Short-Range Order in Amphiboles

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INTRODUCTION

Extensive spectroscopic, diffraction and theoretical work in the last ten years has shown that short-range order (SRO) of both cations and anions is a common feature of amphiboles (Hawthorne et al. 2005). From an experimental perspective, the problem is that SRO does not obey the translational symmetry of the structure in which it occurs, and hence SRO is difficult to detect and decipher directly by standard diffraction methods. There is information on SRO resident in diffuse scattering from a crystal, but this information is quite difficult to extract, particularly when the SRO is complicated, and this approach has only been used for simpler materials. SRO can be detected by several spectroscopic techniques [e.g., infrared spectroscopy, magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy], but the problem is that only part of the local arrangement is derived, and the complete picture of SRO is often not clear. Here, we examine SRO of cations and anions in monoclinic amphiboles, and show that detailed information on SRO can be derived by results from Rietveld and single-crystal diffraction.

LONG-RANGE ORDER

Let us first examine the issue of LRO for a simple (two-dimensional) crystal of general composition M_2SiO_4 where M = Mg, Fe^{2+} , and consider the composition $Mg_{0.8} Fe^{2+}_{1.2} SiO_4$ for the case where there are two distinct sites, M(1) and M(2), in the unit cell (Fig. 1). Maximum order involves complete occupancy of one site by Fe^{2+} and occupancy of the other site by a mixture of Mg and Fe^{2+} . Either M(1) or M(2) can be fully occupied by Fe^{2+} , leading to the two long-range ordered arrangements indicated in Figure 1. Long-range disorder occurs when Mg and Fe^{2+} occur in equal amounts at the M(1) and M(2) sites, indicated in Figure 1. As indicated above, the states of order shown in Figure 1, and any states intermediate between them, can be easily determined by various diffraction and spectroscopic techniques. Why are we interested in such states of LRO? We are interested because the state of LRO affects the stability of the crystal through the associated configurational entropy and enthalpy of order-disorder.

SHORT-RANGE ORDER

Let us now examine the issue of SRO for the same (two-dimensional) crystal shown in Figure 1. LRO involves the occupancies of the sites *averaged over the complete crystal*,

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Figure 1. Sketch of a symbolic (two-dimensional) crystal structure showing a series of unit cells containing two cation sites, M(1) and M(2), together with long-range ordered and long-range disordered site populations for a bulk composition Mg_{0.8} Fe²⁺_{1.2} SiO₄ (from Hawthorne et al. 2005).

whereas SRO involves the occupation of individual (i.e., non-averaged) sites over a scale of a few Å. This situation is illustrated in Figure 2 by a few unit cells of the crystal. The M(1)site in the central unit cell is surrounded by four other sites, two M(1) sites and two M(2)sites. SRO involves the formation of *local* clusters of atoms that occur either more or less than predicted by a random distribution. The four nearest-neighbor M sites surrounding the central M(1) site (Fig. 2) may be occupied by Fe²⁺₄, Fe²⁺₃Mg, Fe²⁺₂Mg₂, Fe²⁺Mg₃, or Mg₄. For a crystal of composition $Mg_{0.8} Fe^{2+}_{1.2} SiO_4$, a random distribution of nearest-neighbor cations will give the frequencies of occurrence of the possible clusters indicated in Figure 2. On the other hand, the local distribution may not be random (i.e., disordered); it may be ordered whereby some clusters occur more often than a random distribution indicates and other clusters may occur less often than a random distribution indicates. This situation is shown in Figure 2 where the cluster Mg_4 occurs much more often and the cluster $Fe^{2+}_2Mg_2$ occurs much less often than for a random distribution (i.e., short-range ordered). What is complete short-range disorder? It is where the frequency of occurrence of each local arrangement conforms to that calculated as the product of the fraction of each component, weighted according to the number of times it occurs in the local arrangement; the resultant values are then normalized to sum to unity. Thus for the example in Figure 2, the calculated relative frequencies for complete short-range disorder are 0.6^4 , $0.6^3 \times$ 0.4, $0.6^2 \times 0.4^2$, 0.6×0.4^3 and 0.4^4 , which normalize to the values given in Figure 2 for the short-range disordered arrangement. The frequencies of occurrence for partial SRO given in Figure 2 are examples (that are compatible with the bulk composition of the crystal).

The above discussion involves SRO of homovalent cations. Of more interest from a crystalchemical and mineralogical perspective is SRO involving heterovalent cations (or anions), as these states of order involve much greater changes in local bond-valence distribution than do



Figure 2. Sketch of a four unit-cell fragment of the symbolic structure of Figure 1, showing the *local* (nextnearest neighbor) environment around one M(1) site, together with short-range ordered and short-range disordered arrangements for a bulk composition Mg_{0.8} Fe²⁺_{1.2} SiO₄ (from Hawthorne et al. 2005).

changes in states of SRO involving homovalent cations (Hawthorne 1997). In turn, the resultant bond-valence constraints on local arrangements may have significant effects on the variation in chemical composition and stability of minerals. Given that short-range order-disorder is quite difficult to characterize experimentally, why should we be interested in SRO? We should be interested in SRO because it will affect the stability of a mineral in the same way as LRO: through its associated configurational entropy and enthalpy of order-disorder, and it will also affect the exchange of elements between coexisting minerals.

BOND-VALENCE ASPECTS OF SRO

Brown (1981, 2002) has developed a simple but powerful approach to chemical bonding in inorganic structures. A crystal is considered as an array of atoms connected by a network of chemical bonds. Any path through this network consists of alternating cations and anions, and the total array is subject to the constraint of electroneutrality. Bond valence is a measure of the strength of a chemical bond, and can be calculated from the curves of Brown and Altermatt (1985) if the bond lengths are known. The valence-sum rule states that the sum of the bond valences incident at each atom is equal to the magnitude of the formal valence of that atom. If the interatomic distances are not known, the bond valences can be approximated by the formal Pauling bond-strengths (Pauling 1929). Bond-valence arguments are normally applied to the long-range aspects of a structure, and Preiser et al. (1999) have shown how bond-valence theory can be derived from an ionic model. However, Burdett and Hawthorne (1993) showed how aspects of the theory can be derived from a localized molecular-orbital description of a solid in which there is a significant energy gap between interacting orbitals on adjacent atoms. This suggests that bond-valence theory can also be applied to local arrangements within a structure, and Hawthorne (1997) applied such arguments to derive the most probable arrangements of SRO in a wide variety of monoclinic amphiboles. A key feature of this approach is the application of the short-range valence-sum rule to all possible short-range arrangements: those arrangements that most closely conform to the valence-sum rule are the short-range arrangements that are most likely to occur.

Of course, except in completely ordered amphiboles (in which the patterns of LRO are also the patterns of SRO), we do not know the local bondlengths. There are two ways in which we can approach this problem: (1) we can use the formal Pauling bond-strengths; (2) we can take the observed bond-valences in an amphibole in which the LRO is similar to that in the structure of interest (usually the structure of the amphibole of interest itself) and modify them by the ratio of the formal aggregate charge of the ions at a site to the formal charge of the ions at that site in the SRO arrangement under consideration.

SRO of heterovalent versus homovalent cations and anions

The valence-sum rule indicates that SRO will be far more common where mixed occupancies at specific sites involve cations or anions of different formal charge than where mixed occupancies involve cations or anions of the same formal charge. Indeed, we predict that SRO will be uncommon where homovalent ions are involved, and common where heterovalent ions are involved.

(OH) AS A PROBE OF LOCAL ORDER IN AMPHIBOLE

The O(3) site and its local environment are illustrated in Figure 3a for the C2/m amphibole structure. When O(3) = (OH), the O-H distance is ~ 0.96 Å (Hawthorne and Grundy 1976) and the associated O-H bond is approximately orthogonal to (100) (Hanisch 1966). The O(3) anion bonds to two M(1) and one M(3) cations. The point symmetry of the O(3) site is *m* in the C2/m amphibole structure, but inspection of Figure 3a shows that there is pseudo-trigonal symme-



Figure 3. The (OH) group in the amphibole structure, associated with the M(1)(dark) and M(3) (stippled) polyhedra. The O atom at the O(3) site is shown as a large black circle, and its associated H atom is shown as a small black starred circle; (a) projected onto (100); (b) projected onto (010) with perspective, the T(2)sites have been omitted for clarity. [Used by permission of Schweizerbart'sche Verlagsbuchhandlung, from Della Ventura et al. (1999), European Journal of Mineralogy, Vol. 11, Fig. 7, p. 88].

try along the O-H bond, a very important factor that affects the resolution of the infrared spectra (Strens 1966). It is notable that the H atom hydrogen-bonds only to one O(7) atom (Fig. 3b).

The exact position (energy) of the principal OH-stretching band in the infrared spectrum of an hydroxyl-bearing mineral is a function of the relative strength of the O-H bond (Huggins and Pimental 1956). As this strength depends on the degree of hydrogen bonding between the H atom and the surrounding O atoms, the relative strength of the O-H bond is sensitive to the local arrangement of atoms around the OH group, i.e., by the cation distribution in the immediate vicinity of the H atom. These arrangements involve the M(1) and M(3) sites, and we will begin by considering the effect on the infrared spectrum of Mg-Fe²⁺ order over the M(1) and M(3) sites.

Mg-Fe²⁺order-disorder over M(1) and M(3) and its effect on the infrared spectrum

Consider two cation species (e.g., Mg and Fe²⁺) at the M(1) and M(3) sites. As O(3) bonds to these M sites, there are 2 $\times 2 \times 2 = 8$ different possible short-range arrangements around an (OH) anion at O(3); these are listed in Table 1. The spectrum that results from this situation (Fig. 4) shows only four absorption bands. This difference in number of bands arises from the pseudo-trigonal nature of the local arrangement: the two M(1) and one M(3) cations are pseudosymmetrically related, introducing an accidental degeneracy into the spectrum (Table 1). The bands in the spectrum of Figure 4 are labeled A, B, C and D, and their assignments are shown in Table 1. The relations between site populations and band intensities for this simple case of Mg- Fe²⁺ are given in Appendix I.

$M^{2+}-M^{3+}$ order-disorder over M(1)and M(3) and its effect on the infrared spectrum

Early crystal-structure studies on calcic amphiboles assumed that C-group



Figure 4. The infrared spectrum in the principal (OH)-stretching region of a synthetic (Mg,Co)potassic-richterite of composition K(CaNa) (Mg₃Co₂)Si₈O₂₂(OH)₂; modified from Hawthorne et al. 1996c.

Table 1. Possible local arrangements around the O(3) site in amphiboles with (Mg, M^{2+}) at M(1) and M(3).

	<i>M</i> (1)	<i>M</i> (1)	<i>M</i> (3)	Band*	Band ⁺
(1)	Mg	Mg	Mg	А	А
(2)	Mg	Mg	M^{2+}	\mathbf{B}'	
(3)	M ²⁺	Mg	Mg	D″	В
(4)	Mg	M^{2+}	Mg	Б	
(5)	M^{2+}	M^{2+}	Mg	C′	
(6)	M^{2+}	Mg	M^{2+}	C''	С
(7)	Mg	M^{2+}	M^{2+}	C	
(8)	M ²⁺	M ²⁺	M ²⁺	D	D

* ideal band-structure; (3) and (4) are symmetry equivalent and give rise to only one band: B"; similarly, (5) and (6) are symmetry equivalent and give rise to only one band: C".

⁺ band structure usually observed; (2) and [(3)+(4)] are pseudo-symmetrically degenerate, and only one band (B) is observed experimentally; similarly, (5) and [(6)+(7)] are pseudo-symmetrically degenerate and only one band (C) is observed experimentally.

trivalent cations are completely ordered at the M(2) site. However, Semet (1973) and Raudsepp et al. (1987a, 1991) showed that this is not the case. Semet (1973) noted the presence of two broad bands centered on 3711 and 3678 cm⁻¹ in synthetic pargasite (Fig. 5a) and magnesiohastingsite, and suggested that these are due to Al-Mg and Fe³⁺-Mg disorder over the M(1) and M(3)sites. Raudsepp et al. (1987a, 1991) presented similar spectra for pargasite and M³⁺ -substituted pargasite (M³⁺ = Cr, Sc, In), and found that the lower-frequency band is shifted to lower wavenumber in the substituted pargasites, in accord with the replacement of Al by a heavier trivalent cation at the M(1,3) sites. This disorder of heavier trivalent cations over the M(1,3) sites was confirmed by Rietveld structure-refinement (Raudsepp et al. 1987a, 1991). Welch et al. (1994) showed an analogous two-peak ¹H MAS NMR spectrum for pargasite (Fig. 5c), indicating disorder of Al over the M(2) and one or both of the M(1,3) sites. Detailed crystal-structure work by Oberti et al. (1995a) showed that ^[6]Al is partly disordered over the M(2) and M(3) sites in Mg-rich pargasite, the degree of disorder increasing with increase in the amount of Mg in the structure. Della Ventura et al. (1998a) showed that ^[6]Al is disordered in synthetic pargasite but completely ordered at M(2) in the Co analogue Na Ca₂ (Co²⁺₄ Al) $(Si_6 Al_2) O_{22} (OH)_2$, i.e., M(1) = M(3) =Co²⁺. However, comparison with the infrared spectrum of tremolite (Fig. 5b) shows the peaks in the pargasite spectrum to be very broad, suggesting the presence of more than two bands (components) in the spectrum. However, inspection of the spectrum of pargasite (Fig. 5a) shows that there is not a lot of information in the envelope on additional components.



Figure 5. The spectra of selected C2/m amphiboles in the principal (OH)-stretching region; (a) the infrared spectrum of synthetic pargasite; (b) the infrared spectrum of synthetic tremolite; (c) the ¹H MAS NMR spectrum of synthetic pargasite [(a) and (b) from Hawthorne et al. 2005, (c) from Welch et al. 1994].

NEXT-NEAREST NEIGHBOR EFFECTS: SRO OF HETEROVALENT-CATIONS IN TREMOLITE

Hawthorne et al. (1996b) first showed that strong SRO of heterovalent cations does occur in monoclinic amphiboles. Figure 6a shows the infrared spectrum of synthetic tremolite of composition close to \Box (Ca_{1.8} Mg_{0.2}) Mg₅ Si₈ O₂₂ (OH)₂ and Figure 6b shows the spectrum of tremolite(56) (Hawthorne 1983), the composition of which is given in Table 2. The spectrum

Figure 6. Infrared absorption spectra in the principal (OH)-stretching region for (a) synthetic tremolite, (b) tremolite (56) of Hawthorne and Grundy (1976), (c) synthetic richterite with a minor tremolite component, (d) synthetic tremolite–potassic-richterite of composition $TR_{80}KR_{20}$. The dashed peaks in (b) represent two component bands of the higher-energy peak (from Hawthorne et al. 1996b).

56.57	Si	7.767
1.41	Al	0.228
0.01	ΣT	7.995
0.01		
0.08	Ti	0.001
0.03	Fe ³⁺	0.001
24.41	Fe ²⁺	0.009
12.25	Mn	0.003
1.44	Mg	4.995
0.68	ΣC	5.009
1.46		
1.52	Ca	1.802
-0.64	Na	0.198
99.23	ΣB	2.000
	Na	0.184
	Κ	0.119
	ΣA	0.303
	(OH)	1.330
		0 (50
	F	0.658
	$\begin{array}{c} 56.57\\ 1.41\\ 0.01\\ 0.03\\ 24.41\\ 12.25\\ 1.44\\ 0.68\\ 1.46\\ 1.52\\ -0.64\\ \hline 99.23\\ \end{array}$	$\begin{array}{ccccc} 56.57 & Si \\ 1.41 & Al \\ 0.01 & \Sigma T \\ 0.01 & & \\ 0.08 & Ti \\ 0.03 & Fe^{3+} \\ 24.41 & Fe^{2+} \\ 12.25 & Mn \\ 1.44 & Mg \\ 0.68 & \Sigma C \\ 1.46 & \\ 1.52 & Ca \\ \hline 0.68 & \Sigma C \\ 1.46 & \\ 1.52 & Ca \\ \hline 0.68 & \Sigma B \\ \hline \end{array}$

Table 2. Chemical composition (wt%) and
unit formula (apfu) for tremolite(56).



of synthetic tremolite consists of an intense narrow band at 3674 cm^{-1} due to the configuration MgMgMg-(OH) [M(1) = M(3) = Mg], together with a narrow shoulder at ~ 3670 cm^{-1} due to the configuration MgMgMg-(OH) with a neighboring M(4) site(s) occupied by Mg rather than by Ca. The spectrum of tremolite in Figure 6b also has an intense band at 3674 cm^{-1} , in accord with the composition of its C-group cations. However, there is also an intense band at 3705 cm^{-1} in the spectrum of Figure 6b, and the composition of this amphibole indicates that this band must be related to occupancy of the A, M(4) and T(1) sites by cations not present in synthetic tremolite [i.e., ${}^{A}(\text{Na}, \text{K})$, ${}^{M(4)}\text{Na}$ and ${}^{T(1)}\text{Al}$]. Hence the bands in the principal (OH)-stretching region of the infrared must also be affected by not just the cations that are nearest neighbors to the O(3) anion, but also by cations that are next-nearest-neighbors of O(3).

