Short-range order of cations in synthetic amphiboles along the richterite-pargasite join

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Abstract: Amphiboles have been synthesized by hydrothermal techniques at 900°C and 3 kbar at nominal compositions along the join richterite-pargasite [Na(CaNa)Mg₅Si₈O₂₂(OH)₂–NaCa₂(Mg₄Al)(Si₆Al₂)O₂₂(OH)₂]. Optical microscopy, SEM and powder X-ray diffraction show that in no cases are the run products single phase except for the end-member compositions. HRTEM shows that the amphiboles synthesized are free of CMFs (chain-multiplicity faults). Cell dimensions increase from Pa(0) to Pa(55) and decrease from Pa(80) to Pa(100) except for the β angle that is linear over the range Pa(0) to Pa(100). The infrared spectrum of richterite in the principal OH-stretching region consists of two bands at 3730 and 3674 cm⁻¹ associated with the local configurations MgMgMg–OH–^ANa and MgMgMg–OH–^A \Box , respectively. As the Pa content of the amphibole increases, several new bands appear at different compositions, and the frequencies of these bands are fixed throughout the series. A total of eight bands are used to fit the spectra, although not all bands occur in all spectra; Pa(100) has the most complex spectrum with six bands. Band positions, widths and intensities were derived by least-squares refinement. The number of bands and their relative intensities are related to local configurations in the structure involving Mg and Al at the M(3) site, Si and Al at the T(1) site, and Mg and Al at the M(2) site.

Key-words: synthetic amphibole, richterite, pargasite, cell dimensions, infrared spectroscopy, short-range order.

Introduction

Infrared spectroscopy in the principal OH-stretching region is sensitive to SRO (Short-Range Order) in OH-bearing materials. Although this was recognized by Strens (1966), infrared spectroscopy has not yet played a role in characterizing SRO in amphiboles. It was used extensively in the late 1960's to characterize LRO (Long-Range Order) of Mg and Fe²⁺ over the M(1) and M(3) sites in amphiboles assuming that no SRO of Mg and Fe²⁺ occurred at these sites (see summary by Hawthorne, 1981). However, the method fell into disuse in amphibole work for two reasons: (1) Law (1976) showed that the equations relating band intensities to site populations were not correct, and work by Whittaker (1979) suggested that the model used by Strens (1966) to develop such equations was not correct; (2) the spectra of many natural amphiboles contained additional bands that could not be assigned with any degree of confidence. Skogby & Rossman (1991) have shown that there is a third problem to be considered in applying infrared spectroscopy in





Fig. 1. SEM images of synthesis products along the pargasite-richterite join. A: Pa(20); B: Pa(40) (note the minor plate-like mica crystals in centre of view); C: Pa(80).

the OH-stretching region to amphiboles: (3) the integrated molar absorptivity of principal OH-stretching bands is not constant, but increases linearly with decreasing frequency (energy). Similar behaviour in other minerals has been shown by Burns & Hawthorne (1994) and Groat *et al.* (1995).

We now have a fairly good understanding of LRO in amphiboles and a concerted effort is being made to resolve the remaining problems (Oberti *et al.*, 1992, 1993a and b, 1995a and b; Hawthorne *et al.*, 1992, 1993a, 1994, 1995, 1996b,c). However, we know very little about SRO in amphiboles, and yet this is a factor that is critical to the evaluation of configurational entropy and the development of accurate activity models for amphiboles. By applying bond-valence theory (Brown, 1981; Hawthorne, 1994) at the local level rather than to the long-range structure, Hawthorne (1997) has proposed that SRO involving polyvalent cations is the rule rather than the exception. The importance of SRO to thermodynamic models makes it essen-

tial that we test whether such large degrees of SRO are present in amphiboles. This being the case, it is important to develop methods that can characterize SRO in amphiboles. Infrared spectroscopy has great potential in this regard if the problems mentioned above can be resolved. Hawthorne et al. (1996a) have addressed problem (1). Della Ventura et al. (1996) have discussed problem (3) for ordering of M2+ cations over the M(1) and M(3) sites, and Hawthorne et al. (1997) examined problem (3) for K-D order-disorder at the A sites and Na-Ca disorder at the M(4) site. Problem (2) can be addressed by working with synthetic amphiboles, as indicated by Robert et al. (1989, 1993), Della Ventura & Robert (1990). Raudsepp et al. (1991) and Della Ventura et al. (1991, 1993a and b). In more complex systems, examining structural variation as a function of chemical variation across the full range of observed chemical composition and structural state (Hawthorne et al., 1993a,b,c and d) has been shown to be more instructive than characterizing isolated compositions. Presumably, the same should hold true for infrared spectroscopy in complex amphibole systems. The infrared spectrum of pargasite has been the subject of several studies (Semet, 1973; Raudsepp *et al.*, 1987, 1991; Welch *et al.*, 1994), and yet is still not understood. Here, we examine the series richterite-pargasite [Na-(CaNa)Mg₅Si₈O₂₂(OH)₂-NaCa₂(Mg₄Al(Si₆Al₂)O₂₂-(OH)₂], develop a model that applies to all compositions along the series, and show that pargasite has extensive SRO of cations within its structure.

