca}_2\text{Mg}_3\text{Al}_2\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$ , although most tschermakite compositions recorded do not approach this formula. We have a fairly good understanding of long-range order of cations in the amphibole structure (Oberti *et al.* 2007), but our knowledge of short-range order lags far behind. Hawthorne *et al.* (1996a) showed that the order–disorder of Na over the  $A(m)$  and  $A(2)$  sites occurs as a result of the short-range (local) bond–valence requirements of the structure, and involves specific arrangements of cations over adjacent  $M(4)$ ,  $O(3)$  and  $A$  sites. Hawthorne *et al.* (1996b) showed that infrared spectroscopy in the principal OH-stretching region is an effective probe of short-range order in amphiboles. Hawthorne (1997) proposed that the valence-sum rule of bond–valence theory must result in short-range order of both cations and anions over the amphibole structure, and extensive work on mainly synthetic amphiboles, primarily by infrared spectroscopy (Della Ventura *et al.* 1996, 1998, 1999, 2001, 2005, 2007, Hawthorne *et al.* 1996c, 1998, 2005, Hawthorne & Della Ventura 2007) has confirmed the common occurrence of SRO (Short-Range Order). A considerable amount of work has been done on synthetic amphiboles approximately along the join tremolite–tschermakite (Oba 1978, Cao *et al.* 1986, Jenkins 1988, 1994, Cho & Ernst 1991, Smelik *et al.* 1994, Jenkins *et al.* 1997, Hawthorne *et al.* 2000, Najorka & Gottschalk 2003), and the more recent work has shown that SRO is a common feature of the amphiboles synthesized. However, comparison with natural amphiboles is lacking. Here, we characterize tschermakite from the ruby locality at Fiskenaeset, Greenland, where tschermakite occurs together with corundum, phlogopite and sapphirine, and is associated with the contact of the anorthosite complex with amphibolite (Rohtert 2006), in order to evaluate aspects of SRO of cations and anions in its structure. In such work, it is critical to derive accurate  $\text{Fe}^{3+}/\text{Fe}^{2+}$  values, as the partitioning of Na between the  $M(4)$  and  $A$  sites is strongly affected by the relative amounts of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in the structure.

## EXPERIMENTAL

*X-ray diffraction*

A small fragment of amphibole was selected for X-ray-diffraction measurements on the basis of optical clarity and freedom from inclusions. The crystal was attached to a tapered glass fiber and mounted on a BRUKER P4 four-circle diffractometer equipped with monochromatic  $\text{MoK}\alpha$  X-radiation and an APEX 4K CCD area detector. The intensities of 2889 reflections were collected to  $\sim 60^\circ 2\theta$  using 15 s per  $0.2^\circ$  frame, with a crystal-to-detector distance of 4 cm. Empirical

absorption corrections (SADABS, Sheldrick 1998) were applied. The unit-cell parameters were obtained by least-squares refinement from the positions of 1192 reflections with  $I > 10\sigma I$ , and are given in Table 1.

The crystal structure was refined with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). The  $R$  indices are of the form given in Table 1, and are expressed as percentages. The structure was refined to an  $R_1$  index of 3.25%, with anisotropic-displacement parameters for all sites except  $A(2)$  and  $A(m)$ . The positional parameters of the H atom were refined with the constraint that the  $O(3)$ –H distance be equal to 0.98 Å. Atom positions and anisotropic-displacement parameters are given in Table 2, selected interatomic distances in Table 3, and refined site-scattering values and assigned site-populations in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data on the MAC website [document Tschermakite CM47\_917].

*Electron-microprobe analysis (EMPA)*

The crystal used for the collection of the X-ray intensity data was subsequently mounted in epoxy, polished, and analyzed with a CAMECA SX-100 electron microprobe operating in wavelength-dispersion mode with the following conditions: excitation voltage: 15 kV, specimen current: 20 nA, beam size: 5  $\mu\text{m}$ , peak-count time: 20 s, background-count time: 20 s. The crystal was analyzed at ten points, and the mean chemical composition is given in Table 5, together with the unit formula calculated on the basis of 24 (O,OH,F,Cl). The contents of FeO and  $\text{Fe}_2\text{O}_3$  were calculated from the  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  value derived from the Mössbauer spectrum.