Infrared absorption in related amphiboles

Inspection of Table 2 shows that the tremolite under consideration has significant (Na, K) at the A site, Na at the M(4) site and Al at the T(1) site. Let us first consider the effect of

(Na, K) at the *A* site on the MgMgMg-(OH) absorption. This may be assessed by examining the infrared spectra of synthetic richterite (Fig. 6c) of nominal end-member composition Na (CaNa) Mg₅ Si₈ O₂₂ (OH)₂ and synthetic tremolite–potassic-richterite solid-solution of nominal composition TR₈₀KR₂₀ (Fig. 6d). In synthetic richterite, the principal absorption occurs at 3730 cm⁻¹ with a minor peak at 3674 cm⁻¹ (Fig. 6c), whereas in synthetic TR₈₀KR₂₀, the principal absorption occurs at 3674 cm⁻¹ with a minor peak at 3735 cm⁻¹ (Fig. 6d). The bands at 3730 and 3735 cm⁻¹ are assigned to the local arrangement MgMgMg-(OH) with a neighboring *A* site occupied by Na and K, respectively, which we will refer to as the richterite (or potassic-richterite) arrangement. In the spectrum of synthetic TR₈₀KR₂₀ (Fig. 6d), the band at 3674 cm⁻¹ can be assigned to the local arrangement. A band due to the tremolite arrangement also occurs in the spectrum of synthetic richterite (Fig. 6c), indicating that it is not of end-member composition, but has significant vacancy at the *A* site.

The effect of next-nearest-neighbor (NNN) cations

Let us now consider the *possible* local arrangements of next-nearest-neighbor cations (Table 3) in tremolite(56) of composition given in Table 2. Obviously, arrangements of the type MgMgMg-F do not give rise to an (OH)-stretching absorption. However, the O(3) sites occur in pairs along the edge of the M(1) octahedron, and the occurrence of (OH)-F arrangements here may or may not give rise to additional bands. Arrangement (1) (Table 3) is the tremolite configuration and gives a band at 3674 cm⁻¹. Substitution of F in tremolite (Robert et al. 1999) does not give rise to any additional bands (one-mode behavior, see section on SRO of (OH) and F in amphiboles later in this chapter) and hence arrangement (2) will not give rise to an (OH) absorption. Arrangement (3) is the richterite (potassic-richterite) configuration and gives a band at 3730 (3735) cm⁻¹. Arrangement (4) involves F at the neighboring O(3) site. As shown by Della Ventura et al. (1998b) and Robert et al. (1999), this arrangement gives rise to an additional band at 3714 cm⁻¹ in both F-bearing richterite and potassic-richterite (two-mode behavior). Substitution of Al for Si in micas reduces the frequency of the principal absorption band by ~ 25 cm⁻¹. Because the local arrangement around (OH) in richterite and potassic-richterite is similar to that in Si-rich micas, substitution of Al for Si in a local richterite configuration will reduce the frequency of the principal (OH)-absorption band by $\sim 25 \text{ cm}^{-1}$: 3730 - 25 = 3705 cm⁻¹. Substitution of Al for Si in a local tremolite configuration [arrangement] (5)] would reduce the frequency of the principal (OH) absorption to give a band at 3674 - 25 =3649 cm⁻¹. Substitution of Al for Si in a local richterite configuration [arrangement (6)] would reduce the frequency of the principal (OH) absorption to give a band at 3730 - 25 = 3705cm⁻¹. Substitution of Al for Si in a local richterite configuration with F at an adjacent O(3) site [arrangement (7)] would reduce the frequency of the principal (OH) absorption to give a band at $3714 - 25 = 3689 \text{ cm}^{-1}$.

		-			
	A	O(3)	<i>T</i> (1)	<i>M</i> (4)	Frequency (cm ⁻¹)
(1)		OH	Si	Ca	3674
(2)		F	Si	Ca	3674
(3)	(Na,K)	OH	Si	Na	3730
(4)	(Na,K)	F	Si	Na	3714
(5)		(OH,F)	Al	Ca	3649
(6)	(Na,K)	OH	Al	Ca	3705
(7)	(Na,K)	F	Al	Ca	3689

 Table 3. Possible local arrangements and predicted band frequencies for tremolite(56).

Derivation of patterns of SRO

We may now compare the band positions and local arrangements of Table 3 with the observed bands in Figure 6b. Arrangement (1), with its band at 3574 cm⁻¹ is obviously the dominant local arrangement in this amphibole. The weak intensity of the band at 3730 cm⁻¹ in Figure 6b is not in accord with all the A cations being involved in arrangement (3). Arrangement (4) would give rise to a band at 3714 cm⁻¹ that is significantly displaced from the maximum at 3705 cm⁻¹; this arrangement may be present in a minor amount, but the spectrum is not compatible with most of the F being involved in this arrangement. Arrangement (5) is obviously not present as there is no trace of a band at 3649 cm⁻¹ in the spectrum. Arrangement (6) will give rise to a band at 3705 cm⁻¹; as the dominant secondary band in the spectrum is at 3705 cm⁻¹ (Fig. 6b), we may conclude that this arrangement is the second most-frequent arrangement in this crystal. There is no band at 3689 cm⁻¹ corresponding to arrangement (7), and hence this does not occur.

Thus the two most important local arrangements in the tremolite(56) of Table 2 are (1) and (6) (Table 3). However, arrangement (3) involves equal amounts of A (Na, K) and ${}^{T(1)}$ Al, and inspection of the formula of the tremolite (Table 2) shows that A (Na, K) exceeds ${}^{T(1)}$ Al. The excess A (Na, K) gives rise to a small amount of arrangement (3) and is in accord with the weak band at 3730 cm⁻¹ in the spectrum (Fig. 6b). As none of the arrangements identified so far as being present involve F, there must be a fourth arrangement that does involve this component. Inspection of Table 3 shows that arrangement (2) is the only possibility. Note that we cannot use the relative intensities of the bands to derive accurate estimates of the amounts of these arrangements present in the amphibole as (1) the absorptivity is related to relative concentration in a complex way that is currently not understood (Skogby and Rossman 1991; Hawthorne et al. 1997); (2) arrangements that involve F have no spectral expression. However, despite this limitation, it is apparent that the non-tremolite components in the amphibole of Table 2 are not randomly distributed within the amphibole structure but show extreme SRO.

SRO of heterovalent cations in tremolite(56): application of bond-valence theory

Let us apply the local version of bond-valence theory to the example of tremolite(56) considered in the previous section. As indicated in Table 2, the principal non-tremolite components in this amphibole are ^{*A*}(Na, K), ^{*M*(4)}Na and ^{*T*(1)}Al. The environment of these sites is shown in Figure 7. Of key importance here are the O(5), O(6) and O(7) anions that link to the *A*(2), *M*(4) and *T*(1) sites, as the bond valences incident at these sites will be strongly affected by the local occupancies of the *A*(2), *M*(4) and *T*(1) sites. Table 4 shows the bond-valences of the cation arrangements of Table 3 (exclusive of those involving F).

Arrangement (1) is the ordered tremolite configuration and has incident bond-valence sums in accord with the valence-sum rule. Arrangement (3) is the richterite configuration; it also has reasonable bond-valence sums, and corresponds with both the chemical composition of the crystal and the weak band at 3730 cm⁻¹ in the spectrum of Figure 6b. Arrangement (5) has Al at T(1), Ca at M(4) and a vacant A-site; the bond-valence sums are very low, indicating that this local arrangement will not occur, in agreement with the absence of a band at 3649 cm⁻¹. For arrangement (6), the bond-valence sum for O(5) is low and the sums for O(6) and



Figure 7. The A(2), M(4) and T(1) sites in tremolite, together with their coordinating anions and neighboring coordination polyhedra.

Arrangement (1)							Arran	gement (3)		
	M(4)Ca	A	T(1)Si	T(2)Si	Σ		M(4)Na	^A Na	T(1)Si	T(2)Si	Σ
O(5)	0.13	_	0.97	0.92	2.02	O(5)	0.06	0.07	0.99	0.91	2.03
O(6)	0.21	_	0.98	0.88	2.07	O(6)	0.10	0.08	0.95	0.86	1.99
O(7)	-	-	$1.02^{x_{2}}$	-	2.04	O(7)	-	0.18	0.96^{x_2}	-	2.10
		Arran	gement (5)				Arran	gement (6)	
	M(4)Ca	$A \square$	$T^{(1)}Al$	T(2)Si	Σ		M(4)Ca	^A Na	T(1)Al	T(2)Si	Σ
0(5)	0.13	_	0.73	0.91	1.77	0(5)	0.13	0.07	0.73	0.91	1.84
O(6)	0.21	_	0.74	0.86	1.81	O(6)	0.21	0.08	0.74	0.86	1.89
O(7)	-	-	0.76 1.02 }	-	1.78	O(7)	-	0.18	0.76 1.02 }	-	1.96

 Table 4. Local bond-valence (vu) patterns for selected local arrangements of Table 3.

O(7) are acceptable. As arrangements (5) and (6) are the only arrangements that include Al at T(1), it is a question of which arrangement is to be preferred. From the sums in Table 4, it is clear that (6) is the preferred arrangement, in accord with the band position at 3705 cm⁻¹ (Fig. 6b). Other arrangements are also possible, specifically those that just involve the addition or replacement of one component, but these are unfavorable from a bond-valence perspective.

NEAREST- AND NEXT-NEAREST-NEIGHBOR EFFECTS

The simple example given above shows that next-nearest-neighbor (NNN) effects give rise to significant bands in the spectra of amphiboles, which is very fortunate as these NNN "effects" are our short-range arrangements of atoms, and the presence and intensities of the resultant bands contain information on SRO. So before we consider any specific amphiboles, we need to characterize the local arrangements of sites that are involved in these possible patterns of SRO, and we also need to develop a nomenclature to denote these site configurations (note that we use the term "configuration" when we are dealing with sites, and the term "arrangement" when we are dealing with atoms).

Nearest-neighbor sites: configuration symbols and atom arrangements

The O(3) site is bonded to two M(1) and one M(3) sites (Fig. 3a), and the H atom of that O(3) site projects out into the *A* cavity. The distance between the H atom and any A cation is of the order of 2.8 Å, and hence one expects a repulsion interaction between the two cations. Comparison of the infrared spectra of amphiboles with M(1) = M(3) = Mg, O(3) = (OH) and A = \Box and Na, respectively, should indicate the effect of the A cation on the spectrum. Comparison of the infrared spectra of synthetic tremolite (Fig. 6a) and synthetic richterite (Fig. 6c) shows that the principal (OH)-stretching band is shifted to higher wavenumber (energy) where H is locally associated with Na at the *A* site. This effect of the A cations is general (e.g., Rowbotham and Farmer 1974; Robert et al. 1989; Hawthorne et al. 1997; Gottschalk and Andrut 2003). Thus we need to incorporate the character of the *A*-site occupancy into any notation describing the local configuration of sites. We may denote this configuration as M(1)M(1)M(3)-O(3)-*A*, and local arrangements of atoms will be written as follows: MgMgMg-OH- \Box ...end-member tremolite arrangement.

NNN sites: the T sites

Consider the local environment of the H atom in the monoclinic amphibole structure (Fig. 3b). The H atom is in such a position as to form a hydrogen bond to the closest O(7) atom (Hawthorne 1983), and it is the strength of this interaction that affects the shift in the frequency of the principal OH-stretching vibration. So what affects the strength of this hydrogen bond? The key issue here is that the valence-sum rule must be satisfied at the O(7) anion, and this is affected only by the atoms occupying the locally associated pair of T(1) sites (Fig. 3b). We can incorporate the T(1)T(1) configuration by appending it to the site configuration symbol: M(1)M(1)M(3)-O(3)-A:T(1)T(1).

NNN sites: the *M* sites

The NN and NNN M sites are shown in Figure 8. The effect of the next-nearest-neighbor M(2) and M(3) sites is subtle to decipher as it produces new bands which usually are poorly resolved in the spectrum and only contribute to the broadening of the main absorptions. Comparison of Figures 8a and 8b indicates that there are two stereochemically distinct types of next-nearest-neighbor polyhedra: (1) polyhedra which share two edges with polyhedra of the NN cluster [M(2)M(2)M(3)] (Fig. 8a), and (2) polyhedra which share one edge with polyhedra of the NN cluster [M(1)M(1)M(2)M(2)] and [M(4)M(4)] (Fig. 8b). It seems reasonable to expect that cation variation in type-1 polyhedra will produce spectral bands that have better resolution that do those resulting from cation variation in type-2 polyhedra.

Della Ventura et al. (1999) discussed this issue, and considered two models: (1) the three NNN *M* sites M(2)M(2)M(3), and (2) the five NNN *M* sites M(2)M(2)M(3)M(2)M(2) which were used to interpret the infrared spectra of synthetic richterite-pargasite amphiboles (Della Ventura et al. 1999) and synthetic aluminous-tremolite solid-solutions (Hawthorne et al. 2000a). However, the M(4) site (Fig. 8b) also has an effect. This is most clearly indicated by Gottschalk et al. (1998, 1999), who resolved bands due to occupancy of the two NNN M(4) sites (Fig. 8b) in synthetic tremolite--Sr-tremolite by Ca, Sr and Mg, and in synthetic tremolite by Ca and Mg. What seems apparent here is that the degree of resolution in amphibole spectra depends on the chemical complexity of the amphibole examined. Hence one needs a flexible site-configuration symbol to cater for these different requirements.



Figure 8. (a) Nearest-neighbor and (b) next-nearest-neighbor octahedra about the O(3) site in the monoclinic amphibole structure; the O(3) site is marked by a large black circle (modified from Della Ventura et al. 1999).

We can incorporate the NNN sites into a site-configuration symbol by appending the NNN sites to the NN symbol as follows:

M(1)*M*(1)*M*(3)-O(3)-A: *T*(1)*T*(1)-*M*(2)*M*(2)*M*(3) (Fig. 8a)

M(1)M(1)M(3)-O(3)-A: T(1)T(1)-M(2)M(2)M(3)-M(2)M(2)

M(1)*M*(1)*M*(3)-O(3)-A: *T*(1)*T*(1)-*M*(2)*M*(2)*M*(3)-*M*(1)*M*(1)*M*(2)*M*(2)-*M*(4)*M*(4)*M*(4)*M*(4) (Fig. 8b)

where we have separated type-1 NNN sites from type-2 NNN sites by a dash.

The number of possible short-range arrangements of cations

Let us examine the site-configuration symbol M(1)M(3)-O(3)-A:T(1)T(1)-M(2)M(2)M(3) to see how many local arrangements are possible. This problem depends on the number of species that are available for incorporation; we will consider this problem for a relatively straightforward example: Let the M(1) and M(3) sites be occupied by Mg and Al, the O(3) site be occupied only by (OH), the A site be occupied by Na, \Box and Ca, and the T(1) site be occupied by Si and Al. Setting pseudosymmetric arrangements as identical, the NN M(1) and M(3) sites give rise to four arrangements: MgMgMg, MgMgAl, MgAlAl and AlAlAl; the A site gives rise to three arrangements: Na, \Box and Ca; the NNN T(1) site pair gives rise to three arrangements: SiSi, SiAl and AlAl; the NNN M(2) and M(3) sites give rise to four arrangements to four arrangement to four arrangements of algebraically possible arrangements is $4 \times 3 \times 3 \times 4 = 144$; if we extend the NNN arrangement of octahedra to the next two M(2) sites, this number rises to $144 \times 3 = 432$. Of course, many of these arrangements will be unstable on bond-valence grounds (Hawthorne 1997), but a random short-range arrangement of cations would give rise to this many arrangements for this particular composition.