Configuration notation

In the amphibole structure, the OH group is directly bonded to two M(1) and one M(3) cations, and the H atom projects into the A-site cavity in which the A site may be occupied or vacant (\Box). The configuration directly around the OH group may thus be represented by the general symbol M(1)M(1)M(3)–OH–^AA; for ordered end-member tremolite and pargasite, the symbols are MgMgMg–OH–^A \Box and MgMgMg–OH–^ANa, respectively.

Materials and methods

Starting materials were prepared as silicate gels according to the method of Hamilton & Henderson (1968). Intermediate compositions were prepared by mixing end-member gels. Synthesis at 900°C and 3 kbar was done in internally-heated pressure vessels. Electron-microprobe analysis was done on a fully-automated CAMECA SX-50 microprobe operating in the wavelength-dispersion mode with the following operating conditions: excitation voltage, 15 kV; beam current, 20 nA: peak count-time, 20 s; background count-time, 10 s; beam diameter, 1 µm. Data reduction was done with the PAP method (Pouchou & Pichoir, 1991). The following crystals, X-ray lines and standards were used: TAP - NaK α , albite; SiK α , diopside; AlK α , kaersutite; MgK α , diopside; PET - KK α , fluor-phlogopite; $CaK\alpha$, diopside. X-ray powder patterns were collected with Fe-filtered CoKa Xradiation. Cell dimensions were refined by wholepowder-pattern refinement using DBW3.2 (Wiles & Young, 1981).

The powdered run products were mounted on carbon tape on a brass substrate to avoid extraneous AlK α X-rays (conventional SEM stubs are Al metal). Quantitative image-analysis work was not possible, as the grey-level contrast-range from topography in the backscattered-electron image of the grains is generally larger than that due to atomic contrast. HRTEM observations were made using a JEOL200CX transmission-electron microscope operated at 200 kV and having $a \pm 30^{\circ}$ tilt about two orthogonal axes. Crystallites were dispersed in dry alcohol and sedimented onto a 3 mm holey carbon Cu grid (Agar products) using a pipette. All samples were very beam-sensitive and a 70 µm condensor-aperture was used to minimize beam damage. High-resolution images were formed from diffracted beams that passed through a 40 μ m (0.45 Å⁻¹) objective aperture. Samples were prepared for FTIR spectroscopy as KBr pellets using the procedure of Robert et al. (1989). FTIR spectra in the OH-stretching region (4000-3000 cm⁻¹) were collected on a Nicolet 800 spectrophotometer equipped with a nitrogen-cooled MCT detector and a CaF₂ beamsplitter; the nominal resolution was 2 cm⁻¹. Spectra are the average of 64 scans. Samples were prepared as KBr pellets with a KBr/mineral ratio = 140/10 as described by Robert et al. (1989).

Results

Experimental products

Run compositions and the amphibole synthesized at these compositions are both referred to by the nominal amount of pargasite component in the nominal composition: richterite-pargasite \rightarrow Pa(0) - Pa(100). This nomenclature does not carry the implication that the amphiboles synthesized are of nominal composition or even lie along the compositional join richterite-pargasite. Initially, intermediate compositions were prepared at 20% molar along the richterite-pargasite join. Nearly single-phase amphibole (~ 98%) was synthesized at nominal end-member compositions. Additional phases, primarily nepheline and mica, were present at all intermediate compositions, but amphibole was by far the dominant phase in Pa(20), Pa(40) and Pa(80) (Fig. 1). The amount of additional phases increases toward the middle of the join, and composition Pa(60) consists primarily of Na-phlogopite + minor diopside and amphibole. Syntheses were subsequently done at intervals of 5% molar in the range Pa(55)-Pa(70) in order to better define the region in which amphibole is a minor phase. The synthesis results for all compositions are given in Table 1.

Pa(0)	amph (~98%)
Pa(20)	amph + nepheline
Pa(40)	amph + nepheline
Pa(55)	amph + diop + (mica)
Pa(60)	mica + diop + amph
Pa(65)	mica + diop + amph
Pa(70)	mica + diop + amph
Pa(80)	amph + nepheline
Pa(100)	amph (~98%)

Table 1. Run products along the join richterite-pargasite at 900°C, 3 kbar, 3 days.

Electron-microprobe analysis

The results of electron-microprobe analysis are given in Table 2; the grain size for Pa(55) was too small to obtain good analyses. The nominal amphibole compositions for each run-product are listed in Table 3. In accord with the low amphibole yields (<90%) for these compositions, the measured compositions (Table 2) depart significantly from the nominal compositions (Table 3). Furthermore, these departures increase toward the middle of the series where amphibole is only a minor phase [Pa(60)–Pa(70)]. In all cases, the principal compositional difference involves Na at the M(4) site, the synthesized amphiboles being somewhat Na-depleted relative to the nominal compositions.

High-resolution transmission electron microscopy

HRTEM shows the amphibole synthesized to be well-ordered with few, if any, discernable defects. This is an extremely important point, as interpreTable 2. Electron-microprobe analyses and unit formulae* of synthetic amphibole solid-solutions along the nominal join richterite-pargasite.