*Mössbauer spectroscopy*

Mössbauer spectroscopy measurements were done in transmission geometry at room temperature (RT) using a  $^{57}\text{Co}(\text{Rh})$  point source. The spectrometer was calibrated with the RT spectrum of  $\alpha$ -Fe. In preparing the Mössbauer absorber, Fiskenaeset amphibole was mixed with sugar and finely ground under acetone to

TABLE 1. CRYSTALLOGRAPHIC DATA AND STRUCTURE-REFINEMENT INFORMATION FOR THE FISKENAESSET TSCHERMAKITE

$a$ (Å)	9.8059(5)	Crystal size ( $\mu\text{m}^3$ )	$170 \times 80 \times 50$
$b$ (Å)	17.9721(8)	Radiation/filter	$\text{MoK}\alpha/\text{graphite}$
$c$ (Å)	5.3012(2)	Unique reflections	1369
$\beta$ ( $^\circ$ )	105.063(1)	$ F_o  > 4\sigma F$	1324
$V$ (Å $^3$ )	902.15	$R_1$ (%)	3.25
Space group	$C2/m$	$wR_2$ (%)	8.52
$Z$	2		

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR_2 = \left[ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right]^{1/2}$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P = (F_o^2 + 2F_c^2) / 3.$$

TABLE 2. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN THE FISKENAESSET TSCHERMAKITE

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
O(1)	0.1066(2)	0.0894(1)	0.2136(3)	0.0101(7)	0.0167(8)	0.0092(7)	-0.0010(6)	0.0031(6)	-0.0020(6)	0.0119(3)
O(2)	0.1189(2)	0.1736(1)	0.7357(3)	0.0073(6)	0.0125(7)	0.0113(7)	0.0014(5)	0.0015(5)	0.0004(5)	0.0106(3)
O(3)	0.10999(23)	0	0.7146(4)	0.0105(10)	0.0125(10)	0.0112(10)	0	0.0032(8)	0	0.0113(4)
O(4)	0.3684(2)	0.2510(1)	0.7918(3)	0.0155(7)	0.0119(7)	0.0144(7)	0.0003(6)	0.0067(6)	-0.0025(6)	0.0134(3)
O(5)	0.35095(16)	0.1402(1)	0.1114(3)	0.0113(7)	0.0171(8)	0.0122(7)	0.0041(6)	0.0015(6)	0.0007(6)	0.0138(3)
O(6)	0.3433(2)	0.1183(1)	0.6045(3)	0.0113(7)	0.0174(8)	0.0135(7)	-0.0046(6)	0.0036(6)	0.0019(6)	0.0140(3)
O(7)	0.3368(3)	0	0.2809(5)	0.0147(11)	0.0150(11)	0.0219(12)	0	0.0041(9)	0	0.0173(5)
T(1)	0.2811(1)	0.08569(3)	0.3017(1)	0.0074(3)	0.0081(3)	0.0076(3)	-0.0004(2)	0.0019(2)	-0.0010(2)	0.0077(2)
T(2)	0.2914(1)	0.17326(3)	0.8136(1)	0.0082(3)	0.0094(3)	0.0080(3)	0.0008(2)	0.0024(2)	0	0.0085(2)
M(1)	0	0.08899(5)	0.5	0.0101(5)	0.0088(5)	0.0071(5)	0	0.0035(3)	0	0.0084(3)
M(2)	0	0.1763(1)	0	0.0066(4)	0.0067(4)	0.0059(4)	0	0.0020(3)	0	0.0063(3)
M(3)	0	0	0	0.0088(6)	0.0067(6)	0.0070(6)	0	0.0016(4)	0	0.0076(4)
M(4)	0	0.2794(1)	0.5	0.0133(3)	0.0137(4)	0.0121(3)	0	0.0064(2)	0	0.0125(2)
M(4')	0	0.243(3)	0.5	0.0133(3)	0.0137(4)	0.0121(3)	0	0.0064(2)	0	0.0125(2)
A(2)	0.5	-0.028(1)	0							0.024(4)
A(m)	0.521(2)	0	0.056(4)							0.024(4)
H(1)	0.213(1)	0	0.782(12)							0.06(2)

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR TSCHERMAKITE FROM FISKENAESSET