SHORT-RANGE ORDER AND SHORT-RANGE DISORDER

Above, we calculated all combinatorially possible arrangements of cations over a specific cluster in the amphibole structure, and it can be shown that many of these arrangements are not stable on bond-valence grounds. Let us consider a series of situations that will illuminate the issues of SRO. (1) Consider the extreme situation where some fraction, x, of the possible number of short-range arrangements are not favored from a bond-valence perspective, and the remaining (1 - x) arrangements are equally favored. There will be extreme SRO as x arrangements will not occur and (1 - x) arrangements will occur as dictated by the statistical distribution of atoms for a specific bulk composition. (2) Consider the situation where some fraction, x, of the possible number of short-range arrangements are not favored from a bond-valence perspective, and the remaining (1 - x) arrangements are unequally favored. There will be extreme SRO as x arrangements will not occur and (1 - x) arrangements will occur as dictated by the preference of occurrence on bond-valence grounds for a specific bulk composition. (3) Consider the situation where all combinatorially possible shortrange arrangements are unequally favored from a bond-valence perspective. There will be extensive SRO as all arrangements may occur as dictated by the preference of occurrence on bond-valence grounds for a specific bulk composition. Of course, other factors, such as structural strain, may affect the fraction of any specific arrangement. However, despite this issue, the three examples outlined above indicate that the situation with regard to SRO is more complicated than it initially appears. For (1), there is extreme SRO from the point of view that many arrangements do not occur, but there is also short-range disorder as the arrangements that do occur will occur as dictated by the statistical distribution of atoms for a specific bulk composition. For (2), there is extensive SRO as for (1), but there is partial SRO of observed arrangements as the fractions of these arrangements do not accord with those dictated by the statistical distribution of atoms for a specific bulk composition. For (3), there is partial SRO as

all arrangements occur, but not in the fractions dictated by the statistical distribution of atoms for a specific bulk composition.

The above discussion indicates a lot of potential complexity in the incorporation of SRO into thermodynamic models of amphiboles, and can also lead to confusion in description, as there may be strong SRO and strong short-range disorder [e.g., example (1) above] involving the same sites in the same crystal.

SPECTRAL VARIATION IN THE INFRARED SPECTRA OF AMPHIBOLES

We are interested in the number and relative intensities of bands in the (OH)-stretching region of the infrared spectra of amphiboles, as they provide us with insight into SRO. The possibility of deriving this information from the spectra depends on the resolution of the bands which, in turn, depends on the positions and widths of the bands. Here, we briefly consider these issues for amphiboles.

Peak width and band width

Here, we will use the word "peak" to designate an envelope in the spectrum with only one maximum, and the word "band" to denote an absorption deriving from a specific single local arrangement in the structure. In optimum circumstances, peak widths of a few wavenumbers can be obtained in amphibole spectra. However, some amphiboles show extremely broad peaks without obvious resolution of any component bands (i.e., without a change in the second derivative of the intensity with respect to energy apart from those required to define the primary peak); this variation in peakwidth is shown in Figures 5a and 5b, and Figures 6a and 6c.

What causes this variation in peakwidth?

- (1) The peak may consist of more that one band, where the bands are not sufficiently resolved to produce subsidiary maxima (or even changes in the second derivative of wavelength with respect to energy); such an example is seen in the spectrum of synthetic pargasite (Fig. 5a) which consists of two very broad peaks, each of which has been shown to contain several bands (Della Ventura et al. 1999).
- (2) Bands that are close in energy and physically close in the structure may couple to produce broadening. This is the case in the spectrum of synthetic richterite (Fig. 6c). The halfwidth of the principal absorption in synthetic richterite is ~ 25 cm^{-1} , whereas the halfwidth of the principal absorption in synthetic tremolite is ~ 2 cm^{-1} (Fig. 6a). The configuration symbol for richterite is as follows: M(1)M(3)-O(3)-A: T(1)T(1)-M(2)M(3)-M(1)M(1)M(2)M(2)M(4)M(4) (Fig. 8b). All sites are ordered except for the two M(4) sites, which results in the possible arrangements: M(4)M(4): CaCa, CaNa, NaNa. Thus the intense peak in the spectrum of synthetic richterite must consist of three bands. As the intrinsic width of the CaCa (i.e., tremolite-type) band is $\sim 2 \text{ cm}^{-1}$, assuming an intrinsic width for the other two arrangements, the three bands will not give rise to a composite peak as wide as ~ 25 cm^{-1} just by overlap. It seems reasonable to propose that arrangements across the occupied A site couple to produce broadening of the component bands. It is this coupling that contributes significantly to the broad peak in the richterite spectrum. In this regard, it should be noted that all A-site-occupied amphiboles have spectra with peaks much broader than those in the spectra of A-site-vacant amphiboles.

Band position (energy) as a function of composition

As discussed above, the exact wavelength (energy) of the principal OH-stretching band in the infrared spectrum of a hydroxyl-bearing mineral is a function of the local arrangement of atoms around the OH group. If we designate the arrangement in tremolite as a reference point, we may list the differences in OH-stretching frequencies for different arrangements, and produce a relation between these differences (often referred to as "shifts") and the local compositional differences of the amphibole structure (Strens 1966; Della Ventura and Robert 1990; Della Ventura 1992). The current status of these relations is given in Table 5.

Resolution in infrared spectra

There are two issues relating to resolution of infrared spectra: (1) how "well-resolved" is the experimental spectrum, and (2) how do we numerically resolve the experimental spectrum to extract the maximum amount of information? With regard to (1), the resolution of the spectrum depends on the degree of structural and chemical complexity of the amphibole. As a rule of thumb, spectral resolution decreases with increasing complexity of order and composition of the amphibole. Simple ordered amphiboles give simple well-resolved spectra. However, any degree of disorder will normally decrease the spectral resolution, which is

	-	
Substitution	Frequency shift (cm ⁻¹)	Reference
$^{A}\Box \leftrightarrow ^{A}A$		
^A Na	+55	Robert et al. (1989)
^A K	+60	Robert et al. (1989)
^A Rb	+60	Della Ventura (1992)
^A Li	+50	Iezzi et al. (2004)
$^{T}Si \leftrightarrow^{T}T$		
^{T(2)} Ti	-13 to -23	Della Ventura et al. (1996b)
T(1)Al	-20	Della Ventura et al. (1999)
$M(1,3)$ $M_{C} (> M(1,3)$ M^{2+}		
M(1,3)N;	-15 to -18	Della Ventura et al. (1006a, 1007)
M(1,3)Co	-15 to -18	Della Ventura et al. $(1990a, 1997)$
M(1,3)Ee2+	-15 to -18	Jerzi et al. (2005)
$M^{(1,3)}Mn^{2+}$	-15	Reece et al. (2002)
$M(1,3)$ Mg $\leftarrow M(1,3)$ M ³⁺		
M(1,3) Δ13+	_33	Della Ventura et al. (1999)
M(1,3)Sc ³⁺	-40	Raudsepp et al. $(1987a b)$
$M^{(1,3)}$ Ga ³⁺	-45	Raudsepp et al. $(1987a b)$
$M^{(1,3)}Cr^{3+}$	-50	Fialips-Guédon et al. (2000)
$M^{(1,3)}$ Fe ³⁺	-50	Raudsepp et al. (1987a)
$M(4)$ C $a \rightarrow M(4)$ M $2+$		
$M(4)$ $M \propto M(4)$ $M $	0	How there at al. (1007)
M(4)Sr	-0	Gottschalk et al. (1997)
	72	Gottschark et al. (1998)
${}^{M(4)}$ Na $\leftrightarrow {}^{M(4)}$ M ⁺		
M(4)Li	-4	Iezzi et al. (2003)
$^{O(3)}OH \leftrightarrow ^{O(3)}F$	-15 to -20	Robert et al. (1999, 2000)
$^{\mathrm{O}(3)}\mathrm{OH} \leftrightarrow ^{\mathrm{O}(3)}\mathrm{O}^{2-}$	-23	Della Ventura et al. (2007)

 Table 5. The differences in OH-stretching frequency for different arrangements of cations, relative to the OH-stretching frequency and cation arrangements in tremolite.
 particularly unfortunate as it is for disordered amphiboles that we look to spectroscopy to give us information on their state of order-disorder. So we must take a pragmatic view to the fitting of spectra: we must extract the information that we can; although we may not necessarily be able to extract all the information pertinent to the structure, we need to extract as much as we can, and complement it with information from other experimental methods and theoretical considerations (e.g., local bond-valence theory).

With regard to (2) above, how do we cope with this problem of complexity in the spectra? This issue was discussed by Della Ventura et al. (1999) who synthesized amphiboles along the richterite-pargasite join. The spectrum of synthetic richterite is well understood, and so this gives us a start in spectrum fitting and assignment. The general approach here is *to fit one model to all the spectra of the series*, as in this way we can considerably increase the number of observations without greatly increasing the number of fitting parameters. We can identify the key features of this approach as follows: (1) numerical fitting of the spectra to component bands must be congruent for all spectra; (2) the intensities of the component bands must vary systematically with changes in chemical composition; (3) the variations in ordering derived from the spectral assignments must be in accord with the variation in cell dimensions across the series.

Here, we have covered the general aspects of SRO with respect to amphiboles. Now we will consider the work that has been done on specific minerals and synthetic systems. It is worth-while pointing out that, due to the work done by all the authors cited here, we know far more about SRO in amphiboles than we do in any other complicated rock-forming mineral group.

SHORT-RANGE DISORDER OF DIVALENT B CATIONS IN TREMOLITE

Chemical analyses of *C2/m* amphiboles (Leake 1968) show that tremolite-actinolite amphiboles commonly have minor amounts of small divalent cations (Mn^{2+} , Fe^{2+} , Mg) at the *M*(4) site (i.e., as B cations). Jenkins (1981) noted the presence of small amounts of Mg as a B cation in their synthesis work on tremolite, and this is commonly expressed as a cummingtonite component (i.e., $\Box Mg_2 Mg_2 Si_8 O_{22} (OH)_2$ in $\Box Ca_2 Mg_2 Si_8 O_{22} (OH)_2$). There have been many subsequent studies of synthetic tremolite (Jenkins 1987, 1988, 1994; Jenkins and Clare 1990; Jenkins et al. 1997; Ahn et al. 1991; Smelik et al. 1994; Chernosky et al. 1998; Gottschalk et al. 1999), and all have confirmed the presence of a cummingtonite component in synthetic tremolite, although the amount of this component has been the subject of some debate until fairly recently, when Gottschalk et al. (1999) showed that the amount of cummingtonite component in synthetic tremolite varies between 0.01 and 0.06. Extensive single-crystal structure refinement of a range of Ca-rich *C2/m* amphiboles (e.g., Oberti et al. 1995a) has shown the presence of a second *M*(4') site with a bond geometry very similar to the analogous arrangement in cummingtonite (Table 6)(see Evans 2007 for additional discussion).

	Synthetic Fluoropargasite	Cummingtonite	Synthetic Fluoropargasite	
<i>M</i> (4)–O(2)	2.413	2.164	2.066	<i>M</i> (4')–O(2)
M(4) - O(4)	2.330	2.023	2.264	M(4')-O(4)
M(4) - O(5)	2.597	3.143	2.878	M(4')-O(5)
M(4)-O(6)	2.561	2.691	2.914	M(4')-O(6)

Table 6. Comparison of *M*(4)-O and *M*(4')-O distances (Å) in synthetic fluoropargasite* and cummingtonite**.

*Oberti et al. 1995b, 1998; ** Hawthorne 1983.

There are three possibilities with regard to incorporation of the cummingtonite component: (1) it occurs as domains or lamellae of cummingtonite in a tremolite host; (2) Ca and Mg are short-range disordered at the M(4) site; (3) Ca and Mg are short-range ordered at the M(4) site. High-Resolution Transmission Electron Microscopy (HRTEM) (Gottschalk et al. 1999) showed no sign of a second (possibly exsolved) phase, and thus possibility (1) can be discounted. Thus we are left with possibilities (2) and (3): are Ca and Mg at M(4) short-range disordered or short-range ordered? Above, we used the valence-sum rule to predict that SRO will be uncommon where homovalent ions are involved, and common where heterovalent ions are involved. Thus we expect Ca and Mg at M(4) and M(4') in tremolite to be short-range disordered.

The infrared spectrum of synthetic tremolite

Gottschalk et al. (1999) presented very detailed spectra for synthetic tremolite synthesized at a variety of experimental conditions. As with previous work, a second peak was observed at ~ 3669 cm^{-1} . However, it was shown that the intensity of this peak varies with the details of synthesis. Moreover, Gottschalk et al. (1999) considered the possible local arrangements of Ca and Mg at the NNN M(4) sites using the configuration symbol M(1)M(1)M(3)-O(3)-A: T(1)T(1)-M(2)M(2)M(3)-M(1)M(1)M(2) M(2)M(4)M(4)M(4)M(4) (where we have bolded the sites involved in the binary occupancy of Ca and Mg). Table 7 shows the possible local arrangements of cations at the quartet of M(4) sites, together with their probabilities of occurrence assuming a random distribution. Inspection of Figure 8b shows that there are two distinct pairs of M(4) sites, and these are distinguished in Table 7 as "nearer" and "further." Inspection of Table 7 shows that bands G, H and I should have almost negligible intensity $(\leq 0.02\%)$ and bands D and E should be extremely weak (0.23%) due to the small amount of ^BMg present in tremolite. Thus we expect to observe three distinct bands of significant intensity in the tremolite spectrum, and this is indeed the case. Figure 9 shows the spectrum of synthetic tremolite with close to the maximum observed content of ^BMg. There are two discrete peaks (at 3674.7 and 3669.2 cm⁻¹), but fitting of the spectra shows the presence of two additional bands of significant intensity. The highest-energy band (3676.4 cm⁻¹) is assigned to the presence of minor amounts of talc in the run product (a common feature of amphibole synthesis, Raudsepp et al. 1991). The intense band at 3674 cm⁻¹ was assigned to the arrangement M(4)M(4)-M(4)M(4) = CaCa-CaCa, and the bands at 3672.4 and 3669.2 cm⁻¹ were assigned to the arrangements CaCa-CaMg and CaMg-CaCa (some of the very weak bands were also assigned, but the presence of these bands cannot be evaluated without the associated

	M(4)-sites: distance from H		Probability of cation	Proba calculated	Probabilities calculated for $X^{M(4)}_{Ca}$	
	nearer	further	arrangement	0.95	0.90	
А	CaCa	CaCa	x^4 _{Ca}	81.45	65.61	
В	CaMg	CaCa	$2 x_{Mg} x_{Ca}^3$	8.57	14.58	
С	CaCa	CaMg	$2 x_{Mg} x_{Ca}^3$	8.57	14.58	
D	MgMg	CaCa	$x^2_{Mg} x^2_{Ca}$	0.23	0.81	
Е	CaCa	MgMg	$x^2_{Mg} x^2_{Ca}$	0.23	0.81	
F*	CaMg	CaMg	$4 x_{Mg}^2 x_{Ca}^2$	0.90	3.24	
G	CaMg	MgMg	$2 x_{Mg}^3 x_{Ca}$	0.02	0.18	
Н	MgMg	CaMg	$2 x_{Mg}^3 x_{Ca}$	0.02	0.18	
Ι	MgMg	MgMg	x^4 Mg	0.00	0.01	

Table 7. Probabilities for random distribution of M(4) cation arrangements in the C2/m amphibole structure.

*Cis and trans arrangements are not distinguished.