	Pa(20)	Pa(40)	Pa(80)
SiO.	56.61	52 23	45.36
	2.66	6.28	14 90
MaO	24.19	24.52	20.84
CaO	8.14	10.66	12.42
Na ₂ O	6.12	4.71	3.90
Total	97.72	98.40	97.42
Si	7.72	7.15	6.32
Al	0.28	0.85	1.68
ΣΤ	8.00	8.00	8.00
Al	0.15	0.16	0.76
Mg	4.85	4.84	4.24
ΣC	5.00	5.00	5.00
Mg	0.07	0.16	0.09
Ca	1.19	1.56	1.86
Na	0.74	0.28	0.05
ΣВ	2.00	2.00	2.00
Na	0.91	0.97	1.00

* calculated on the basis of 23 Ox; each composition is the average of two analyses.

tation of the infrared spectra is hence not complicated by the presence of microstructures that may give rise to additional bands in the principal OHstretching region. A typical image is shown in Fig. 2; for Pa(80), a well-ordered image is apparent with both (020) and (040) fringes present due to slight variation in thickness across the crystal.

Table 3. Nominal compositions of amphiboles synthesized in this work.

Sample	Α	M(4)	M(1,2,3)	T(1,2)	Total Al (apfu)
Pa(0)	Na	NaCa	Mg ₅	Si _a	
Pa(20)	Na	Na _{0.6} Ca _{1.2}	Mg _{4.8} Al _{0.2}	Si7.6Al0.4	0.6
Pa(40)	Na	Na _{0.6} Ca _{1.4}	Mg _{4.6} Al _{0.4}	Si _{7.2} Al _{0.8}	1.2
Pa(55)	Na	Na0.45Ca1.55	Mg _{4.45} Al _{0.55}	Si _{6.9} AI _{1.1}	1.65
Pa(80)	Na	Na0.2Ca1.8	Mg _{4.2} Al _{0.8}	Si _{6.4} Al _{1.6}	2.4
Pa(100)	Na	Ca₂	Mg₄Al₁	Si ₆ Al ₂	3.0



Fig. 2. Typical high-resolution transmission electron micrograph of amphibole synthesized along the join richterite-pargasite: Pa(80).

IR spectroscopy

The IR spectra for the synthesized amphiboles are shown in Fig. 3; the amount of mica in the amphibole-dominant run-products is not sufficient to significantly contribute to the infrared spectra shown in Fig. 3. Richterite (Robert *et al.*, 1989) shows a single main band at 3730 cm⁻¹, assigned to the local configuration MgMgMg–OH–^ANa. It also shows a minor band at 3674 cm⁻¹ due to vacant A sites in the structure. Taking the spectrum of richterite as a starting point, there are two main features in the spectra of Fig. 3: (1) with increasing pargasite component in the solid-solution up to compositions close to Pa(55), the main band at



Fig. 3. Infrared spectra in the principal OH-stretching region of run products synthesized along the join rich-terite-pargasite.

Table 4. Refined cell dimensions for synthetic amphiboles along the join richterite-pargasite.

Sample	a (Å)	b (Å)	c (Å)	β (°)	V (ų)
Pa(0)	9.9076(6)	17.988(1)	5.2706(4)	104.252(4)	910.45
Pa(20)	9.9051(6)	18.000(1)	5.2727(4)	104.534(4)	910.00
Pa(40)	9.9107(7)	18.008(1)	5.2735(4)	104.857(4)	909.73
Pa(55)	9.903(2)	18.013(5)	5.275(4)	105.00(4)	909.02
Pa(80)	9.9056(6)	17.975(1)	5.2780(4)	105.407(6)	906.01
Pa(100)	9.890(6)	17.940(5)	5.274(2)	105.54(4)	901.5(4)



3730 cm⁻¹ broadens and linearly decreases in wavenumber down to 3713 cm⁻¹, but it is still the most intense feature of each spectrum; (2) at compositions close to Pa(80), a new intense band appears at 3680 cm⁻¹, and an additional lower-frequency band is present at approximately 3655 cm⁻¹ in composition Pa(100).

Cell parameters

The refined cell-parameters are given in Table 4 and their variation as a function of nominal amphibole composition is shown in Fig. 4. All cell edges linearly increase in the compositional range Pa(0)-Pa(55) except *a* which is constant in this range. In the central region around Pa(60), singlephase amphibole could not be synthesized. On the other side of this gap, the cell dimensions decrease with increasing pargasite component from Pa(80) to Pa(100). The β angle increases linearly with increasing pargasite component, without the prominent discontinuity that the other cell parameters exhibit around the composition Pa(60). The cell volume (Fig. 4b) is linear with increasing pargasite content from Pa(0) to Pa(40), there is a significant discontinuity at the central gap, and the volume then decreases with increasing pargasite component from Pa(80) to Pa(100).