T(1)-O(1)	1.653(2)	M(2)-O(1) ×2	2.050(2)
T(1)-O(5)	1.675(2)	M(2)-O(2) ×2	2.043(2)
T(1)-O(6)	1.668(2)	M(2)-O(4) ×2	1.962(2)
T(1)-O(7)	1.648(1)	<M(2)-O>	2.018
<T(1)-O>	1.661		
T(2)-O(2)	1.634(2)	M(3)-O(1) ×4	2.083(2)
T(2)-O(4)	1.607(2)	M(3)-O(3) ×2	2.074(2)
T(2)-O(5)	1.645(2)	<M(3)-O>	2.080
T(2)-O(6)	1.661(2)		
<T(2)-O>	1.637		
M(1)-O(1) ×2	2.055(2)	M(4)-O(2) ×2	2.403(2)
M(1)-O(2) ×2	2.116(2)	M(4)-O(4) ×2	2.323(2)
M(1)-O(3) ×2	2.092(2)	M(4)-O(5) ×2	2.628(2)
<M(1)-O>	2.088	M(4)-O(6) ×2	2.548(2)
		<M(4)-O>	2.476
A(m)-O(6) ×2	2.88(1)	A(2)-O(5) ×2	2.648(15)
A(m)-O(7)	2.41(2)	A(2)-O(6) ×2	2.78(1)
A(m)-O(7)	2.53(2)	A(2)-O(7) ×2	2.503(5)
<A(m)-O>	2.675	<A(2)-O>	2.644
T(1)-O(5)-T(2)	133.6(1)		
T(1)-O(6)-T(2)	138.8(1)		
T(1)-O(7)-T(1)	138.4(2)		

TABLE 4. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR THE FISKENAESSET TSCHERMAKITE

Site	Refined site-scattering ( <i>epfu</i> )	Assigned site-populations ( <i>apfu</i> )	Calculated site-scattering ( <i>epfu</i> )	<M-O> <sub>calc</sub> (Å)
T(1)	-	1.33 Al + 2.67 Si	-	-
T(2)	-	0.23 Al + 3.77 Si	-	-
M(1)	25.7	1.86 Mg + 0.14 Fe <sup>2+</sup>	26.0	2.083(3)
M(2)	27.8	0.96Mg + 0.76 Al + 0.19 Cr + 0.09 Fe <sup>3+</sup>	28.3	2.016(5)
M(3)	13.4	0.84 Mg + 0.05 Al + 0.11 Fe <sup>2+</sup>	13.6	2.078(6)
M(4)	40.1	1.80 Ca + 0.05 Na + 0.15 Fe <sup>2+</sup>	40.5	2.470(11)
A(2)	2.9	0.28 Na	3.1	-
A(m)	1.9	0.13 Na + 0.05 K	2.4	-

avoid oxidation. The mixture was then loaded into a Pb ring (2 mm inner diameter) and covered by tape on both sides. Assuming a recoilless fraction of 0.7 for the Mössbauer absorber, the amount of sample corresponds to an absorber thickness of  $\sim 4$  mg Fe/cm<sup>2</sup>. The spectra were analyzed using a Voigt-based quadrupole-splitting distribution (QSD) method (Rancourt & Ping 1991). To account for absorber-thickness effects, we allowed the Lorentzian linewidth ( $\Gamma$ ) of the symmetrical elemental doublets of the QSD to be an adjustable parameter during the spectrum fitting (Rancourt 1994). However, a full correction for thickness was applied to the Mössbauer data (Rancourt *et al.* 1993), and similar results ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) were obtained from fitting of the thickness-corrected spectrum.

Figure 1a shows the RT Mössbauer spectrum of the Fiskenaeset tschermakite. It is adequately fitted by a model having two generalized sites, one for  $\text{Fe}^{2+}$  and one for  $\text{Fe}^{3+}$ , each with two Gaussian components. The center shift (CS) was taken to be linearly correlated to the quadrupole splitting (QS) for both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sites. The resultant Mössbauer hyperfine parameters are listed in Table 6. The QSD profile for  $\text{Fe}^{2+}$  is shown in Figure 1b. It displays two well-resolved Gaussian components with average QS values of 2.65 and 1.85 mm/s, respectively. Following the site assignments of Goldman (1979) for calcic amphiboles, we assign the component with a QS of 2.65 mm/s (43% relative area) to  $\text{Fe}^{2+}$  at the  $M(1)$  and  $M(3)$  sites. The QS value (1.85 mm/s) of the second component (36% relative area) is very close to that of  $\text{Fe}^{2+}$  at the  $M(4)$  site in amphiboles (Goldman 1979, Hawthorne 1983a, Della Ventura *et al.* 2005). Therefore, we assigned this component to  $\text{Fe}^{2+}$  at the  $M(4)$  site. Using the Mössbauer relative areas and the total amount of Fe in the formula unit (Table 5), the

$\text{Fe}^{2+}$  populations at the  $M(1) + M(3)$  and  $M(4)$  sites are 0.18(1) and 0.15(1) *apfu*, respectively.