Figure 9. The infrared spectrum of tremolite (synthesized at 700 °C and 500 MPa from a mixture of CaCO₃, MgO and SiO₂ in a solution of 30 mg of H₂O and 63 mg of AgC₂O₄). Note the presence of a talc band (a common product in the synthesis of tremolite) at 3670.6 cm⁻¹. [Used by permission of Schweizerbart'sche Verlagsbuchhandlung, from Gottschalk et al. (1999), European Journal of Mineralogy, Vol. 11, Fig. 6, p. 977.]

standard deviations for their relative intensities from the least-squares fitting procedure). The relative band intensities from the fitted spectrum of Figure 9 are in accord with the probabilities of the arrangements calculated from a random distribution (Gottschalk et al. 1999). Hence Ca and Mg are short-range disordered in tremolite, as predicted from the short-range valence-sum rule of bond-valence theory.

The Sr analogue of tremolite can be synthesized and Gottschalk et al. (1998) examined the solid-solution of Ca and Sr at the M(4) site in synthetic tremolite and the synthetic Sranalogue of tremolite. HRTEM showed well-ordered structures for most run conditions, and complete solid-solution along the Ca-Sr join. Infrared spectra of end-member compositions gave two distinct bands, whereas intermediate compositions gave additional bands. Gottschalk et al. (1998) interpreted these bands in terms of the configuration symbol M(1)M(1)M(3)-O(3)-A: T(1)T(1)-M(2)M(2)M(3)-M(1)M(1)M(2)M(2)M(4)M(4) [with two less M(4) sites than were used to interpret the spectrum in Figure 9). The spectra of Ca-rich synthetic tremolites were interpreted assuming a random distribution of Ca and Mg over the two nearest M(4) sites, with the probabilities given by $p(CaCa) = x_{Ca} x_{Ca}$, $p(CaMg) = 2 x_{Ca} x_{Mg}$, $p(MgMg) = x_{Mg} x_{Mg}$. The spectra of Sr-rich synthetic analogue-tremolites were interpreted assuming a random distribution of Ca, Sr and Mg over the two nearest M(4) sites with zero occurrence assumed for the arrangement CaMg, with the probabilities given by $p(SrCa) = 2x_{Ca} x_{Ca}$, $p(SrMg) = 2 x_{Ca} x_{Mg}$, $p(SrSr) = x_{Sr} x_{Sr}$. Across the series, the band intensities calculated for a random distribution (within the constraints of the initial assumptions: CaMg and MgMg do not occur at Sr-dominant compositions) are in close agreement with the observed intensities, indicating that there is no SRO in this series (apart from the anti-order assumed with regard to CaMg and MgMg at Sr-dominant compositions). This result is further supported by Andrut et al. (2000), who examined the lattice-vibrational modes in this solid-solution series. They showed that the stretching frequencies for the $[Si_4 O_{11}]$ unit show one-mode behavior (see section on SRO of (OH)-F in amphiboles), indicating that there cannot be any short-range order of Ca and Sr at the M(4) sites.

SRO IN RICHTERITE-PARGASITE SOLID-SOLUTIONS

Early crystal-structure studies on pargasite assumed that ^[6]Al is completely ordered at the M(2) site. However, Semet (1973) showed that the infrared spectrum of pargasite consists of two broad bands centered on 3711 and 3678 cm⁻¹ and suggested that these are due to Al-Mg disorder over the M(1) and M(3) sites. This conclusion was supported by later infrared and Rietveld work (Raudsepp et al. 1987a, 1991) and MAS NMR spectroscopy (Welch et al. 1994). Detailed crystal-structure work by Oberti et al. (1995a) showed that ^[6]Al is partly disordered over the M(2) and M(3) sites in Mg-rich pargasite, the degree of disorder increasing with increase in the amount of Mg in the structure. Della Ventura et al. (1998a) showed that ^[6]Al is disordered in synthetic pargasite but completely ordered at M(2) in the Co analogue: Na Ca₂ (Co²⁺⁴ Al) (Si₆ Al₂) O₂₂ (OH)₂.

The very broad peaks in the spectrum of synthetic pargasite (Fig. 5a) suggest that each is an envelope that consists of more than one band. There is little information in this spectrum

to support fitting of more than one component to each peak, even though the width of the peaks suggests that they consist of several component bands. However, this problem was, if not overcome, somewhat alleviated by fitting a single model (i.e., the same set of components with the same positions and widths) to the spectra of a series of samples along the synthetic-amphibole join richteritepargasite (Della Ventura et al. 1999). The spectra of this series are shown in Figure 10. The fitting process started with the top spectrum of Figure 10, and then proceeded through to the bottom spectrum of Figure 10, fixing the positions of the peaks present in the previous spectra (these constraints were relaxed somewhat once all the spectra were fitted); the results are shown in Figure 11. How do we assign these bands?

The number of stable arrangements

Above, we showed that there are 144 algebraically distinct arrangements for the configuration symbol *M*(1)*M*(1)*M*(3)-O(3)-A:*T*(1)*T*(1)-M(2)M(2)M(3), and 432 distinct arrangements for the configuration symbol M(1)M(3)-O(3)-A: T(1)T(1)-M(2)M(2)M(3) M(2)M(2). Let us consider the case for the simpler configuration. Using the bond-valence arguments of Hawthorne (1997), we can reduce this number somewhat to what is possible with regard to the local valence-matching principle. Any arrangement with two or three Al at M(1)M(1)M(3) will lead to an unacceptable excess in bond valence at O(3) (1.33 and 1.50 vu using Pauling bond-strengths), and hence only MgMgMg and MgMgAl can occur, reducing the number to 144/2 = 72. Although Ca can occur at the A site in monoclinic amphiboles (Hawthorne et al. 1995), it is unlikely that such an arrangement is possible in the absence of F, as Ca would get too close to the H



Figure 10. The infrared spectrum of amphiboles, synthesized along the join richteritepargasite, in the principal (OH)-stretching region; modified after Della Ventura et al. (1999).

atom of the (OH) group at O(3). Examination of pargasitic amphiboles (plus fluorocannilloite, Hawthorne et al. 1996d) shows that F is always in excess of ${}^{A}Ca \times 2$. Thus only Na and \Box are possible at the A site, reducing the number of arrangements to $72 \times 2/3 = 48$. The local arrangements to $72 \times 2/3 = 48$.



Figure 11. Resolution of the infrared spectra of richterite-pargasite solid solutions into component bands A to H. [Used by permission of Schweizerbart'sche Verlagsbuchhandlung, from Della Ventura et al. (1999), European Journal of Mineralogy, Vol. 11, Fig. 5, p. 85.]

f arrangements to $72 \times 2/3 = 48$. The local arrangement T(1)T(1) = AlAl cannot occur as it requires local association of Ca at the *A* site (which above we show does not occur in the absence of F) to avoid unacceptably low bond-valence sums at the O(7) site, and hence the number further decreases to $48 \times 2/3 = 32$. The four possible arrangements of NNN cations [at the M(2)M(2)M(3) sites] are MgMgMg, MgMgAl, MgAlAl and AlAlAl; neither AlAlAl nor MgAlAl can occur with the NN arrangement MgMgAl as an excess of bond valence results at the anions linked to two Al cations, reducing the number to 32/2 = 16.

Band assignment

Note that in end-member pargasite, the arrangement T(1)T(1) = SiSi cannot occur as the bulk composition of the crystal would also force an equal number of arrangements of the type T(1)T(1) = AlAl, and these cannot occur because of the absence of F (and hence ^ACa), resulting in low bond-valence sums incident at the O(7) anion. This argument is in accord with the spectra of Figures 10 and 11: Band A, which we assign to the MgMgMg-(OH)-Na: SiSi-MgMgMg arrangement in richterite, decreases in intensity with increasing pargasite content in the amphibole to disappear at end-member pargasite (and hence the number of possible local arrangements in end-member pargasite reduces to 16/2 = 8). Bands B and C involve NN arrangements of the form MgMgMg-OH-Na; they also have to incorporate [4]Al and hence have the NNN arrangement T(1)T(1) =SiAl. Bands D and F involve NN arrangements of the form Mg-MgAl-OH-Na; they also have to incorporate ^[4]Al and hence have the NNN arrangement T(1)T(1) =SiAl. So what distinguishes between bands B and C, and between bands D and F? This is the NNN arrangement involving the M(2) and M(3) sites: MgMgMg and AlMgMg, respectively. The G and H bands occur only in end-member pargasite, and were assigned to NNN M configurations involving two Al atoms (Della Ventura et al. 1999). The alternative is that bands G and H could be due to configurations involving partly vacant A-sites in the structure, as their frequencies correspond closely to that of bands B and B' of synthetic magnesiohornblende (see below). However, it is difficult at the moment to argue convincingly for one assignment versus the other.

Thus short-range order is extensive in amphiboles of the richterite-pargasite series. The short-range arrangements that occur are those which most closely obey the valence-matching principle applied to local arrangements.

SRO IN TREMOLITE-MAGNESIOHORNBLENDE SOLID-SOLUTIONS

There has been a considerable amount of work on the synthesis of amphiboles nominally along the join tremolite-tschermakite (Jasmund and Schäfer 1972; Oba 1978; Cao et al. 1986; Jenkins 1981, 1983, 1988, 1994; Jenkins et al. 1997; Cho and Ernst 1991; Smelik et al. 1994; Hoschek 1995; Quirion and Jenkins 1998; Hawthorne et al. 2000a; Najorka and Gottschalk 2003). Careful characterization of the run products has shown that amphiboles cannot be synthesized in the tschermakite-dominant part of the system (i.e., more aluminous than aluminohornblende). Furthermore, Mg is incorporated at the M(4) site, leading to Ca contents below the ideal value of 2 apfu. Considerable efforts have been made to characterize the resultant amphiboles (Jenkins et al. 1997; Hawthorne et al. 2000a; Najorka and Gottschalk 2003), but the situation is still not completely clear. However, what is clear is that there is considerable short-range order involving some cation arrangements, and there may also be short-range disorder involving different cation arrangements.

Jenkins et al. (1997) reported infrared spectra and ²⁹Si and ²⁷Al MAS NMR spectra of amphiboles (run products) in the compositional range Al = 0 (0) to 1.84(2.0) apfu. The MAS NMR spectra are shown in Figure 12. The ²⁷Al MAS NMR spectra (Fig. 12a) shows a single peak at 68 ppm, assigned to [4]-coordinated Al, and a doublet at ~0 ppm assigned to [6]-coordinated Al. There is no sign of two components in the 68 ppm peak, and hence there is no information about site occupancy for [4]-coordinated Al. The doublet at ~0 ppm indicates that [6]-coordinated Al occurs at (at least) two sites, in accord with the infrared spectra, but we cannot distinguish between sole occupancy of *M*(1), sole occupancy of *M*(3), or occupancy of both *M*(1) and *M*(3) by Al. Jenkins et al. (1997) interpret the ²⁹Si MAS NMR spectra (Fig. 12b) as indicating complete disorder of Al over the *T*(1) and *T*(2) sites. However, their calculations take no account of SRO, a situation that the bond-valence arguments of Hawthorne (1997) and the experimental observations of Della Ventura et al. (1999) indicate as most unlikely. Moreover, the neutron structure work of Welch and Knight (1999) shows that ^[4]Al is ordered at *T*(1) in synthetic pargasite, a compositionally similar amphibole synthesized at similar conditions.

Hawthorne et al. (2000a) reported infrared and triple-quantum MAS NMR spectra of synthetic aluminous amphiboles nominally along the join tremolite-tschermakite with a small ($\leq 10\%$ content of cummingtonite component) but extending only as far as aluminohornblende. Figure 13 shows the ²⁷Al MAS NMR spectra of an amphibole with ^[4]Al = ^[6]Al = 0.4 apfu. The ²⁷Al MAS NMR spectrum (Fig. 13a) is conformable with those of Jenkins et al. (1997) (see Fig. 12) and is interpreted in the same fashion. The 3Q MAS NMR spectrum has an isotropic component that allows Al bands that overlap in the MAS NMR spectrum to be resolved (this is usually not possible for the single-pulse spectrum because of significant quadrupolar components of the spectrum that lead to considerable peak-overlap). The 3Q spectrum (Fig. 13b) clearly resolves two distinct signals for [6]-coordinated Al, indicating that Al occurs at only two of the *M*(1,2,3) sites. The single-crystal structure-refinement results of Oberti et al. (1995a) indicates that these two sites are *M*(2) and *M*(3).

The infrared spectra of these amphiboles are shown in Figure 14. Based on the argument that it is only statistically justified to fit a component if there is a change in sign of the second derivative of intensity with respect to energy (wavenumber), Hawthorne et al. (2000a) identified 5 distinct bands (A, B, B', C and C', Fig. 14a) and fit all spectra of the series to these bands (Fig. 14b). As only 5 bands were resolved, Hawthorne et al. (2000a) interpreted the spectra in terms of the configuration symbol M(1)M(1)M(3)-O(3)-A: T(1)T(1)-M(2)M(2)M(3). Figure 15a shows the relevant cluster of octahedra, Figure 15b shows a graphical representation of this



Figure 12. MAS NMR spectra for amphiboles along the nominal join tremolite-aluminohornblende; (a) ²⁷Al; (b) ²⁹Si (from Jenkins et al. 1997).



Figure 13. MAS NMR spectra for an amphibole along the nominal join tremolite-aluminohornblende with ${}^{[4]}Al = {}^{[6]}Al = 0.4$ apfu; (a) ${}^{27}Al$ MAS NMR spectrum; (b) triple-quantum (3Q) ${}^{27}Al$ MAS NMR spectrum (from Hawthorne et al. 2000a).



Figure 14. Infrared spectra of synthetic tremolite-aluminohornblende amphiboles in the principal (OH)stretching region; (a) raw spectra; (b) spectra resolved (from Hawthorne et al. 2000a).

cluster, and Figure 15c shows the possible NN and NNN cation-arrangements for occupancy of these octahedra by Mg and Al [with Al restricted to M(2) and M(3)]. Inspection of Figure 15c shows 8 arrangements that are acceptable from a bond-valence perspective (those marked by a central black diamond). However, there is also distinct symmetry and pseudosymmetry among these arrangements (i.e., those arrangements connected by broken and dotted lines). Incorporating these equivalences results in 4 distinct arrangements: (1) MgMgMg-O(3)- $\Box: T(1)T(1)-MgMgMg; (2) MgMgMg-O(3)-\Box: T(1)T(1)-MgMgAl; (3) MgMgAl-O(3)-\Box:$ T(1)T(1)-MgMgMg; (4) MgMgAl-O(3)- \Box : T(1)T(1)-MgMgAl. This leaves the T(1)T(1) part of the configuration to be considered. As discussed by Della Ventura et al. (1999) for synthetic amphiboles of the richterite-pargasite series, the possible cation arrangements for T(1)T(1) are SiSi and SiAl (AlAl can only occur where A = Ca, Hawthorne et al. 1996d). These arguments result in the eight arrangements given in Table 8. There are only five resolved components in the spectra of Figure 14b, and Hawthorne et al. (2000a) assigned the arrangements to the component absorptions using the frequency shifts listed in Table 5. Although Hawthorne et al. (2000a) could not derive band intensities for all eight bands listed in Table 8 (as only five components were resolved), the small number of bands observed (compared with the large number of combinatorially possible bands) indicates strong short-range order arising from local bond-valence requirements.



Figure 15. NN and NNN cation arrangements in synthetic amphiboles (approximately) along the join tremolite-aluminohornblende (with a small cummingtonite component); (a) polyhedron representation of the cluster of octahedra; (b) graphical representation of the cluster shown in (a); (c) possible NN and NNN arrangements in the cluster shown in (a), (b) under the constraint that Al does not occur at M(1); undecorated nodes represent Mg, shaded circles represent Al. The NN cations are indicated above each graph [M(1)M(3) = MgMgMg or MgMgAl]; the NNN cations are shown below each graph [M(2)M(2)M(3) = MgMgMg, AlMgMg (=MgAlMg = MgMgAl), AlAlMg (= AlMgAl = MgAlAl) and AlAlAl. The most stable arrangements from a bond-valence perspective are shown by occupancy of the central node by a black diamond. Symmetrically equivalent arrangements are connected by broken lines, pseudosymmetrically equivalent arrangements are form Hawthorne et al. 2000a).