Spectrum fitting

The infrared spectrum of pargasite has long been somewhat of an enigma. The two main peaks were initially assigned by Semet (1973) and Raudsepp et al. (1987), but there is a low-energy shoulder on the lower-energy peak that indicates a third component. In addition, the main peaks are much broader than the bands observed in other synthetic amphiboles (Della Ventura, 1992; Della Ventura et al., 1993a, 1996; Robert et al., 1989), suggesting the presence of other local arrangements that give rise either to discrete additional bands or to strong coupling that produces very broad bands. However, the pargasite spectrum itself does not contain sufficient information to allow a completely independent and unique fit of component bands (Hawthorne & Waychunas, 1988). The situation is somewhat different for the

Fig. 4. Variation in refined cell-dimensions of amphiboles synthesized along the join richterite-pargasite; (a) a, b, c and β ; (b) V. Standard deviations are less than the size of the symbols used.

solid-solution series synthesized here, as there are additional constraints to the spectrum-fitting process: (1) numerical fitting of the spectra to component bands must be congruent for all spectra; (2) the component-band intensities must vary systematically with changes in chemical composition, (3) the variations in ordering apparent from the spectral assignments must be in accord with the variation in cell dimensions across the series.

The variation in band positions and intensities across the series may be followed in Fig. 5 where the bands are labelled A-H. The A band is strongest in Pa(0), decreases in relative intensity with increasing pargasite content and has zero intensity in the spectrum of Pa(100). The B band is absent in Pa(0) but gives rise to the strong peak asymmetry in the spectrum of Pa(20); it is the most intense band in Pa(40) and remains prominent in the spectra of Pa(100). Band C is absent in Pa(0) and weak in Pa(20); indeed, one might be uncertain as to its existence just from the spectra of Pa(0) and Pa(20). However, it is an essential component of the remaining spectra (Fig. 5), gradually increasing in relative intensity to a maximum in the spectrum of Pa(100). The D band is absent in the spectra of Pa(0), but must be present in Pa(40) and Pa(55) to give rise to the intensity between the two main peaks; it is a prominent well-resolved feature of the spectra of Pa(80) and Pa(100). The E band is a prominent well-resolved feature of the spectra of Pa(0) to Pa(40). However, in the spectra of Pa(80) and Pa(100), it is not possible to discern whether or not an E band is present because its position coincides with the tail of a very strong and asymmetric absorption peak. It is here that we must consider the origin of the E band. It is due to the configuration MgMgMg-OH-A associated with a hexagonal $[T(1)_4T(2)_2 = Si_6]$ ring of tetrahedra. The E band indicates that nominal synthetic end-member richterite is not of end-member composition, a feature that is also characteristic of natural richterites. This being the case, we do not expect to observe the E band in Pa(100) as the $[T(1)_4T(2)_2 = Si_6]$ ring configuration does not occur (see later discussion); hence our fitting model for Pa(80) and Pa(100) does not include an E band. In the spectrum of Pa(0), band E has a small shoulder to the low-wavenumber side (Fig. 3 and 5). Although this corresponds in position to band F that occurs in Pa(40)-Pa(100), this band cannot be F because the latter band is assigned to a configuration involving Al, whereas Pa(0) contains no Al at all. The only possible assignment



Fig. 5. Resolution of the infrared spectra in the principal OH-stretching region into component bands by least-squares refinement. The band nomenclature (A–H) is shown at the top and bottom of the figure.

for this band is as an MgMgMg–OH–^A⊡:SiSi and occurring next to another MgMgMg–OH– ^A□:SiSi. This occurrence of the band at lower wavenumber is in accord with the association with another □ at an adjacent A site. The lack of intensity of this band is also in accord with this assignment, as most of the E configurations will tend to be spatially associated with A configurations rather than E configurations. Bands F and G

Table 5. Positions (cm^{-1}) , widths (cm^{-1}) and relative intensities for the bands A–H in the infrared OH-stretching spectra of synthetic amphiboles along the join richterite-pargasite.

Band	Parameter	Pa(0)	Pa(20)	Pa(40)	Pa(55)	Pa(80)	Pa(100)
	Position	3730.7	3729.4	3729.4	3729.4	3729.2	_
	Width	17.0	16.7	17.0	17.0	16.7	_
	Intensity	0.93	0.60	0.28	0.08	0.04	-
в	Position	-	3717.7	3719.1	3719.1	3716.2	3716.3
	Width	-	16.9	16.9	16.9	16.8	16.5
	Intensity	-	0.22	0.36	0.38	0.31	0.20
с	Position		3705.2	3707.0	3707.3	3704.9	3705.2
	Width	-	17.2	16.9	16.9	17.0	17.0
	Intensity	-	0.06	0.16	0.26	0.14	0.22
D	Position	-	3687.2	3687.8	3687.8	3683.5	3684.0
	Width	-	18.4	18.3	18.3	18.6	18.4
	Intensity	-	0.03	0.11	0.15	0.36	0.23
Е	Position	3674.8	3674.7	3674.3	3675.6	-	_
	Width	9.7	9.7	10.0	10.0	-	-
	Intensity	0.07	0.09	0.07	0.04	-	-
F	Position	-	-	3671.4	3671.4	3670.7	3672.6
	Width		-	18.3	18.3	18.8	18.8
	Intensity	-	-	0.02	0.09	0.15	0.20
G	Position	-	-	-	-	-	3656.8
	Width	-	_	-	-		19.6
	Intensity		-	-	-	-	0.12
н	Position	-	_	_	-	-	3640.0
	Width	-	-	-		-	19.4
	Intensity	-	-	-	_	-	0.03

are not present in the Pa(0)-Pa(40) spectra, but band F is prominent in the spectra of Pa(80) and Pa(100), and band G is prominent in the spectrum of Pa(100). Possibly there is also a weak band, H, at the extreme low-energy side of the absorption in Pa(100).