The QSD for  $\text{Fe}^{3+}$  also has two components, a major component with a relative area of 19% and a very minor component having a relative area of 2%, giving a  $\text{Fe}^{3+} : \text{Fe}_{\text{tot}}$  ratio of 21%. The center shifts (0.41 and 0.47 mm/s for the major and minor components, respectively) are characteristic of a high-spin  $\text{Fe}^{3+}$  in octahedral coordination. Ferric iron preferentially enters the  $M(2)$  site in amphiboles (Hawthorne 1983a, 1983b), and we assign the major component of  $\text{Fe}^{3+}$  to the  $M(2)$  site. Assignment of the minor component is more problematic, as the actual amount of  $\text{Fe}^{3+}$  involved is small, 0.01 *apfu*. This could occur at  $M(1)$ , associated with very minor  $\text{O}^{2-}$  at  $\text{O}(3)$ , or it could occur at  $M(2)$  and be associated with a short-range arrangement involving Al at  $M(3)$ . However, because of the minor amount present, we have no way of deciding between these two possibilities. Thus we go with the simpler solution and assign this small amount of  $\text{Fe}^{3+}$  to  $M(2)$  as well.

## SITE POPULATIONS

### The T sites

The unit formula indicates that significant Al occurs at the T sites, and the  $\langle T\text{-O} \rangle$  distances should reflect this occupancy. This issue has been addressed by Papike *et al.* (1969), Hawthorne & Grundy (1973a, 1973b, 1977), Robinson *et al.* (1973), Bocchio *et al.* (1978), Hawthorne (1981, 1983a, 1983b), Oberti *et al.* (1995a) and Hawthorne & Oberti (2007). Hawthorne (1976) and Ungaretti (1980) suggested that variations in  $\langle T\text{-O} \rangle$  distances occur as a result of other cation substitutions in the amphibole structure, a feature that complicates the assignment of site populations. Hawthorne & Oberti (2007) considered this issue in some detail and presented relations between mean  $T\text{-O}$  bond-lengths and Al site-populations. In particular, they showed that the grand  $\langle T\text{-O} \rangle$  distance is strongly affected by inductive effects of the rest of the structure where  $^{14}\text{Al}$  is less than 0.50 *apfu*, but varies linearly with  $^{14}\text{Al}$  content where  $^{14}\text{Al}$  exceeds 0.50 *apfu*. Using their equation

TABLE 5. AVERAGE CHEMICAL COMPOSITION AND UNIT FORMULA OF THE FISKENAESSET TSCHERMAKITE

SiO <sub>2</sub> , wt. %	45.90	Si <i>apfu</i>	6.43
TiO <sub>2</sub>	0.44	Al	1.57
Al <sub>2</sub> O <sub>3</sub>	14.43	$\Sigma T$	8.00
Cr <sub>2</sub> O <sub>3</sub>	1.73		
* Fe <sub>2</sub> O <sub>3</sub>	0.82	Al	0.81
* FeO	2.79	Ti	0.05
MnO	0.25	Cr	0.19
MgO	17.50	Fe <sup>3+</sup>	0.09
CaO	11.99	Fe <sup>2+</sup>	0.33
Na <sub>2</sub> O	1.70	Mg	3.65
K <sub>2</sub> O	0.25	Mn	0.03
F	0.10	$\Sigma C$	5.15
** H <sub>2</sub> O	2.09	<sup>26</sup> C	0.15
O=F,Cl	-0.04	Ca	1.80
		Na	0.05
Total	99.94	$\Sigma B$	2.00
		Na	0.41
		K	0.05
		$\Sigma A$	0.46
		F	0.04
		OH	1.96

\* Determined by Mössbauer spectroscopy. \*\* Calculated as  $\text{OH} = 2 - \text{F} \text{ apfu}$ .

TABLE 6. MÖSSBAUER HYPERFINE PARAMETERS FOR THE FISKENAESSET TSCHERMAKITE DERIVED FROM THE VOIGT-BASED QUADRUPOLE SPLITTING DISTRIBUTION (QSD) ANALYSIS

Site	CS (mm/s)	QS (mm/s)	$\sigma_{\text{QS}}$ (mm/s)	Area (%)
Fe <sup>2+</sup> $M(1)+M(3)$	1.13(2)	2.65(2)	0.11(4)	43(2)
Fe <sup>2+</sup> $M(4)$	1.13(2)	1.85(4)	0.24(4)	36(2)
Fe <sup>3+</sup> $M(2)$	0.41(4)	0.71(5)	0.30(8)	19(2)
Fe <sup>3+</sup> $M(3)$	0.47(4)	1.55(22)	*0	2(2)

Note that the line width of the elemental components,  $\Gamma$ , is equal to 0.17 mm/s. The CS (relative to  $\alpha\text{-Fe}$ ) is allowed to correlate linearly to the QS;  $\sigma_{\text{QS}}$  is the distribution width. \* This value was close to zero (0.00x) with a large standard deviation, and hence was set to zero.