Najorka and Gottschalk (2003) also examined synthetic amphiboles nominally along the join tremolite-aluminohornblende; their spectra are very similar to those of Hawthorne et al. (2000a), but the fitting and interpretation are different. The cluster used to interpret the spectra is shown in Figure 16, the usual constraints [^[4]Al at T(1) only, ^[6]Al at M(2,3) only] were used, and thirty-six possible cation arrangements were identified (Fig. 17). A maximum of twelve bands were fitted to the IR spectra (Fig. 18). There do not appear to be a sufficient number of changes in the second derivative of the spectral envelope to justify this number of components (Hawthorne and Waychunas 1988). On the other hand, one can extract more information from a spectrum that is present in the raw information if one can input additional correct information in the fitting model (e.g., the width of the component bands, the relative positions of the component bands, the number of component bands, of which one may have information independent of the spectrum).

No.	Configuration	Observed	Band frequency (cm ⁻¹)
1	[MgMgMg]–SiSi–MgMgMg	3675	А
2*	[MgMgMg]–SiSi–MgMgAl	3671	A'
3	[MgMgMg]–SiAl–MgMgMg	3655	В
4*	[MgMgMg]–SiAl–MgMgAl	3642	B'
5	[MgMgAl]–SiSi–MgMgMg	3642	B'
6*	[MgMgAl]–SiSi–MgMgAl	3625	С
7	[MgMgAl]–SiAl–MgMgMg	3625	С
8*	[MgMgAl]-SiAl-MgMgAl	3608	C'

 Table 8. Possible cation arrangements around the OH group in synthetic amphiboles of the tremolite-magnesiohornblende series, together with the assigned bands and observed band frequencies.

*M(2)M(3)M(2) = MgMgAl and MgAlMg are indistinguishable.



Figure 16. NN and NNN cation arrangements in the amphibole structure at which Al occurs in tremolite-aluminohornblende solid-solutions. [Used with kind permission of Springer Science and Business Media, from Najorka and Gottschalk (2003), Physics and Chemistry of Minerals, Vol. 30, Fig. 10, p. 120.]

Najorka and Gottschalk (2003) divide their cation arrangements into groups under the assumption that the spectral shift from the tremolite arrangement is proportional to the distance from the proton at which the Al occurs. This results in three groups (Fig. 17): I: ^{*T*(1)}Si only, ^[6]Al = 1-2 at M(2) and/or $M(3)_{far}$; II: ^{*T*(1)}Al = 1, ^[6]Al = 1-3 at M(2) and/or $M(3)_{far}$; III: ^[6]Al = 1-4 at M(2) and either Al at $M(3)_{near}$ or ^{*T*(1)}Al = 2. Furthermore, they assume that groups I-III correspond to the three groups of bands with different half-widths (Fig. 18). The variation in relative intensity of these groups of bands is shown in Figure 19, where they are compared with the variation calculated assuming a statistical distribution of cations. The agreement is closer assuming a random distribution of Al over M(2) and M(3) rather than a random distribution of Al and Mg at M(2).

It is apparent that there are different philosophies of spectral fitting operative in this area, and there has not been sufficient work done on complicated amphiboles to evaluate which approach is more profitable (note that we do no use the rather emotive term 'correct'). This issue must await resolution, if indeed it can be resolved. One may be restricted to a more pragmatic approach where one extracts what insight one can from the infrared spectrum, and appeals to other experimental methods for additional information.



Figure 17. The 36 possible cation arrangements for (Mg,Al) and (Si,Al) occurrence in the cluster of Fig. 16 for the occupancy constraints discussed in the text; unshaded polyhedra are occupied by Mg or Si, shaded polyhedra are occupied by Al; the numbers to the bottom right of each arrangement indicate the multiplicity of that arrangement; the arrangements are divided into four types, indicated by the Roman numbers. [Used with kind permission of Springer Science and Business Media, from Najorka and Gottschalk (2003), Physics and Chemistry of Minerals, Vol. 30, Fig. 11, p. 121.]

SRO IN PARVO-MANGANO-EDENITE

Oberti et al. (2006) described recently two new group-5 amphiboles with a *B*-site composition intermediate between that of calcic and Mg-Fe-Mn-Li amphibole (Oberti et al. 2007a). Application of the bond-valence approach (Hawthorne 1997) suggests three possible local arrangements in edenite based on the site-configuration symbol M(1)M(1)M(3)-O(3)-A: T(1)T(1): (1) MgMgMg-OH-Na: SiAl, (2) MgMgMg-OH- \Box : SiSi, (3) MgMgMg-OH-Na: SiSi. The first two arrangements are part of a neutral formula, whereas the third arrangement is charged: it is equivalent to a tremolite-like arrangement with additional Na, and thus implies additional bond-valence incident at the O(5) and O(6) anions that could be accommodated by relaxation of bond lengths. The FTIR spectrum of parvo-mangano-edenite (Fig. 20) was modeled using eight Gaussian components, labeled A to H, the assignment of which is reported in Table 9. The spectrum is in accord with this model; bands B and C (Table 9) are associated with the edenite(1) configuration, and bands D to G are associated with the edenite(2) configuration. The strong intensity of these latter bands accords with the Si excess measured by EMP analysis. The edenite(3) configuration is assigned to band A. The presence

TS-93

absorbance [arbitrary units]

3500





Figure 18. Infrared spectra of selected amphiboles along the join tremolite-aluminohornblende (expressed as the fraction of tschermakite, TS); the cation arrangements associated with each band or group of bands is shown in the top spectrum, and the type of arrangement is indicated by the Roman numbers in the spectrum for TS-30. [Used with kind permission of Springer Science and Business Media, from Najorka and Gottschalk (2003), Physics and Chemistry of Minerals, Vol. 30, Fig. 9, p. 120.]

Figure 19. Comparison of observed (points) and calculated (lines) relative absorbances for the groups I-III (Fig. 17) for (a) random distribution of (Mg,AI) at M(2), and (b) random distribution of (Mg,AI) over M(2) and M(3); shaded circles = Group I, dotted circles = Group II, unshaded circles = Group III. [Used with kind permission of Springer Science and Business Media, from Najorka and Gottschalk (2003), Physics and Chemistry of Minerals, Vol. 30, Fig. 12, p. 122.]

of all configurations predicted on bond-valence grounds by Hawthorne (1997) is in accord with significant short-range order in this composition.

SHORT-RANGE ORDER-DISORDER OF (OH) AND F IN AMPHIBOLES

Many monoclinic amphiboles show solid solution of (OH) and F, but little has been published on the mechanism of this solid solution: do (OH) and F show complete shortrange disorder, or is this substitution associated with SRO? Infrared spectroscopy can provide



Figure 20. Fitted infrared spectra in the principal (OH)-stretching region for parvo-mangano-edenite (from Oberti et al. 2006).

Table 9. Band labels,	position (cm ⁻¹), and assignment for
the spectrum	of parvo-mangano-edenite.

Band	Wavenumber (cm ⁻¹)	Configuration
А	3725	^A Na–MgMgMg–SiSi
В	3711	^A Na–MgMgMg–AlSi
B*	3709	^A Na–MgMgMn–SiSi
С	3692	^A Na-MgMgMn-AlSi
C^*	3693	^A Na-MgMnMn-SiSi
D	3672	^A D–MgMgMg–SiSi
D*	3677	^A Na-MnMnMn-SiSi
Е	3659	^A □–MgMgMn–SiSi
F	3641	^A □–MgMnMn–SiSi
G	3621	^A □–MnMnMn–SiSi
Н	3603	^A □–MgMgM ³⁺ –SiSi

*Values calculated with a constant negative shift of 16 cm^{-1} for the different (Mg,Mn) configurations at M(1,3) (e.g., Reece et al. 2002)

us with a window into this type of behavior. Robert et al. (1989, 1999) examined (OH)-F solid-solutions in synthetic tremolite--fluorotremolite, synthetic richterite--fluororichterite and synthetic potassic-richterite--potassic-fluororichterite. The salient feature of all these amphiboles is that the M(1), M(2) and M(3) sites are occupied only by Mg; hence the only NN M(1)M(1)M(3) arrangement that occurs is MgMgMg, and the NNN *M*-site arrangements involve only Mg. Similarly, the T(1) sites are occupied only by Si. Hence all local arrangements are as follows: MgMgMg-(OH)- \Box :SiSi-MgMgMg and MgMgMg-(OH)-Na:SiSi-MgMgMg, and their F-analogues MgMgMg-F- \Box :SiSi-MgMgMg and MgMgMg-F-Na:SiSi-MgMgMg that are invisible in the infrared. The only potential for local order involves (OH) and F at O(3) sites adjacent to the (OH) group of the arrangement.

One-mode and two-mode behavior

In amphiboles of the tremolite-fluorotremolite series, there is a single (OH)-stretching band at 3674 cm⁻¹. The position of this band does not change significantly with decreasing F content

of the amphibole, and the band intensity decreases monotonically with decreasing F content. This type of spectrum is called one-mode behavior. In the amphiboles of the richterite-fluororichterite series, the spectra are more complicated (Fig. 21). The richterite spectrum (Fig. 21a) contains a single intense band A at 3730 cm⁻¹ due to the arrangement MgMgMg-(OH)-Na:SiSi-MgMgMg, together with a weak band C at 3674 cm⁻¹ due to the arrangement MgMgMg-(OH)-□:SiSi-MgMgMg from the minor tremolite component in the amphibole. The spectrum of fluororichterite with a nominal F content of 1.2 apfu (Fig. 21b) contains a single intense band A at 3730 cm⁻¹ due to the arrangement MgMgMg-(OH)-Na:SiSi-MgMgMg, together with a weak band C at 3674 cm⁻¹ due to the arrangement MgMgMg-(OH)-D:SiSi-MgMgMg from the minor tremolite component, plus an additional band B of intermediate intensity at 3711 cm⁻¹. This appearance of a new band in such circumstances is known as two-mode behavior (Chang and Mitra 1968). Moreover, with increasing F content of the amphibole, the intensity of the B band increases at the expense of the A band.

The stereochemistry of local coupling within the amphibole structure

The one-mode behavior of the synthetic tremolite-fluorotremolite solid-solution indicates that local arrangements involving an (OH) group



Figure 21. Infrared spectra in the principal (OH)-stretching region for (a) an amphibole of intermediate composition in the tremolite-fluorotremolite solid-solution; (b) an amphibole of intermediate composition in the richterite-fluororichterite solid-solution (from Robert et al. 1999).

are not significantly affected by adjacent arrangements involving F. Thus we may conclude that in tremolite-fluorotremolite, there is no coupling between adjacent O(3) anions, either through the O(3)-O(3) edge in the octahedral strip or across the vacant A cavity. The two-mode behavior of richterite-fluororichterite solid-solutions indicates that the local arrangement involving an (OH) group is significantly affected by adjacent arrangements involving F. The only local difference between tremolite and richterite is that the A cavity is vacant in tremolite and is occupied by Na in richterite, indicating that the two-mode behavior in the latter is due to coupling of arrangements across the A cavity through the resident Na atom.

What factors are pertinent to the possibility of coupling across the *A* cavity? First, comparison of the principal (OH)-stretching frequency in tremolite (3674 cm^{-1}) and richterite (3730 cm^{-1}) indicates that there is a strong repulsive interaction between H and Na at the *A* site. Second, comparison of the electron-density arrangements in the *A* cavity when O(3) = (OH) and when O(3) = F (Fig. 22) indicates that Na occupies a more central position in the cavity when O(3) = (OH) than when O(3) = F. In turn, this indicates that an (OH) group will interact less strongly with Na when the opposing O(3) site is occupied by F rather than by (OH). Hence Na will move toward F and away from (OH), reducing the repulsive interaction between H and Na and causing the constituent (OH) group to absorb at a lower frequency [as is observed for band B in the spectrum of fluororichterite (Fig. 21b)]. Thus local coupling of arrangements occurs across an occupied *A* cavity but not across an unoccupied *A* cavity. This is an important generalization as it provides constraints on what bands can and cannot occur in amphibole solid-solutions.



Figure 22. Electron-density distribution in the *A* cavity projected on to $(\overline{2}01)$ in (a) fluoro-arfvedsonite, and (b) arfvedsonite; contour interval is 1 e/Å³ (from Haw-thorne et al. 1996a).

Local arrangements in (OH,F)-bearing amphibole solid-solutions

In order to quantitatively interpret the spectra presented here, we have to understand what is happening around the *A* site in these amphiboles. This issue is examined in Figure 23 which shows sketches of all possible arrangements around the *A* cavity in richterite and tremolite. In richterite, where both O(3) sites are occupied either by (OH) [arrangement (1)] or by F [arrangement (3)], Na interacts equally with each (OH) group, whereas when one O(3) site is occupied by (OH) and the other is occupied by F, Na moves toward F [and away from (OH)], giving rise to the second band. In tremolite, the occupancy of one O(3) site does not affect the other O(3) site as there is no A cation to transmit this effect across the cavity.

Testing for SRO of (OH) and F in richterite

Let us now consider the quantitative effect of the arrangements in Figure 23 on the infrared spectra. There are two important points here: (1) arrangements (3) and (6) are invisible to infrared in the principal (OH)-stretching region; (2) arrangements 4 and 5 will give rise to degenerate principal (OH)-stretching bands; (3) the sum of the relative proportions of the six



Figure 23. Local arrangements in the *A* cavity involving (OH) and F: (a) (OH,F)-bearing richterite; (b) (OH,F)-bearing tremolite. White circles: O atoms of (OH) groups; small black starred circles: H atoms; large black circles: F atoms; black square: Na at the A(m) site; white square: vacant A(m) site (modified from Robert et al. 1999).

arrangements is unity. There are six arrangements and only three bands in the spectrum, and we cannot explicitly derive quantitative information on SRO. In addition, the bands due to richterite have different molar absorptivities than the bands due to tremolite (Hawthorne et al. 1997), and hence the intensities of the richterite and tremolite bands do not relate to the frequency of occurrence of local arrangements in the same way. Despite these problems, we can test a model for complete local disorder using the relative intensities of bands A and B, as the arrangements involved couple through the Na at the *A* site and hence have the same molar absorptivities.

Let *X* be the proportion of richterite component [arrangement (4)], (1 - X) be the proportion of tremolite component, *x* be the fraction of F [$x = X_F = F / (OH + F)$], n_i be the probability of occurrence of local arrangement (i) (i = 1-6) such that $\Sigma n_i = 1$. Assuming no SRO, the probabilities of occurrence of these arrangements can be written as follows:

 $n_{1} = X(1 - x)^{2}$ $n_{2} = 2X(1 - X)x$ $n_{3} = Xx^{2}$ $n_{4} = (1 - X)(1 - x)^{2}$ $n_{5} = 2(1 - X)(1 - x)x$ $n_{6} = (1 - X)x^{2}$ (1)

The individual band intensities should vary as follows:

$$I_A \propto 2n_1 = 2X(1-x)^2 \approx X(1-x)$$

$$I_B \propto n_2 = 2X(1-x)x \approx Xx$$

$$I_C \propto 2n_4 + n_5 = 2(1-X)(1-x)^2 + 2(1-X)(1-x)x \approx 1-X$$
(2)

where the approximation assumes that the extinction coefficients of bands A, B and C are equal [i.e., that the total band intensity $I_A + I_B + I_C$ is 2(1 - x)]. The constituent arrangements for bands A and B have the same molar absorptivities, and hence we can test a model of complete local disorder using the intensities of the two bands. We do not know the value of *X*, but *X* is not involved in the *relative* intensities of the A and B bands:

$$I_A / (I_A + I_B) = X(1 - x) / [X(1 - x) + Xx] = 1 - x$$

$$I_B / (I_A + I_B) = Xx / [X(1 - x) + Xx] = x.$$
(3)

Figure 24 compares the calculated and observed intensity ratios for the A and B bands in richterite-fluororichterite solid-solutions; the agreement is in accord with complete short-range disorder of (OH) and F in these amphiboles.