Spectra were fitted by interactive optimization followed by least-squares refinement. A symmetrical Gaussian line-shape was used, and all bands except E were constrained to have the same width across the series; band E is associated with a vacancy at the A site and hence has a different intrinsic width (Hawthorne *et al.*, 1997). In some cases, we were forced to fix the positions of weak bands to produce a stable refinement; in these cases, the weak bands were fixed at the positions derived from spectra in which the same bands are prominent features with well-determined positions. The refined band positions, widths and intensities are given in Table 5, and the fitted spectra are shown in Fig. 5.

Band assignment

Preliminary considerations

Next-nearest-neighbour interactions

If end-member pargasite had maximal LRO (Long-Range Order) with M(1) = M(3) = Mg, M(2) = 0.5 Mg + 0.5 Al and T(1) = 0.5 Si + 0.5 Al, and the OH-stretching band were affected only by the nearest cation neighbours, then the infrared spectrum of pargasite would show a single band

due to the configuration MgMgMg-OH-ANa. The spectrum of pargasite is far more complicated than a single band, and previous work has established that there is Mg-Al disorder over some of the M sites in the structure (Raudsepp et al., 1987; Welch et al., 1994). Oberti et al. (1995a) showed that ^[6]Al is partly to almost completely disordered over the M(2) and M(3) sites in a series of pargasites from mantle peridotites. The spectrum of pargasite (Semet, 1973; Raudsepp et al., 1987; Welch et al., 1994, this work Fig. 5) shows two main bands of almost equal intensity at 3709 and 3678 cm⁻¹. These are assigned to the local configurations MgMgMg-OH-ANa and MgMgAl-OH-ANa. As the ensuing discussion is based on this assignment, it is crucial that the assignment is correct. Raudsepp et al. (1987) refined the site populations in nominal end-member scandiumpargasite and obtained the following site populations: M(1) 2.00 Mg; M(2) 1.58 Mg + 0.42 Sc; M(3) 0.79 Mg + 0.21 Sc. If the above assignment is correct, the infrared spectrum of the same sample of scandium-pargasite should consist of two bands with an intensity ratio of 4:1 (i.e., 0.79:0.21) corresponding to the local arrangements MgMgMg and MgMgSc [M(1)M(1)M(3)], respectively. The infrared spectrum of scandiumpargasite (Raudsepp et al., 1987) corresponds reasonably to this pattern; the lower frequency band is more intense than the above argument would predict, but as we show below, this is due to over-

results for scandium-pargasite give semi-quantitative support for the conventional assignment of the 3709 and 3678 cm⁻¹ bands in pargasite. It is well-established that there are two NN

lap with some MgMgMg configurations. Thus the

(Nearest-Neighbour) cation configurations around the O(3) site. If this were the only factor affecting the infrared spectrum of pargasite, the spectrum would contain two bands only. It is apparent from Fig. 5 that there are more than two bands in the pargasite spectrum, and hence the spectrum must also be affected by NNN (Next-Nearest-Neighbour) configurations.

Next-nearest-neighbour configurations: the T sites

Bond-valence considerations indicate that Al–O– Al linkages only occur in amphiboles with Ca at the A site (Hawthorne, 1997; Hawthorne *et al.*, 1996b), and hence the composition of end-member pargasite forces the partly ordered chain ar-

T(1) T(1) Fig. 6. The partly ordered Si₆Al₂ tetrahedral chain in pargasite; the state of LRO is $T(1) = Si_2Al_2$ and $T(2) = Si_4$. All T(1)–O(7)–T(1) dimers are Al–O(7)–Si or Si–O(7)–Al but there is orientational disorder of these dimers relative to the +*b* direction; the chain thus shows a high (but not complete) degree of SRO. The T(2) tetrahedra are unshaded, $T^{(1)}Si$ tetrahedra are random-dot-shaded and $T^{(1)}Al$ tetrahedra are black.

rangement of Fig. 6. All T(1) dimers are of the form Al–O(7)–Si. These dimers can disorder with regard to orientation along the b axis, but all hexagonal rings must be of composition Si₄Al₂. Note that there *cannot* be any rings of composition Si₅Al in end-member pargasite, or the bulk composition of Si₄Al₂ would force a corresponding number of Si_3Al_3 rings which require either (1) Al–O(7)–Al linkages or (2) Al occupancy of the T(2) site. Neither Al-O(7)-Al linkages (Welch et al., 1994) nor Al occupancy of the T(2) site (Oberti et al., 1995b) occur in end-member pargasite which hence can only contain Si₄Al₂ rings. However, the amphiboles of intermediate composition must contain Si₅Al rings, and yet this configuration seems to have no spectral expression; why is this the case? We may understand this by considering the local environment of the OH group in pargasite (Fig. 7). The H atom is in such a position as to form an H-bond to the closest





Fig. 7. The local environment of the H atom in pargasite, viewed down (010) with perspective; the T2 sites have been omitted for clarity.