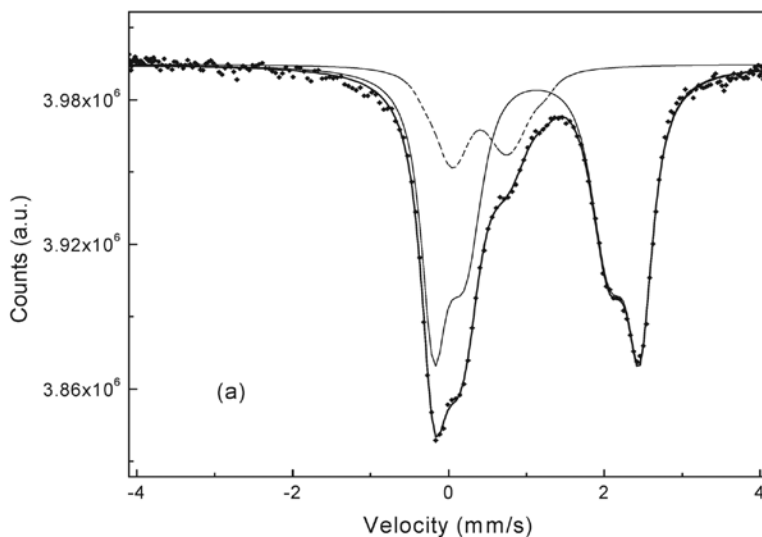


FIG. 1a. Room-temperature Mössbauer spectrum of Fiskenaeset tschermakite, fitted by the Voigt-based quadrupole-splitting distribution (QSD) method, solid subspectrum:  $\text{Fe}^{2+}$  site; dashed subspectrum:  $\text{Fe}^{3+}$  site.

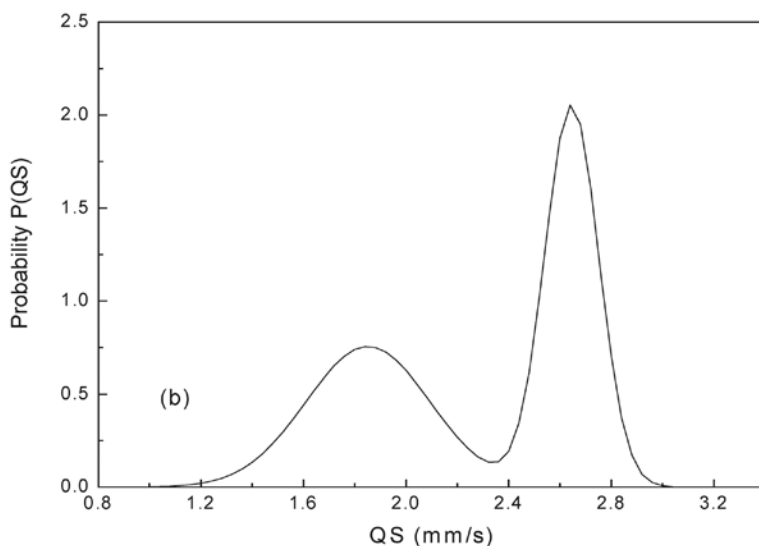


FIG. 1b. Profile of Voigt-based quadrupole-splitting distribution (QSD) for  $\text{Fe}^{2+}$ .

$[\text{grand } \langle T\text{-O} \rangle = 1.6250 + 0.0153 [^{41}\text{Al}]^{(>0.50 \text{ apfu})}]$  gives a predicted grand  $\langle T\text{-O} \rangle$  distance of 1.649 Å, in exact accord with the observed value (Table 3). Using their equation  $[^{41}\text{Al}]^{(>0.50 \text{ apfu})} = -103.7 + 63.86 \langle T\text{-O} \rangle$  gives a predicted  $^{41}\text{Al}$  content of 1.52 apfu, in reasonable

accord with the value of 1.57 apfu indicated by the unit formula (Table 5). Hawthorne & Oberti (2007) also presented relations between mean  $T\text{-O}$  bond-lengths and Al site-populations for the  $T(1)$  and  $T(2)$  tetrahedra  $[^{T(1)}\text{Al}]^{(>0.50 \text{ apfu})} = -52.120 + 32.177 \langle T(1)\text{-O} \rangle$ ;

$T(2)Al^{(>0.50\text{ apfu})} = -47.613 + 29.228 <T(2)-O>$  that give the predicted site-populations shown in Table 4. The sum of these two values,  $1.56^{[4]Al}$ , agrees closely with the analytical value of  $1.57\text{ apfu}$  (Table 5).