The spectra discussed above indicate that (OH) and F are short-range disordered. However, we must emphasize that this disorder is with regard to each other (i.e., they are randomly disordered with regard to each other). Hawthorne et al. (1996a) showed that local arrangements of atoms at the M(4) and O(3) sites are preferentially associated with Na at the A(2) and A(m) sites. This issue has recently been addressed by Hawthorne et al. (2006) on a series of F-rich amphiboles from Bear Lake, Ontario (Canada), in which there are significant to complete short-range associations of the type Na-F^{M(4)}Na and \Box -(OH)- $^{M(4)}$ Ca. Thus (OH)



Figure 24. Variation in the observed band intensities and the values calculated for complete short-range disorder of (OH) and F in richterite-fluororichterite solid-solutions (from Robert et al. 1999).

and F may be randomly arranged with respect to each other, but they can also show SRO involving other atoms in the amphibole structure.

Testing for SRO of (OH) and F in pargasite

Richterite, potassic-richterite and tremolite are characterized by the M(1)M(1)M(3) arrangement MgMgMg, and we examined the short-range behavior of (OH) and F with respect to each other. The presence of the M(1)M(1)M(3) arrangements MgMgMg and MgMgAl in pargasite (see above) allows us to test the potential for SRO of both (OH) and F with respect to these to NN arrangements.

Robert et al. (2000) examined the (OH,F) substitution in synthetic pargasite; the infrared spectra of the amphiboles are shown in Figure 25. As shown above, the spectrum of synthetic end-member pargasite consists of six bands, but Robert et al. (2000) fitted only three aggregate bands because the appearance of the spectra in Figure 25 make it apparent that the principal changes relate to the NN arrangements MgMg-Mg and MgMgAl (and not to the NNN arrangements). The spectra of the F-bearing amphiboles were resolved into four bands; bands A and B in F-free pargasite can also be identified in the spectra of the F-bearing pargasite, and it is notable that the intensity of band B decreases strongly with increasing F content of the amphibole (Fig. 25). Moreover, the A' and B' bands increase rapidly in intensity with increasing F, indicating that the associated arrangements involve F, and that these bands are the result of two-mode behavior. The greater decrease in intensity of band B [MgMgAl-OH] relative to that of band A [MgMgMg-OH] indicates a relative decrease in the number of MgMgAl-OH arrangements with increasing F content. There are two possibilities here: (1) F occurs preferentially at the MgMgAl arrangement; (2) Al is displaced to the M(2) site by F occurring at O(3). Single-crystal structure refinement of fluoropargasite (Oberti et al. 1995b) shows all Al ordered at M(2), indicating that mechanism (2) is operative in these amphiboles.



Figure 25. Infrared spectra in the principal (OH)stretching region for pargasite-fluoropargasite solid-solution (from Robert et al. 2000).

Della Ventura et al. (2001) examined amphiboles of nominal composition [richterite_{0.60}pargasite_{0.40}] with varying amounts of (OH) and F: Na (Na_{0.6} Ca_{1.4}) (Mg_{4.6} Al_{0.4}) (Si_{7.2} Al_{0.8}) O₂₂ (OH,F)₂. The infrared spectra are shown in Figure 26. Comparison of the spectrum of Fbearing richterite (Fig. 26a) with that of end-member richterite (Fig. 26b) shows the addition of a new band in the former at 3711 cm⁻¹, a result of the new arrangement in which F replaces (OH) at the O(3) site across the *A* cavity (see above). The spectrum of end-member pargasite (Fig. 26e) has two (composite) bands at 3710 and 3678 cm⁻¹, and addition of F gives rise two new bands at 3694 and 3658 cm⁻¹ (Fig. 26d, also see above). The spectrum of Ri_{0.40}Pa_{0.60} (Fig. 26c) shows a broad absorption at 3705 cm⁻¹ and a weaker absorption at 3674 cm⁻¹. Comparison with the other spectra of Figure 26 suggests that the 3705 cm⁻¹ band corresponds to overlap of the 3711 band in richterite [from association of (OH) and F at neighboring sites across the A cavity], the 3710 cm^{-1} band in pargasite [from the arrangement MgMgMg-(OH)-(OH)], and the 3694 cm⁻¹ band in pargasite [from the arrangement MgMgMg-(OH)-F]. The band due to the arrangement MgMgAl-(OH)-F (at 3658 cm⁻¹) and the 3730 cm⁻¹band in richterite are not present in the spectrum of (OH,F)bearing Ri_{0.40}Pa_{0.60} (Fig. 26c). These spectra thus show that F completely replaces (OH) in local MgMgMg-(OH)-Na:SiSi (richteritelike) arrangements, and partly replaces (OH) groups in MgMgMg-(OH)-Na:SiAl (one of the pargasite-like) arrangements. Note that in MgMgAl-(OH):SiAl arrangements, F cannot replace (OH). The latter is to be expected on bond-valence grounds: MgMgAl will provide incident bond-valence significantly greater than 1 vu, and the (OH) group can accommodate this because the O-H bond can adjust its length to provide whatever bond valence is needed (i.e., 1.0-0.7 vu). On the other hand, F needs to receive exactly 1 vu from its coordinating cations; there is no problem when these are MgMgMg (≈ 0.33 \times 3 = 1 vu), but when they are MgMgAl, the resulting sum (0.33 + 0.33 + 0.50 = 1.17 vu) is too large to be accommodated by F.

SHORT-RANGE DISORDER OF Ti⁴⁺ AND Si

It has long been known that K-bearing richterite from lamproites often shows Si + Al less than 8 apfu, and it was customary to assign Ti to the *T*-group cations to bring the total to 8 apfu (e.g., Papike et al. 1969; Wagner and Velde 1986). XAS (Mottana et al. 1990; Paris et al. 1993) and infrared spectroscopy (Della Ventura



Figure 26. Infrared spectra in the principal (OH)-stretching region for the synthetic solid-solution Richterite_{0.40}Pargasite_{0.60}(OH, F). [Used by permission of Schweizerbart'sche Verlagsbuchhandlung, from Della Ventura et al. (2001), European Journal of Mineralogy, Vol. 13, Fig. 7, p. 846.]

et al. 1991, 1993a) showed that Ti is indeed a tetrahedrally coordinated cation in synthetic Tibearing potassic-richterite. Site-scattering refinement of a series of Ti-bearing richterite crystals (Oberti et al. 1992) showed that Ti⁴⁺ is a T cation and is completely ordered at the T(2) site. However, the question now arises as to whether there is short-range order involving Ti⁴⁺ and Si at the T(2) site. This issue was examined by Della Ventura et al. (1996b) who synthesized amphiboles along the join potassic-richterite [K (Ca Na) Mg₅ Si₈ O₂₂ (OH)₂] – Ti⁴⁺-bearing potassic-richterite [K (Ca Na) Mg₅ (Si₇ Ti⁴⁺) O₂₂ (OH)₂] and characterized them by infrared spectroscopy. Their spectra are shown in Figure 27. There is prominent multi-mode behavior and the spectra were fitted to four bands, A, B, C and T; bands A, B and C were assigned to Asite-full arrangements and band T was assigned to the tremolite arrangement (see above). There is also a very weak band in the spectrum of Ti-free potassic-richterite (Fig. 27a) at ~ 3720 cm⁻¹; this is due to slight asymmetry in the band (which was fitted by a symmetrical Gaussian curve),



Figure 27. Infrared spectra in the principal (OH)-stretching region for synthetic amphiboles along the join potassic-richterite–K CaNa Mg_5 (Si₇ Ti⁴⁺) O_{22} (OH)₂ (from Della Ventura et al. 1996b).

and was ignored in the following arguments as it is less than 5% of the total intensity.

Band assignment

The occurrence of multi-mode behavior suggests the existence of distinct local arrangements, and the increase in intensity of bands B and C with increasing Ti (Fig. 28) indicates that these local arrangements must involve Ti⁴⁺. There are two T(2) sites in each ring of six tetrahedra (Hawthorne and Oberti 2007, Fig. 3), and each of these may be occupied by Si or Ti⁴⁺. Thus there are only three possible arrangements around each (OH) group: SiSi, SiTi⁴⁺ and Ti⁴⁺Ti⁴⁺. The intensity of an (OH)-stretching band is proportional to the number of (OH) groups in each arrangement. Assuming a random distribution of Si and Ti⁴⁺ over the two sites, the probability of occurrence of each T(2)T(2) pair as a function of bulk composition is as follows:

SiSi:
$$(1 - x / 4)^2$$

SiTi⁴⁺: $2(1 - x / 4) (x / 4)$ (4)
Ti⁴⁺Ti⁴⁺: $(x / 4)^2$

where $x = \text{Ti}^{4+}$ apfu. Figure 29 shows the observed relative intensities of the three resolved bands as a function of the calculated probabilities of occurrence of the three possible arrangements for a random distribution. There is close accord between the observed and calculated values, and this agreement leads us to assign band B to the SiTi⁴⁺ arrangement and band C to the Ti⁴⁺Ti⁴⁺ arrangement. The close agreement between the observed and calculated values indicates that there is complete short-range disorder of Si and Ti⁴⁺ over the *T*(2) sites in the double chain of tetrahedra in the structure of potassic-richterite.

Local stereochemistry

The Ti⁴⁺ \rightarrow Si substitution does not modify the charge distribution around the locally associated (OH) groups, and hence the appearance of the lower-frequency

bands must be caused by the different local distortions of the six-membered rings of tetrahedra resulting from the different T(2) arrangements.

SHORT-RANGE ORDER OF Ti⁴⁺ AND O²⁻

The association between Ti⁴⁺ and deficiency in monovalent anions has long been recognized in kaersutitic amphiboles (Leake 1968; Saxena and Ekstrom 1970). However, the situation is complicated by the fact that dehydrogenation in amphiboles can proceed by oxidation of Fe²⁺ to Fe³⁺ (e.g., Barnes 1930; Addison et al. 1962; Ernst and Wai 1970; Dyar et al. 1993; Popp et al. 1995), and hence other factors *can* affect the amount of monovalent anions in the amphibole structure. Site-scattering refinement with neutron-diffraction data (Kitamura and Tokonami 1971; Kitamura et al. 1973, 1975; Jirak et al. 1986; Pechar et al. 1989) has shown that Ti is partly to completely ordered at the M(1) site. The same conclusions have been made



from crystal-structure refinement with X-rays, focusing on the stereochemistry of the M(1) site. Hawthorne et al. (1998) showed that there is a very strong correlation between the Ti content of a suite of sodic-calcic and sodic amphiboles from Coyote Creek, California (Fig. 30), where the H contents were determined by SIMS. The slope of the line in Figure 30 is in accord with the equation (note that this is **not** a chemical reaction!)

$${}^{M(1)}\text{Ti}^{4+} + 2 {}^{O(3)}\text{O}^{2-} = {}^{M(1)}(\text{Mg},\text{Fe}^{2+}) + 2 {}^{O(3)}\text{OH}^{-}$$
 (5)

Oberti et al. (1992) proposed that the atoms involved are locally associated in the amphibole structure. This proposal makes sense from a local bond-valence perspective, as the absence of a H atom from the coordination of O(3) necessitates incidence of considerable additional bond valence from the locally coordinating cations. The association of a high-valence cation with the occurrence of a divalent anion at the O(3) site is a notable feature in amphiboles. In addition to kaersutite, there are several other amphiboles with dominant O^{2-} at the O(3) site (Table 10). All of them except ungarettiite have Ti⁴⁺as an essential constituent, and in all of them, the local version of bond-valence theory indicates that there local association of Ti⁴⁺at M(1) with O^{2-} at O(3). For ungarettiite, the situation is somewhat different. Here, Mn^{3+} is dominant at the M(1) and M(3) sites; moreover, Mn^{3+} is a Jahn-Teller cation when in octahedral coordination, and it forms very short bonds to the O(3) site (Hawthorne et al. 1995), providing the necessary bond valence for O^{2-} at the O(3) site.



Figure 30. Variation in Ti⁴⁺ as a function of the O^{2–} content of the O(3) site in amphiboles from Coyote Peak (from Hawthorne et al. 1998).

Table 10. Amphibole end-member	s with O ²	^{2–} dominant at	the $O(3)$ site.
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Name	Formula	Ref.
Obertiite	Na Na ₂ (Mg ₃ Fe ³⁺ Ti ⁴⁺) Si ₈ O ₂₂ O ₂	(1)
Dellaventuraite	Na Na ₂ (MgMn ³⁺ ₂ Ti ⁴⁺ Li) Si ₈ O ₂₂ O ₂	(2)
Ungarettiite	Na Na_2 (Mn^{2+}_2Mn^{3+}_3) Si_8 O_{22} O_2	(3)

References: (1) Hawthorne et al. (2000b); (2) Tait et al. (2005); (3) Hawthorne et al. (1995).

Della Ventura et al. (2007) studied a suite of well-characterized Ti-rich pargasites from the Lherz peridotite, previously characterized by Zanetti et al. (1996). A combination of XREF, EMPA and SIMS data showed all amphiboles to be Ti-rich pargasites of fairly constant *M*-site composition, with ${}^{[6]}Al_{tot} \sim 0.55$ apfu, ${}^{[6]}Ti \sim 0.45$ apfu and ${}^{[6]}Fe^{3+} \sim 0.40$ apfu, and an anion composition at O(3) = OH \approx O²⁻ \approx 1.0 apfu, with negligible F (max. = 0.06 apfu). The principal variation in these amphiboles involves the different degree of ^CAl disorder between the M(2) and M(3) sites. The FTIR spectra of these amphiboles (e.g., Fig. 31c) are significantly different from those of both synthetic pargasite (Fig. 31a) and natural pargasite (Fig. 31b), both of which show a characteristic pattern of two peaks. The Lherz spectrum is very similar to spectra of synthetic OH-F exchanged pargasite (Fig. 31d). Della Ventura et al. (2007) assign the component bands in the spectra of the Lherz pargasites to local arrangements involving OH-OH (components A, C and E, Fig. 32) and OH-O²⁻ (components B and D, Fig. 32). This suggests that FTIR spectroscopy is an effective way to detect the presence of O^{2-} at O(3). Moreover, the OH-bearing local arrangements visible in the IR spectra are exclusively of the type MgMgMg or MgMgM³⁺ with M³⁺ predominantly Al, in accord with the complete local association of ${}^{M(1)}$ Ti⁴⁺ and ${}^{M(1)}$ Fe^{3+ M(3)}Fe³⁺ with O²⁻ at O(3).

SHORT-RANGE ORDER OF CATIONS AROUND THE A SITE

C2/m amphiboles

The A site in C2/m amphiboles may be occupied by Na, K or \Box (vacancy), and rarely by Ca. As discussed in Oberti et al. (2007b), the A cations do not occupy the central A2/m





Figure 31 (to the left). Infrared spectra in the principal (OH)stretching region for (a) synthetic pargasite; (b) pargasite from Finero; (c) Ti-rich pargasite from Lherz (sample HR3); (d) synthetic fluorpargasite with (OH_{0.8} $F_{1.2}$) (from Della Ventura et al. 2007).

Figure 32 (above). Infrared spectra in the principal (OH)stretching region for Ti-rich pargasite from Lherz (sample HR3) (modified from Della Ventura et al. 2007).

site: K always occupies the A(m) site, whereas Na can occupy the A(m) and/or the A(2)sites. Hawthorne et al. (1996a) showed that the various occupancies of the A(m) and A(2)sites by Na are controlled by the short-range bond-valence requirements of the cations involved in the disorder and the anions to which they are bonded. Figure 27 of Hawthorne and Oberti (2007) shows the distribution of electron density in a series of amphiboles, the compositions of which are given in Table 11. In this regard, it is important to recognize that the factors influencing ^ANa order are short range rather than long range, and the presence of significant SRO may significantly affect the long-range data that we derive from crystalstructure refinement. This situation is illustrated schematically in Figure 33, where the O(3)site is occupied by two anions, X^- and Y^- . The A(2/m) site (Fig. 33a) is equidistant from the two closest O(3) sites, whereas the A(m) site (Fig. 33b) is displaced toward one of the two nearer O(3) sites. Consider the situation where (1) occupancy of O(3) by Y⁻ couples to local occupancy of A(m) by Na, (2) occupancy of O(3) by X⁻ couples to local occupancy of A(2) by Na, and (3) arrangement (1) is energetically preferable to arrangement (2). Let us sum the local arrangement in Figure 33b over the crystal: $\Sigma(A(m)Na - O(3)Y + A(2)\Box - O(3)X) =$ $A^{(m)}$ Na_{1.0} $A^{(2)}$ $\Box_{1.0} - X_{1.0}Y_{1.0} = A^{(m)}$ Na $- X_1Y_1$. The variation in A(m) and A(2) site-populations as a function of bulk composition of the crystal is shown in Figure 33c. At X = 2 apfu, all ^ANa must be associated with X at O(3), and Na occupies the A(2) site. As Y increases, all Y couples to ^ANa and causes ^ANa to occupy A(m). At a composition $O(3) = X_1Y_1$, all ^ANa is coupled to Y at the O(3) site, and hence all ^ANa occupies A(m), even though O(3) is only half-occupied by Y. This example shows how the pattern of A Na order can change in a non-linear fashion as a function of chemical composition of the crystal, an important issue to bear in mind where considering SRO of A cations in amphiboles.