O(7) atom (Hawthorne, 1983a and b), and *it is the* strength of this interaction that affects the shift in frequency of the principal OH-stretching vibration. Thus it is not the hexagonal-ring composition that affects the position of MgMgAl-OH-^ANa vibration, it is the dimer composition coordinating the nearest O(7) atom. This T(1)-O(7)-T(1) dimer may be Si-O(7)-Si, as in band A, or Si-O(7)-AI [= Al-O(7)-Si]; the O(7) anion in the second arrangement requires a stronger H-bond, and hence the band shifts to lower frequency.

Next-nearest-neighbour configurations: the M sites

There are two ways in which one can model the NNN-cation variations in the amphibole structure: (1) the NNN sites are considered to be the triplet of M(2)M(2)M(3) sites, the coordination polyhedra of which share edges with two octahedra of the M(1)M(1)M(3) triplet that coordinates the O(3) site (Fig. 8a); (2) the NNN sites are considered to be the nine sites that link to any octahedra of the M(1)M(1)M(3) triplet that coordinates



Fig. 8. Nearest-neighbour and next-nearest-neighbour octahedra about the O(3) site in the C2/m amphibole structure: (a) six-site model; (b) twelve-site model. The O(3) site is marked by a large black circle; NN octahedra are unshaded, NNN octahedra are shaded.

the O(3) site (Fig. 8b). For case (2), M(1) = Mgand M(4) = (Ca, Na); we know from the spectra of richterite-tremolite amphiboles (Hawthorne et al., 1997) that Na \leftrightarrow Ca substitution at M(4) does not produce additional fine-structure (bands) in the infrared spectra. Hence only the M(2) and M(3)sites are involved in producing different bands from NNN-cation arrangements; there are five of these NNN sites, four M(2) + one M(3). Three of the NNN octahedra share two edges with the NN octahedra (as in Fig. 8a) and two of the NNN octahedra each share one edge with the NN octahedra (Fig. 8b). Whether this stereochemical distinction between NNN octahedra influences their effect on the fine structure of the principal OHstretching band in the infrared is not known.

The geometrically possible NN- and NNN-cation arrangements with M(1) = Mg, M(2) = (Mg,Al)and M(3) = (Mg,Al) may be derived by permuting Mg and Al over the sites in the cluster. Hawthorne (1997) has shown that cation arrangements with trivalent cations occupying adjacent sites are unlikely from a bond-valence viewpoint, and we discard these arrangements as unlikely. The distinct arrangements, combined with the two distinct cations arrangements at the adjacent pair of T(1) sites (SiSi and SiAl), are listed in Table 6.

Representation of NNN configurations

Next-nearest-neighbour configurations may be represented by the string of cation species involved, and may be appended to the NN-cation configuration: M(1)M(1)M(3)–OH–A: T(1)T(1)–M(2)M(2)M(3)M(2)M(2). Thus for tremolite: MgMgMg–OH–^A:SiSi–MgMgMgMgMg, and for ideally ordered end-member pargasite: MgMgMg–OH–^ANa:SiAl–AlMgMgAlMg. All five NNN M cations are shown; if one wishes to consider only three of these (as in Fig. 8a), then the last two terms are omitted.

Band A

This is due to the configuration MgMgMg–OH– ^ANa:SiSi–MgMgMgMgMg, the configuration in ideal end-member richterite. This band decreases in intensity with increasing pargasite component and is absent in the end-member pargasite spectrum (Fig. 3 and 5). This means that pargasite *cannot* have the MgMgMg–OH–^ANa:SiSi– MgMgMgMgMg configuration. Table 6. Local configurations involving NN and NNN arrangements within the octahedral strip of the C2/m amphibole structure.

(1)	MgMgMg-OH-A : SiSi - MgMgMgMgMg
(2)	MgMgMgOHA : SiSi AlMgMgMgMg
(3)	MgMgMg–OH–A : SiSi AlAlMgMgMg
(4)	MgMgMg–OH–A : SiSi – AlAlAlMgMg
(5)	MgMgMgOHA : SiSi - AlAlMgAlAl
(6)	MgMgMgOHA:SiAI-MgMgMgMgMg
(7)	MgMgMgOHA : SiAl - AlMgMgMgMg
(8)	MgMgMg–OH–A : SiAl – AlAlMgMgMg
(9)	MgMgAl-OH-A : SiSi - MgMgMgMgMg
(10)	MgMgAl–OH–A : SiSi – AlMgMgMgMg
(11)	MgMgAl–OH–A : SiSi – AlAlMgMgMg
(12)	MgMgAl–OH–A : SiSi – AlAlAlMgMg
(13)	MgMgAl-OH-A : SiSi - AlAlMgAlAl
(14)	MgMgAlOHA : SiAl MgMgMgMgMg
(15)	MgMgAl-OH-A : SiAl - AlMgMgMgMg
(16)	MgMgAI-OH-A : SiAI AlAIMgMgMg