#### The $M(1,2,3)$ sites

The strip of octahedra is the most compliant part of the amphibole structure and shows the greatest variation in size and valence of substituent cations and anions (Hawthorne 1981, 1983a, 1983b). There has been considerable diffraction and spectroscopic work on cation and anion order in this part of the amphibole structure, syntheses of which are given by Hawthorne & Oberti (2007), Hawthorne & Della Ventura (2007) and Oberti *et al.* (2007).

The total refined scattering at the  $M(1,2,3)$  sites ( $66.9\text{ epfu}$ , Table 4) is in close agreement with the total effective scattering of the  $C$ -group cations in the structural formula:  $67.8\text{ epfu}$  (Table 5), allowing use of the unit formula (Table 5) as a guide for assigning the  $M(1,2,3)$  site populations. We adjusted the refined site-scattering values slightly such that their sum corresponds to that from the structural formula:  $M(1)$  26.0,  $M(2)$  28.2,  $M(3)$  13.6  $epfu$ . There are seven species of  $C$ -group cations (Table 5). The amount of  $Mn^{2+}$  is minor, and we incorporate this in with  $Fe^{2+}$ . Inspection of Table 5 shows that  $0.15\text{ apfu}$  of  $C$ -group cations must occur at the  $M(4)$  site. Work on Mg–Fe–Mn amphiboles (Ghose 1961, Hafner & Ghose 1971, Ghose & Yang 1989, Hirschmann *et al.* 1994, Reece *et al.* 2000) shows that medium-size divalent transition-metals have the  $M(4)$  site-preference  $M^{2+} \gg Mg$ ; hence we assign  $0.15\text{ apfu}$   $Fe^{2+}$  to  $M(4)$ . There is no evidence of significant  $O^{2-}$  at  $O(3)$ , and hence we initially assign all trivalent cations to  $M(2)$ . It is probable that there is some disorder of Al between  $M(2)$  and  $M(3)$ , as shown for Mg-rich amphiboles by Oberti *et al.* (1995b) and for synthetic Fe-free amphiboles by Della Ventura *et al.* (1999), Hawthorne *et al.* (2000) and Jenkins *et al.* (2003), but this may be evaluated later using relations involving mean bond-length and constituent-cation radii. These initial assignments mean that we may assign  $Mg^*$  ( $= Mg + Al$ ) and  $Fe^*$  ( $= Fe + Cr + Ti$ ) to the  $M(1)$ ,  $M(2)$  and  $M(3)$  sites according to the refined site-scattering values (Table 4). For the  $M(1)$  site, this is quite straightforward; the adjusted site-scattering value of  $26.0\text{ epfu}$  (Table 5) indicates a site population of  $1.86\text{ Mg} + 0.14\text{ Fe}$ , and the equation of Hawthorne & Oberti (2007) relating  $<M(1)-O>$  to constituent-cation radius (values from Shannon 1976) shows that Fe is divalent at this site. Initial assignment of  $Mg^*$  and  $Fe^*$  to  $M(2)$  and  $M(3)$  was done using the adjusted site-scattering values. The observed  $<M(2)-O>$  and  $<M(3)-O>$  values of 2.018 and 2.080 Å indicate that the majority of the trivalent and tetravalent  $C$ -group cations occur at  $M(2)$ . However, using the equations of Hawthorne & Oberti (2007),

such an assignment results in calculated  $<M(2)-O>$  and  $<M(3)-O>$  values of 2.010 and 2.086 Å, compared with the observed values of 2.018 and 2.080 Å, respectively, indicating that some Al occurs at  $M(3)$ , as found for pargasite by Oberti *et al.* (1995b) and Tait *et al.* (2001), and synthetic magnesiohornblende by Hawthorne *et al.* (2000). The amounts of Al and Mg at  $M(2)$  and  $M(3)$  were adjusted such that the calculated  $<M(2)-O>$  and  $<M(3)-O>$  distances are similar to the observed values. The resulting site-populations and calculated  $<M-O>$  distances for the  $M(1)$ ,  $M(2)$  and  $M(3)$  sites are given in Table 4.