			Table 11. Form	ulae (apfu) of <i>C</i>	2/m amphiboles o	f Figures 34 and	35.*		
	Fluoro- nyböite	Fluoro- ** arfvedsonite	Syn. fluoro- edenite	Syn. fluoro- pargasite	$\mathbf{Arfvedsonite}^{\dagger}$	Pargasite	Taramite	Fluoro- taramite	Nyböite
Si	7.178	7.825	7.000	6.000	7.855	6.187	6.238	6.592	6.908
Al	0.822	0.141	1.000	2.000	0.137	1.813	1.762	1.408	1.092
ΣT	8.000	7.966	8.000	8.000	7.992	8.000	8.000	8.000	8.000
AI	1.251	0.000	I	1.000	0.000	0.937	1.120	0.851	1.384
Τi	0.014	0.116	I	I	0.059	0.018	0.040	0.017	0.031
Fe^{3+}	0.262	1.252	I	I	1.334	0.070	0.500	0.836	0.380
Fe^{2+}	0.836	1.887	I	I	3.255	0.756	0.411	0.832	0.502
Mn	0.008	0.923	I	I	0.147	0.001	I	0.019	0.001
Mg	2.612	0.759	5.000	4.000	0.005	3.413	2.929	2.426	2.773
ΣC	4.986	5.187	5.000	5.000	5.002	5.195	5.000	4.988	5.073
Fe,Mn	0.000	0.187	I	I	0.002	0.195	I	0.000	0.073
Ca	0.484	0.066	2.000	2.000	0.065	1.760	1.062	0.793	0.401
Na	1.516	1.747	Ι	Ι	1.933	0.045	0.938	1.207	1.526
ΣB	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.787	0.833	1.000	1.000	0.362	0.791	1.000	0.905	0.746
K	0.035	0.183	I	I	0.589	0.018	I	0.004	0.043
ΣA	0.822	1.016	1.000	1.000	0.951	0.809	1.000	0.909	0.789
Ļ	1.135	1.616	I	I	0.187	I	0.004	1.020	0.228
НО	(0.865)	0.384	2.000	2.000	1.813	(2.000)	(1.996)	(0.980)	(1.772)
*from Hawth ** includes 0 * includes 0.18	orne et al. (1993, 247 Li and 0.003 86 Li and 0.016 Z	1996a); nominal form i Zn apfu; in apfu.	ulae are given for sy	nthetic amphiboles;					

Short-Range Order in Amphiboles



Figure 33. Possible local order at the *A* site: (a) Sketch of the A(2/m) site sandwiched between two octahedral strips, with the closest O(3) sites indicated; (b) occupancy of O(3) sites by anions X^- and Y^- , with ^{*A*}Na preferentially occupying the A(m) site where locally associated with Y^- , rather than the A(2) site where locally associated with X^- ; (c) the resulting variation in A(m) and A(2) site-populations as a function of bulk anion composition (from Hawthorne et al. 1996a).

The effects of variation in ^T(Al,Si) and ^C(M²⁺, M³⁺)

In order to understand the possible effects of variation in ^T(Al,Si) and ^C(M²⁺, M³⁺), we need to compare the patterns of *A*-site electron density in structures with different values of ^T(Al,Si) and ^C(M²⁺, M³⁺). In Figure 34a, b, this is done for fluoro-arfvedsonite [C \approx (M²⁺₄ M³⁺), T \approx (Si₈)] and fluoronyböite [C \approx (M²⁺₃ M³⁺₂), T \approx (Si₇Al)]. Inspection of the formulae of fluoronyböite and fluoro-arfvedsonite (Table 11) indicates significant variation at the O(3) site; however, in the following section, we will see that variation in (OH,F) does not affect ordering of Na over the *A*(2) and *A*(*m*) sites. Inspection of Figures 34a, b shows that Na is ordered at the *A*(*m*) site in both crystals, and hence the compositional difference between these two crystals [i.e., C \approx (M²⁺₃ M³⁺₂), T \approx (Si₇ Al) versus C \approx (M²⁺₄ M³⁺), T \approx (Si₈)] does not result in any difference in ordering of ^ANa.

Figure 34c, d show the *A*-site electron density in synthetic fluoro-edenite $[C \approx M^{2+}_{5}, T \approx (Si_{7} Al)]$ and synthetic fluoropargasite $[C \approx (M^{2+}_{4} M^{3+}_{1}), T \approx (Si_{6} Al_{2})]$, the nominal compositions of which are given in Table 11. Both crystals have similar patterns of electron density at the *A*(*m*) and *A*(2) sites, and hence we can conclude that the compositional differences between fluoro-edenite and fluoropargasite [i.e., $C \approx M^{2+}_{5}, T \approx (Si_{7} Al)$ versus $C \approx (M^{2+}_{4} M^{3+}), T \approx (Si_{6} Al_{2})]$ does not result in any difference in ordering of ^ANa. Note that fluoropargasites from Oberti et al. (1995) have significant Ca at the *A* site, which modifies the distribution of the electron density (similar to that of cannilloite).

Both these examples show that compositional variations at the M(1,2,3) and T sites do not correlate directly with A-site ordering of Na in amphiboles (this result is also apparent in comparisons of other compositions in C2/m amphiboles). Of course, electroneutrality compels compositional variation at these sites to correlate with compositional variations at other sites that do correlate strongly with the distribution of Na over the A(m) and A(2) sites. However, below we will see that variation in B cations has a much more direct correlation with ordering of ^ANa than variation of C or T cations, as one would expect from local bondtopology and the ensuing local bond-valence requirements of the anions: (1) The majority of the anions bonded to A cations are also bonded to B cations, whereas this is not the case for C cations. Hence one does not expect such a direct correlation between bond-valence variations at the M(1,2,3) sites and the A sites as between the M(4) site and the A sites. The situation is not so clearcut at the T sites, as the T cations bond to all the anions coordinating the A sites. However, the examples given above show no change in the A-site electron-density with variation in T-cation composition and constant B-cation composition (fluoronyböite versus



Figure 34. Difference-Fourier sections through the *A* cavity for (a) fluoro-arfvedsonite, (b) fluoronyböite, (c) synthetic fluoro-edenite, (d) synthetic fluoropargasite [(a), (b), (d) from Hawthorne et al. 1996a, (c) from Boschmann et al. 1994].

fluoro-arfvedsonite and fluoro-edenite versus fluoropargasite), whereas they do show change in the *A*-site electron-density with variation in B-cation composition and constant T-cation composition (fluoronyböite versus fluoro-edenite).

The effects of variation in ^{O(3)}(OH,F)

Comparison of the electron-density distribution in arfvedsonite (Fig. 35a, Table 11) and fluoro-arfvedsonite (Fig. 34a) shows that ordering of ^ANa at A(m) is not affected by variation in (OH,F) where M(4) =Na. However, the A(m) site is displaced much further from the center of the *A* cavity where O(3) = F than where O(3) = (OH), indicating significant repulsion of ^ANa and H.

In pargasite (Fig. 35b, Table 11), ^ANa is ordered at A(2), whereas arfvedsonite (Fig. 35a) has ^ANa ordered at A(m). Both amphiboles have $C \approx (M^{2+}_4 M^{3+})$ and $O(3) \approx (OH)$, and hence the difference in *A*-site order must be due to either Ca versus Na at M(4) or Al versus Si at *T* (or both). However, above we saw that variation in (Al,Si) does not correlate strongly with variation in ^ANa order. Hence, in hydroxy-amphiboles, Na at M(4) causes ^ANa to occupy A(m) and Ca at M(4) causes ^ANa to occupy A(2). We may write this in the following way: ^{M(4)}Na-^{O(3)}(OH)-^{A(m)}Na and ^{M(4)}Ca-^{O(3)}(OH)-^{A(2)}Na are preferred local arrangements.

As fluoro-arfvedsonite (Fig. 34a) has Na at A(m) and F at O(3), we may also conclude that $^{M(4)}$ Na- $^{O(3)}$ F- $^{A(m)}$ Na is a preferred local arrangement. Next, compare the electron density in fluoronyböite (Fig. 34b) and nyböite (Fig. 35c). In fluoronyböite, $M(4) \approx Na_{1.5}Ca_{0.5}$ (Table 11), O(3) \approx F, and only the A(m) site is occupied; hence the possible schemes of local order in fluorony-



Figure 35. Difference-Fourier sections through the *A* cavity for (a) arfvedsonite, (b) pargasite, (c) nyböite, (d) taramite (from Hawthorne et al. 1996a).

böite are ${}^{M(4)}$ Na- ${}^{O(3)}$ F- ${}^{A(m)}$ Na, ${}^{M(4)}$ Na- ${}^{O(3)}$ (OH)- ${}^{A(m)}$ Na and ${}^{M(4)}$ Ca- ${}^{O(3)}$ F- ${}^{A(m)}$ Na (we know from pargasite, Fig. 35b, that the arrangement ${}^{M(4)}$ Ca- ${}^{O(3)}$ (OH)- ${}^{A(m)}$ Na does not occur). In nyböite (Fig. 35c), $M(4) \approx Na_{1.6}$ Ca_{0.4} (Table 11), O(3) \approx (OH), and the A(m) and A(2) sites are about equally occupied; hence the possible schemes of local order in nyböite are ${}^{M(4)}$ Na- ${}^{O(3)}$ (OH)- ${}^{A(m)}$ Na and ${}^{M(4)}$ Ca- ${}^{O(3)}$ (OH)- ${}^{A(m)}$ Na (above, we showed that ${}^{M(4)}$ Na- ${}^{O(3)}$ F- ${}^{A(2)}$ Na and ${}^{M(4)}$ Ca- ${}^{O(3)}$ (OH)- ${}^{A(m)}$ Na do not occur). In nyböite (Table 11), there is sufficient Ca at M(4) to be locally associated with Na at A(2) where half the A Na occurs at A(m). In fluoronyböite, the arrangement ${}^{M(4)}$ Ca- ${}^{O(3)}$ (OH)- ${}^{A(m)}$ Na cannot occur as only A(m) is occupied (Fig. 34b). From these considerations, we may conclude that ${}^{M(4)}$ Ca- ${}^{O(3)}$ (OH)- ${}^{A(2)}$ Na is preferred over ${}^{M(4)}$ Na- ${}^{O(3)}$ (OH)- ${}^{A(m)}$ Na.

We may test this prediction with an amphibole that has M(4) = NaCa and O(3) = OH; taramite is such an amphibole, and we thus predict that in taramite, ${}^{M(4)}\text{Ca}-{}^{O(3)}(OH)-{}^{A(2)}\text{Na}$ should occur (being preferred to ${}^{M(4)}\text{Na}-{}^{O(3)}(OH)-{}^{A(m)}\text{Na}$). In accord with this prediction, the electron density in the *A* cavity of taramite (Fig. 35d) has ^ANa completely ordered at *A*(2). Consider next fluorotaramite (which shows the same electron-density distribution as fluoronyböite, Fig. 34b) with $M(4) \approx \text{Na}_{1.2}\text{Ca}_{0.8}$, $O(3) = \text{F}_1(OH)_1$ and Na ordered at *A*(*m*), an arrangement dramatically different from that in taramite (cf. Figs. 34b and 35d). As noted, the local arrangement of ^ANa in fluorotaramite cannot involve Ca or (OH) as the *A*(2) site is not occupied, and hence the arrangements that occur must be more favorable than ${}^{M(4)}\text{Ca}-{}^{O(3)}(OH)-{}^{A(2)}\text{Na}$. The possible local arrangements in fluorotaramite are ${}^{M(4)}\text{Na}-{}^{O(3)}\text{F}-{}^{A(m)}\text{Na}$ and ${}^{M(4)}\text{Ca}-{}^{O(3)}\text{F}-{}^{A(m)}\text{Na}$. The ordering of ^ANa in synthetic fluoro-edenite (Fig. 34c) and synthetic fluoropargasite (Fig. 34d) indicates that ${}^{M(4)}\text{Ca}-{}^{O(3)}\text{F}-{}^{A(m)}\text{Na}$ locally couples to ${}^{M(4)}\text{Ca}-{}^{O(3)}\text{F}-{}^{A(2)}\text{Na}$, and does not occur as an isolated arrangement. As the *A*(2) site is not occupied by Na in fluorotaramite (which has the same pattern of electron density as in fluoronyböite, Fig. 34b) the local arrangement must be ${}^{M(4)}$ Na- ${}^{O(3)}$ F- ${}^{A(m)}$ Na. Comparison of the electron density in fluorotaramite with that in taramite (Fig. 35d) thus shows that arrangement ${}^{M(4)}$ Na- ${}^{O(3)}$ F- ${}^{A(m)}$ Na is preferred over arrangement ${}^{M(4)}$ Ca- ${}^{O(3)}$ (OH)- ${}^{A(2)}$ Na.

Consider next the electron density in fluoro-edenite (Fig. 34c) and fluoropargasite (Fig. 34d). The A(m) and A(2) sites are equally occupied by Na in both crystals, indicating that the local arrangements $^{M(4)}Ca^{-O(3)}F^{-A(2)}Na$ and $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na$ occur in equal amounts. Boschmann et al. (1994) suggested that these two arrangements are locally coupled, accounting for their occurrence in equal amounts on crystals with $M(4) = Ca_2$ and $O(3) = F_2$. Now consider fluorotaramite with $M(4) = Na_{1,2}Ca_{0,8}$ and $O(3) = F_1(OH)_1$; this crystal has all ^ANa ordered at A(m) (which shows the same electron-density distribution as fluoronyböite, Fig. 34b), and hence arrangements involving $^{M(4)}Ca$, $^{O(3)}F$ and an occupied A site cannot occur (or there would be Na at A(2), which there is not) owing to local coupling to $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na$. As this is not the case, we can conclude that the arrangements $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na$ and $^{M(4)}Ca^{-O(3)}F^{-A(2)}Na$ are less favorable than $^{M(4)}Na^{-O(3)}F^{-A(m)}Na$.

It is difficult to evaluate the relative stability of $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na + ^{M(4)}Ca^{-O(3)}F^{-A(2)}Na$ versus $^{M(4)}Ca^{-O(3)}(OH)^{-A(2)}Na$ and $^{M(4)}Na^{-O(3)}(OH)^{-A(m)}Na$. For $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na + ^{M(4)}Ca^{-O(3)}F^{-A(2)}Na$ versus $^{M(4)}Ca^{-O(3)}(OH)^{-A(2)}Na$, Nature has not provided us with the appropriate amphibole compositions. For $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na + ^{M(4)}Ca^{-O(3)}F^{-A(m)}Na$, we will be compositions. For $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na + ^{M(4)}Ca^{-O(3)}F^{-A(m)}Na$ would occur instead, as the resulting composition of the crystal would be similar. However, the fact that natural amphiboles of appropriate composition to resolve this problem do not occur (or are extremely rare and have not yet been found) suggests that the arrangement $^{M(4)}Ca^{-O(3)}F^{-A(m)}Na + ^{M(4)}Ca^{-O(3)}F^{-A(2)}Na$ is less favorable than either $^{M(4)}Ca^{-O(3)}(OH)^{-A(2)}Na$ or $^{M(4)}Na^{-O(3)}(OH)^{-A(m)}Na$.

The relative stability of local arrangements

We are now in a position to summarize the relative stability (preference of occurrence) of local arrangements for the configuration symbol M(4)-O(3)-A, listed in order of decreasing preference (Table 12): (1) > (2) > (3) >> (4) \approx (5).