* NNN arrangements are listed for the cluster of Fig. 8b; for the cluster of Fig. 8a, the last two elements of the NNN term are discarded, thus configurations (4) = (5) and (12)= (13)

Bands B, C, D, F, G and H

The composition of pargasite, together with the ordering information derived from Rietveld structure-refinement of M^{3+} ($M^{3+} = Cr^{3+}$, Sc, In) analogues, indicates that pargasites must have MgMgMg–OH–^ANa configurations. Therefore, the absence of the A band in Pa(100) indicates that end-member pargasite does not have the NNN T(1)T(1) configuration SiSi, in accord with the argument given above (Fig. 6).

There is an important fact that can be established from the Pa(80) and Pa(100) spectra. There are broad peaks at 3710 and 3678 cm⁻¹ in each spectrum (Fig. 3), and these are assigned to local configurations involving MgMgMg-OH-ANa and MgMgAl-OH-ANa, respectively (Semet, 1973; Raudsepp et al., 1987). It is important to note that in both the Pa(80) and Pa(100) spectra, these two peaks have approximately the same relative intensities. The fact that the peaks have the same intensity within each spectrum indicates that there are an equal number of MgMgMg-OH-ANa and MgMgAl–OH–^ANa configurations (omitting, for the moment, any consideration of differences in molar absorptivity as a function of absorption energy); in turn, this indicates that the M(3) siteTable 7. Final assignment of bands in amphiboles synthesized nominally along the join richterite-pargasite.

Band	Configuration
A	MgMgMg-OH-^Na:SiSi-MgMgMgMgMg
в	MgMgMg-OH- ^A Na : SiAl-MgMgMgMgMg
С	MgMgMg-OH- ^A Na : SiAl-AlMgMgMgMg
D	MgMgAl-OH-^Na : SiAl-MgMgMgMgMg
E	MgMgMg–OH–^□ : SiSi–MgMgMgMgMg
F	MgMgAl-OH- ^A Na : SiAl-AlMgMgMgMg
G	MgMgAI-OH- ^A Na : SiAI-AIMgMgAIMg
Н	MgMgAlOH- ^A Na : SiAl-AlMgMgAlAl

population is approximately 0.50 Al + 0.50 Mg in *both* Pa(80) and Pa(100).

There are two bands, B and C, under the peak that has previously been assigned to the MgMgMg-OH-ANa configuration in the pargasite spectrum and there are two peaks, D and F, under the peak previously assigned to the MgMgAl-OH-ANa configuration; why are there two bands under each of these peaks rather than one band? The two pairs of bands, B-C and D-F, must be due to differences in NNN arrangements involving cations at the M sites, as all bands must involve the T(1)T(1) configuration SiAl in pargasite.

Inspection of Fig. 5 shows that the intensity of the B band increases most rapidly from $Pa(0) \rightarrow Pa(20) \rightarrow Pa(40)$ while the principal variation in the NNN cations involves Al \rightarrow Si at the T(1) site (Table 2). Thus the B band may be assigned to the configuration MgMgMg–OH–^ANa:SiAl–MgMg-MgMgMg.

As discussed above, the D and F bands must be due to configurations involving Al at M(3). The D band is assigned to MgMgAl-OH-^ANa:SiAl-MgMgMgMgMg and F is assigned to MgMgAl-OH-ANa:SiAl-AlMgMgMgMg. Note the relative intensities B:C and D:F in Pa(80) and Pa(100): it is apparent that in Pa(80), [6]Al is strongly ordered at M(3) relative to M(2), and that most ^[6]Al entering the pargasite structure between Pa(80) and Pa(100) goes into the M(2) site. Thus the G and H bands must arise from NNN configurations involving more than one [6]Al: G = MgMgAl-OH-ANa:SiAl-AlMgMgAlMg and H =MgMgAl–OH–^ANa: SiAl-AlMgMgAlAl, although the H band is very weak (~ 3% of the total intensity) and its presence in the spectra may be an artifact due to slight errors in fitting the background. These final assignments are listed in Table 7.