#### The $M(4)$ site

The excess  $C$ -group cations ( $0.15\text{ apfu}$ ) and the presence of residual electron density at the  $M(4)$  site indicate that a significant amount of intermediate-size divalent cations ( $Mn^{2+}$  and  $Fe^{2+}$ ) occupy the  $M(4)$  site. The refined site-occupancies at the  $M(4)$  and  $M(4')$  sites are not reliable, as the separation of the two sites is considerably less than the wavelength of the X-rays used in the diffraction experiment. However, the sum of the occupancies  $M(4) + M(4')$  is an accurate measure of the average scattering at this aggregate site (Oberti *et al.* 1993). The observed total scattering at  $M(4)$  is  $40.1\text{ epfu}$ , indicating the presence of cations heavier than Ca: either  $Fe^{2+}$  or  $Mn^{2+}$  or both. The  $Fe^{2+}$  occupancy at the  $M(4)$  site obtained from Mössbauer spectroscopy,  $0.15(1)\text{ apfu}$ , is in excellent agreement with the excess amount of  $C$ -group cations (Table 5). Therefore, we assign  $0.15\text{ apfu}$   $Fe^{2+}$  to the  $M(4)$  site together with Ca and Na as indicated by the unit formula (Table 5).

#### The $A$ site

In accord with the work of Hawthorne *et al.* (1996a) on Na at the  $A$  site in monoclinic amphiboles, we assign Na to the  $A(2)$  site and (Na + K) to the  $A(m)$  site (Table 4), with the K content taken from the unit formula. The aggregate site-scattering value from the refinement ( $4.8\text{ epfu}$ ) (Table 4) agrees quite well with that indicated by the unit formula ( $5.4\text{ epfu}$ ).

### SHORT-RANGE ORDER

Short-range order involves local clusters of atoms that occur either more or less frequently than predicted by a random distribution. The short-range arrangements that can occur are constrained by the *local* version of the valence-matching principle (Hawthorne 1997, Hawthorne *et al.* 2005). Of particular importance in controlling short-range arrangements in amphiboles is the role of the  $A$  site and its constituent cations. Hawthorne *et al.* (1996a) showed that  $^4Na$  couples with different combinations of cations at  $M(4)$  and anions at  $O(3)$ , and that certain arrangements are preferred over

others; this information is summarized in Table 7, where the arrangements are listed in decreasing order of preference. Arrangement (1) will thus occur rather than any other arrangement, until one component of arrangement (1) is totally used up [e.g., F at O(3)]. Then arrangement (2) will occur rather than any other subsequent arrangement, until one component of arrangement (2) is totally used up [e.g., Na at the A(2) site], etc. The information given in Table 7 is modified slightly from that given by Hawthorne *et al.* (1996); the stoichiometry of the cluster is also indicated (Table 8), and the configuration of sites is shown in Figure 2.

It is apparent from the above discussion that we may calculate the amounts of the short-range arrangements occurring in the crystal from the site populations. Consider first arrangement (1)  $M^{(4)}Na_2 - O^{(3)}F - A^{(m)}Na$ . Inspection of Tables 4 and 5 shows that the least abundant constituent of arrangement (1) is  $M^{(4)}Na$ . Note that the stoichiometry of the cluster (see Fig. 2) requires twice as much  $M^{(4)}Na$  as  $O^{(3)}F$  and  $A^{(m)}Na$ :  $M^{(4)}Na = 0.05 \text{ apfu}$ , and hence the fraction of arrangement (1) is 0.025. Consider next arrangement (2)  $M^{(4)}Ca_2 - O^{(3)}(OH) - A^{(2)}Na$ . Inspection of Tables 4 and 5 shows that the least abun-