Assignment of local arrangements in structures

As the sum of the short-range arrangements has to be equal to the bulk composition of the crystal, we may use the chemical composition and the measured electrondensity at the A sites to derive the relative amount of each arrangement. Hawthorne et al. (2006) have done this for fluorotremolite, fluororichterite and two potassian fluoroTable 12. Patterns of SROinvolving cation sitesadjacent to the A cavity, inorder of preference*.

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

*from Hawthorne et al. (1996a).

magnesiokatophorite crystals from Bear Lake, Ontario; the chemical formulae are given in Table 13. All of these crystals have Na ordered at the A(m) site, and they also contain significant amounts of K (Table 13). As the A(2) site is not occupied in these amphiboles, local arrangements (2) and (5) in Table 12 do not occur. Thus arrangement (1) will be preferred, with arrangements (3) and (4) occurring only if there are residual chemical components after assignment to arrangement (1). Inspection of Table 12 shows that arrangements (1) and (3) have Na at both M(4) and A, and that the amount of F at O(3) always exceeds the amount of Na at M(4) and A (Fig. 36a); hence the amount of local arrangement (1) is not restricted by the amount of F in the amphibole. Figure 36b shows the variation of ${}^{A}(Na + K)$ as a function of ${}^{M(4)}Na$ in the Bear Lake amphiboles. As the amount of Na at M(4) always equals amount of Na at A, local arrangement (1) accounts for all Na at M(4) and Na at A in these crystals. The remaining arrangements can only involve ${}^{M(4)}Ca, {}^{O(3)}(OH,F)$ and ${}^{\Box}$, and the amounts of these arrangements are dictated by the amount of (OH) and the remaining amounts of ${}^{O(3)}F$. The amounts of local arrangements in the Bear Lake amphiboles are given in Table 14.

	757	761	721	762
Si	8.035	7.909	7.374	7.362
Al	0.000	0.091	0.626	0.638
ΣT	8.035	8.000	8.000	8.000
Al	0.016	0.020	0.030	0.053
Ti	0.002	0.004	0.063	0.081
Fe ³⁺	0.000	0.061	0.478	0.486
Fe ²⁺	0.249	0.215	0.908	1.007
Mn	0.022	0.013	0.052	0.049
Mg	4.644	4.700	3.427	3.276
Zn	0.004	0.006	0.006	0.003
Li	0.000	0.000	0.023	0.023
ΣC	4.937	5.019	4.987	4.978
	0.000	0.019	0.000	0.000
Ca	1.610	1.466	1.232	1.177
Na	0.390	0.515	0.768	0.823
ΣB	2.000	2.000	2.000	2.000
Na	0.176	0.342	0.506	0.507
Κ	0.177	0.174	0.297	0.315
ΣΑ	0.353	0.516	0.803	0.822
F	0.584	0.721	1.210	1.277
OH	1.416	1.279	0.790	0.723

 Table 13. Chemical compositions (wt%) and unit formulae (apfu) of the Bear Lake amphiboles.



Figure 36. Bear Lake amphiboles: (a) The variation in F as a function of ${}^{A}(Na + K)$; the black line is drawn as a guide to the eye, the broken line indicates a 2:1 relation; (b) The variation of ${}^{A}(Na + K)$ as a function of ${}^{M(4)}Na$ in the Bear Lake amphiboles of Table 6; the line indicates a 1:1 relation (from Hawthorne et al. 2006).

	757	761	721	762
Richterite	0.37	0.43	0.16	0.18
Tremolite	0.63	0.48	0.21	0.18
Katophorite	0.00	0.09	0.63	0.64

Table 14. Proportion of SRO arrangements inthe Bear Lake amphiboles.

Hawthorne (1997) examined the issue of SRO in amphiboles from a bond-valence perspective and emphasized the importance of defining an FBB (Fundamental Building Block) for patterns of SRO. The FBB involves all symmetrically distinct sites in the structure, and thus the arrangements of atoms in the configuration symbol M(4)-O(3)-A dictate the composition of the rest of the crystal. Arrangement (1) involves patterns resembling richterite and katophorite (Hawthorne 1997), and arrangements $^{M(4)}$ Ca- $^{O(3)}$ (OH,F)- A can involve patterns resembling those in tremolite, aluminohornblende and tschermakite. We may identify which patterns of order are present from the other (C and T) cations in the crystal. Consider crystal 757 (Tables 12, 13, 14), with 0.37 $^{M(4)}$ Na- $^{O(3)}$ F- $^{A(m)}$ Na and 0.63 $^{M(4)}$ Ca- $^{O(3)}$ (OH,F)- A . There is no T Al in this crystal, and hence the local arrangements must be if the richterite type and the tremolite type (with Si = 8 apfu). The amounts of these SRO arrangements are shown for each crystal in Table 14.

Oberti et al. (2003a, b) noted the preferential order of the A-site cation at A(m) in ^{B,C}Lirich amphiboles. Figure 37 shows electron-density maps through the A site for a series of amphiboles with increasing ^A(Na,K):^CLi and ^BLi:^CLi ratios, in which the A(m)-A(m) separation increases strongly. ^BLi occurs at the M(4') site and has a weaker interaction with O(5) and O(6) than Na (or Ca) at M(4). The local version of the valence-sum rule at O(5) and O(6) indicates that where Li occurs at M(4'), the O(6) anion requires additional bond-valence, and ^ANa at A(m) moves away from A(2/m), increasing the bond valence received at O(6) from ^ANa, and Oberti et al. (2003b) show that the bond valences are in accord with this behavior. They also emphasize that the presence of F at O(3) is an important factor in allowing ^ANa to shift within the A cavity without the steric hindrance of the presence of H present as (OH) at O(3). Oberti



Figure 37. Difference-Fourier sections through the *A* cavity (parallel to $\overline{2}01$) for (a) leakite (A2 from Hawthorne et al. 1994: ^A(Na,K) = 0.69, ^BLi = 0.00, ^CLi = 0.74, F = 0.49 apfu), (b) ferriwhittakerite and (c) ferri-ottoliniite (Oberti et al. 2004: ^A(Na,K) = 0.77, ^BLi = 0.62, ^CLi = 0.73, F = 0.72 and ^A(Na,K) = 0.45, ^BLi = 1.24, ^CLi = 0.42, F = 0.47 apfu, respectively, (d) sodic ferri-ferropedrizite and (e) ferriclinoferroholmquistite (Oberti et al. 2003b: ^A(Na,K) = 0.56, ^BLi = 1.82, ^CLi = 0.58, F = 0.52 and ^A(Na,K) = 0.028, ^BLi = 1.90, ^CLi = 0.28, F = 0.024 apfu, respectively (modified from Oberti et al. 2003b).

et al. (2003b) conclude that the sequence of preferred local arrangements in ^BLi is $^{M(4')}$ Li- $^{O(3)}$ F- $^{A(m)}$ Na > $^{M(4')}$ Li- $^{O(3)}$ OH- $^{A(m)}$ Na, similar to the sequence $^{M(4)}$ Na- $^{O(3)}$ F- $^{A(m)}$ Na > $^{M(4)}$ Na- $^{O(3)}$ OH- $^{A(m)}$ Na observed in ^BNa-bearing ^TAl-free amphiboles by Hawthorne et al. (1996a).

SUMMARY

Extensive work in the last ten years has shown that short-range order is a common feature of synthetic amphiboles, is present in some natural amphiboles, and is probably an extremely common feature of natural amphiboles. The results described here also suggest that short-range order may be common in other rock-forming minerals such as micas and pyroxenes. To summarize the results on the amphiboles:

- (1) LRO (Long-Range Order) involves the occurrence of atoms at different crystallographic sites in a structure such that the average arrangement over all the unit cells in the crystal does not concur with that predicted by a random distribution;
- (2) SRO (Short-Range Order) involves the formation of local clusters of atoms that occur either more or less frequently than predicted by a random local distribution.
- (3) Infrared spectroscopy in the principal OH-stretching region is particularly effective in characterizing local (short-range) arrangements of atoms in amphiboles.
- (4) Extension of bond-valence theory to local arrangements (Hawthorne 1997) shows that short-range bond-valence requirements exert strong constraints on the local arrangements of atoms that can occur (i.e., that are stable).
- (5) Infrared spectroscopy and bond-valence constraints show that local ordering of cations is very pronounced in a crystal of tremolite with significant Na and Al contents.
- (6) The results mentioned in (5) show that the principal OH-stretching frequency in amphiboles is affected by the cations at both nearest-neighbor and next-nearest-neighbor sites.
- (7) A site-configuration symbol can be used to denote the sites affecting the principal (OH)-stretching frequency in amphiboles: M(1)M(3)-(OH)-A:T(1)T(1)-M(2)M(2)M(3); local arrangements of atoms can then be denoted by inserting the atoms at the relevant sites: e.g., MgMgMg-(OH)-Na:SiAl-MgMgMg or MgMgAl-(OH)-Na:SiAl-MgMgAl.
- (8) Synthesis and infrared spectroscopy show that monoclinic calcium-rich amphiboles in the system tremolite-cummingtonite and synthetic amphiboles in the system tremolite--Sr-tremolite show short-range disorder involving divalent cations at the M(4) [and M(4')] site.
- (9) Synthesis, infrared spectroscopy and local bond-valence arguments show that monoclinic amphiboles in the systems richterite-pargasite, tremolite-pargasite and tremolite~hornblende show strong SRO involving T, C and A cations.
- (10) Synthesis and infrared spectroscopy for amphiboles with (OH)-F solid-solution show that amphiboles with \Box (vacancy) at the *A* site (e.g., tremolite-fluorotremolite) show one-mode behavior, whereas amphiboles with Na or K at the *A* site (e.g., richterite-fluororichterite) show two-mode behavior; it is apparent from this observation that nearest-neighbor arrangements of atoms couple through an occupied *A* site, but do not couple through a vacant *A* site.
- (11) The relative band intensities in (OH)-F amphibole solid-solutions showing two-mode behavior indicate that (OH) and F are completely short-range disordered *with respect to each other* in the amphibole series examined thus far.

- (12) Synthesis, infrared spectroscopy and local bond-valence arguments show that monoclinic amphiboles in the system pargasite-fluoropargasite show strong SRO of (OH) and F with regard to the cations occupying the associated nearest-neighbor M(1)M(1)M(3) sites: arrangements involving MgMgAl-(OH) are far more common than arrangements involving MgMgAl-F.
- (13) Synthesis and infrared spectroscopy for Ti-bearing richteritic amphiboles show that ^[4]Ti⁴⁺ and Si are short-range disordered with regard to each other.
- (14) Crystal-structure refinement, SIMS analysis and local bond-valence requirements suggest that ${}^{[6]}\text{Ti}^{4+}$ and ${}^{O(3)}\text{O}^{2-}$ are locally associated at adjacent M(1) and O(3) sites in nearly all amphiboles with a significant oxo-component related to primary crystallization.
- (15) The variation in occupancy of the *A*(*m*) and *A*(2) sites by Na in *C2/m* amphibole is caused by the occurrence of a number of preferred arrangements of cations and anions at the adjacent *M*(4) and O(3) sites. The arrangements and their relevant stabilities are as follows: ${}^{M(4)}Na - {}^{O(3)}F_{-}A^{(m)}Na > {}^{M(4)}Ca - {}^{O(3)}(OH) - {}^{A(2)}Na > {}^{M(4)}Na - {}^{O(3)}(OH) - {}^{A(m)}Na > {}^{M(4)}Ca - {}^{O(3)}F_{-}A^{(m)}Na \approx {}^{M(4)}Ca - {}^{O(3)}F_{-}A^{(m)}Na$, and they can be understood in terms of local bond-valence requirements within the amphibole structure.
- (16) It is apparent from this review of recent results that SRO is very common in monoclinic amphiboles. Although much work remains to be done to fully characterize SRO across the complexities of amphibole composition-space, the general features are already emerging: local bond-valence requirements seem to be the (principal) factor controlling this type of order.
- (17) SRO 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 is not yet clear, but what is clear is that future thermodynamic models need to consider SRO in amphiboles and probably in other minerals in which heterovalent substitutions are common.

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APPENDIX I: (Mg,Fe²⁺) ORDER-DISORDER AND BAND INTENSITIES IN THE IR SPECTRUM

As the bands A, B, C and D are related to different short-range arrangements of the M(1) and M(3) cations around O(3), then the relative intensities of these bands are related to the relative frequencies of occurrence of these short-range arrangements in the structure; moreover, the sum of all the short-range arrangements must be equal to the bulk composition. Strens (1966, 1974) derived the criteria for identifying both LRO and SRO, but Law (1976) showed that these criteria are not correct. Law (1976) developed a model for LRO assuming no SRO is present, but application to two amphiboles characterized by crystal-structure refinement and Mössbauer spectroscopy showed poor agreement between the various site-occupancies.

Following Strens (1966, 1974) and Law (1976), we may write the site occupancies and *C*-group-cation composition as follows:

$$y_{M(1)} = M^{2+} \text{ at } M(1)$$

$$y_{M(3)} = M^{2+} \text{ at } M(3)$$

$$x_{M(1)} = Mg \text{ at } M(1)$$

$$x_{M(3)} = Mg \text{ at } M(3)$$

(A1)

$$X = \text{total Mg at } M(1,3) = 2 x_{M(1)} + x_{M(3)}$$

$$Y = \text{total } M^{2+} \text{ at } M(1,3) = 2 y_{M(1)} + y_{M(3)}$$
(A2)

We may express all occupancies in terms of x and y by manipulating Equations (A1) and (A2):

$$\begin{aligned} x_{M(1)} &= 1 - y_{M(1)} = 1 - \frac{1}{2} \left[Y - y_{M(3)} \right] \\ y_{M(1)} &= \frac{1}{2} \left[Y - y_{M(3)} \right] \\ x_{M(3)} &= 1 - y_{M(3)} \end{aligned}$$
(A3)

For no SRO, the relative intensities of the bands, ICA, B, C, D are given by

$$I_{A}^{C} = x_{M(1)}^{2} x_{M(3)}$$

$$I_{B}^{C} = x_{M(1)}^{2} y_{M(3)} + 2 x_{M(1)} y_{M(1)} x_{M(3)}$$

$$I_{C}^{C} = y_{M(1)}^{2} x_{M(3)} + 2 x_{M(1)} y_{M(1)} y_{M(3)}$$

$$I_{D}^{C} = y_{M(1)}^{2} y_{M(3)}$$
(A4)

where the superscript C on the band intensities denotes that they are *calculated* values. Substituting (A2) into (A3) gives the following:

$$\begin{split} & [C_{A} = 1 - \frac{1}{2} \left[Y - y_{M(3)} \right]^{2} \left(1 - y_{M(3)} \right) \\ & [C_{B} = \left(1 - \frac{1}{2} \left[Y - y_{M(3)} \right] \right)^{2} y_{M(3)} + 2 \left(1 - \frac{1}{2} \left[Y - y_{M(3)} \right] \right) \frac{1}{2} \left[Y - y_{M(3)} \right] \left(1 - y_{M(3)} \right) \\ & [C_{C} = \frac{1}{4} \left[Y - y_{M(3)} \right]^{2} \left(1 - y_{M(3)} \right) + 2 \left(1 - \frac{1}{2} \left[Y - y_{M(3)} \right] \right) \frac{1}{2} \left[Y - y_{M(3)} \right] y_{M(3)} \\ & [C_{D} = \frac{1}{4} \left[Y - y_{M(3)} \right]^{2} y_{M(3)} \end{split}$$
(A5)

Equation (A5) give the calculated band intensities as a function of cation order (i.e., $y_{M(3)}$) for a specific composition *Y* where there is no SRO present (i.e., there is short-range disorder). Following Law (1976), we may assume that there is no SRO and use Equation (A5) to derive the state of LRO from the observed values of the band intensities ($I^{O}_{A,B,C,D}$). Alternatively, we may measure the state of LRO (i.e., $y_{M(3)}$) by some other method (e.g., Rietveld refinement, Raudsepp et al. 1987a,b; Della Ventura et al. 1993a, b) and use the observed ($I^{O}_{A,B,C,D}$) and calculated ($I^{C}_{A,B,C,D}$) band intensities to derive information on SRO of divalent cations over the M(1) and M(3) sites (Hawthorne et al. 1996c; Della Ventura et al. 1996a).