dant constituent of this arrangement is  $A^{(2)}Na$ : 0.28 *apfu*; hence the fraction of arrangement (2) is 0.28. Arrangement (3),  $M^{(4)}Na_2 - O^{(3)}(OH) - A^{(m)}Na$  cannot occur, as all  $M^{(4)}Na$  is already involved in arrangement (1). The least abundant constituent of arrangement (4) is  $O^{(3)}F$ : there is 0.04 F *apfu* in the structure (Table 5) and 0.025 F *apfu* is involved in arrangement (1), leaving 0.015 F *apfu* to be involved in arrangement (4); hence the fraction of arrangement (4) is 0.015. Arrangement (5),  $M^{(4)}Ca_2 - O^{(3)}F - A^{(2)}Na$  cannot occur as all  $O^{(3)}F$  is already involved in arrangements (1) and (4). We no longer know the sequence of preference for the remaining arrangements, but this knowledge is not necessary to derive their compositions and amounts as the sites  $M^{(4)}$  and  $O^{(3)}$  can only be occupied by Ca and (OH), respectively. Hence the remaining arrangements are  $M^{(4)}Ca_2 - O^{(3)}(OH) - A^{(2)}Na$ ,  $M^{(4)}Ca_2 - O^{(3)}(OH) - A^{(m)}K$  and  $M^{(4)}Ca_2 - O^{(3)}(OH) - A^{(m)}Na$ , and their amounts are dictated by the amounts of  $A^{(2)}Na$  (0.54 *pfu*) and  $A^{(m)}K$  (0.05 *apfu*), and the remaining amount of  $A^{(m)}Na$  (0.09

TABLE 7. PATTERNS OF SHORT-RANGE ORDER INVOLVING CATION SITES ADJACENT TO THE A CAVITY, IN DECREASING ORDER OF PREFERENCE

(1)	$M^{(4)}Na - O^{(3)}F - A^{(m)}Na$	(4)	$M^{(4)}Ca - O^{(3)}F - A^{(m)}Na$
(2)	$M^{(4)}Ca - O^{(3)}OH - A^{(2)}Na$	(5)	$M^{(4)}Ca - O^{(3)}F - A^{(2)}Na$
(3)	$M^{(4)}Na - O^{(3)}OH - A^{(m)}Na$		

Taken from Hawthorne *et al.* (2006).

TABLE 8. SHORT-RANGE ARRANGEMENTS IN TSCHERMAKITE FROM FISKENAESSET

(1)*	$M^{(4)}Na_2 - O^{(3)}F - A^{(m)}Na$	0.025
(2)	$M^{(4)}Ca_2 - O^{(3)}(OH) - A^{(2)}Na$	0.28
(3)	$M^{(4)}Na_2 - O^{(3)}(OH) - A^{(m)}Na$	0
(4)	$M^{(4)}Ca_2 - O^{(3)}F - A^{(m)}Na$	0.015
(5)	$M^{(4)}Ca_2 - O^{(3)}F - A^{(2)}Na$	0
	$M^{(4)}Ca_2 - O^{(3)}(OH) - \square$	0.54
	$M^{(4)}Ca_2 - O^{(3)}(OH) - K$	0.05
	$M^{(4)}Ca_2 - O^{(3)}(OH) - A^{(m)}Na$	0.09

\* numbering from Hawthorne *et al.* (1996).

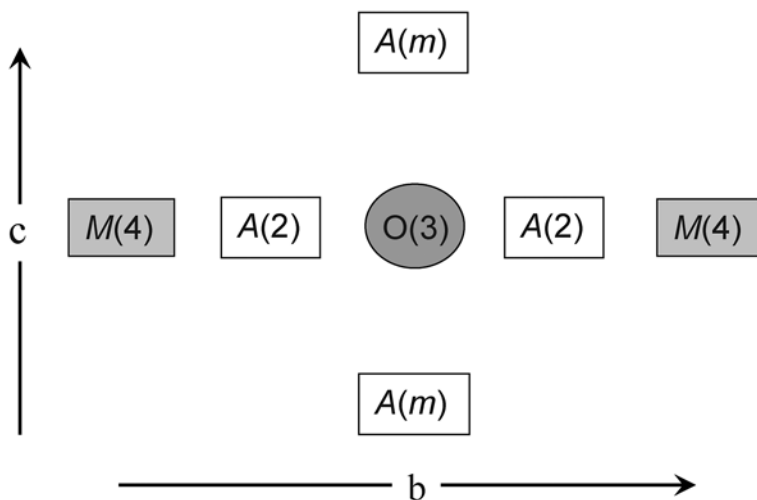


FIG. 2. The configuration of sites involved in the short-range arrangements described in Table 8.

*apfu*). The content of the various arrangements is given in Table 8.

Although much work remains to be done to fully characterize SRO in amphiboles, the general features are already emerging: local bond-valence requirements seem to be the principal factor controlling this type of order. Short-range order is of significance in that it will affect the stability of amphiboles (and other minerals in which it occurs) through its entropy and enthalpy effects. The way in which these effects can be formulated for such a complicated case as the amphibole structure is not yet apparent, but what is clear is that future thermodynamic models need to consider SRO in amphiboles in which heterovalent substitutions are common.

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