Discussion

Cell dimensions

It is apparent from both the variation in cell dimensions and infrared spectra that the amphiboles synthesized in this work are not a simple binary solid-solution between richterite and pargasite. From $Pa(0) \rightarrow Pa(55)$, the principal additional bands in the infrared region are B and C (Fig. 5). According to the band assignments discussed above, the principal compositional change affecting the spectrum is the substitution of $T^{(1)}Al$ for ^{T(1)}Si. The relative intensity of the C band in this compositional region indicates that the substitution $M^{(2)}Al \rightarrow M^{(2)}Mg$ is less than that indicated by the nominal composition. The Al \rightarrow Si substitution must be balanced primarily by the $M^{(4)}$ Ca $\rightarrow^{M(4)}$ Na substitution in Pa(0)–Pa(55). This is in accord with the variation in cell dimensions (Fig. 4). As established by Colville et al. (1966), the *b* dimension is related primarily to the mean radius of the constituent M(2) cations. Hence significant $^{M(2)}Al \rightarrow ^{M(2)}Mg$ substitution will significantly reduce the b dimension of an amphibole; in agreement with this, the b dimension of pargasite $[M(2) = MgAl, \langle r \rangle = 0.628 \text{ Å}; \text{ radii from Shan-}$ non, 1976] is significantly less than that of richterite $[M(2) = Mg_2, \langle r^{M(2)} \rangle = 0.72 \text{ Å}]$ (Table 4). Nevertheless, from $Pa(0) \rightarrow Pa(20) \rightarrow Pa(55)$, the b dimension increases, in accord with the suggestion that the $^{M(2)}Al \rightarrow ^{M(2)}Mg$ substitution in this range is less than the nominal amount, and the $^{T(1)}Al \rightarrow ^{T(1)}Si$ substitution is dominant, enlarging the cell dimensions as ^[4]Al (0.39 Å) is larger than ^[4]Si (0.26 Å).

Consider now the substitutions occurring at the other end of the 'series': Pa(100) Pa(80). As discussed above, the infrared band intensities indicate that M(3) = 0.5 Mg + 0.5 Al in both Pa(100) and Pa(80). Thus the possible substitutions from Pa(100) \rightarrow Pa(80) are ^{M(2)}Mg \rightarrow ^{M(2)}Al, ^{T(1)}Si \rightarrow ^{T(1)}Al and ^{M(4)}Na \rightarrow ^{M(4)}Ca. The strong decrease in the intensity of bands C and F relative to bands B and D indicate that the ^{M(2)}Mg \rightarrow ^{M(2)}Al substitution is significant here. As noted above, the relative intensities of these bands are conformable with an M(2) site-population of 1.7 Mg + 0.3 Al in Pa(80). As the ^{M(2)}Mg \rightarrow ^{M(2)}Al substitution reTable 8. Bond-valence tables for proposed short-range arrangements in pargasite.

Pargasite: arrangement (1)								
	<i>M</i> (1)	<i>M</i> (2)	<i>M</i> (3)	<i>M</i> (4)	A	<i>T</i> (1)	<i>T</i> (2)	Σ
O(1)	0.41 ^{x2} ↓	0.52 ^{x2} i	0.33 ^{x4} i			0.75		2.01
O(2)	0.25 ^{x2} ↓	0.46 ^{x2} 1		0.28 ^{x2} 1			1.01	2.00
O(3)	0.34 ^{x2} ↓-	•	0.33 ^{x2} i					1.00
O(4)		0.52 ^{x2} 1		0.35 ^{x2} i			1.08	1.95
O(5)				0.14 ^{x2} ↓	0.15 ^{x2} ↓	0.75	0.96	2.00
O(6)				0.23 ^{x2} 1	0.10 ^{x2} 1	0.75	0.95	2.03
O(7)					0.25 ^{x2} 1	0.75/1.00		2.00
Σ	2.00	3.00	1.98	2.00	1.00	3.00	4.00	
			Parga	site: arran	gement (2)		
	M (1)	M (2)	<i>M</i> (3)	<i>M</i> (4)	A	<i>T</i> (1)*	T(2)	Σ
O(1)	0.33 ^{x2} 1	0.27 ^{x2} ↓	0.33 ^{x4} 1			1.10		2.03
O(2)	0.33 ^{x2} 1	0.33 ^{x2} ↓		0.30 ^{x2} ↓			1.05	2.01
O(3)	0.34 ^{x2} 1-	•	0.33 ^{x2} 1					1.00
O(4)		0.40 ^{x2} ↓		0.36 ^{x2} 1			1.10	1.86
O(5)				0.13 ^{x2} i	-	1.00	0.95	2.08
O(6)				0.21 ^{x2} ↓	-	0.96	0.90	2.07
O(7)					-/0.21 ^{x2}	0.94 ^{x2} →		2.09
Σ	2.00	2.00	1.98	2.00		4.00	4.00	
			Parga	site: arran	gement (3)		
	<i>M</i> (1)	<i>M</i> (2)	<i>M</i> (3)	<i>M</i> (4)	Α	<i>T</i> (1)*	T(2)	Σ
O(1)	0.40 ^{x2} i	0.32 ^{x2} ↓	0.50 ^{x4} 1			0.75		1.97
O(2)	0.36 ^{x2} 1	0.30 ^{x2} ↓		0.30 ^{x2} ↓			1.00	1.96
O(3)	0.24 ^{x2} i-	•	0.50 ^{x2} ↓					0.98
O(4)		0.38 ^{x2} ↓		0.35 ^{x2} ↓			1.10	1.83
O(5)				0.14 ^{x2} ↓	0.15 ^{x2} 1	0.75	0.96	2.00
O(6)				0.21 ^{x2} ↓	0.10 ^{x2} 1	0.75	0.94	2.00
<u>O(7)</u>					0.25 ^{x2} ↓	0.75/1.00		2.00
Σ	2.00	2.00	3.00	2.00	1.00	3.00	4.00	

	Pargasite: arrangement (4)								
	<i>M</i> (1)	<i>M</i> (2)	<i>M</i> (3)	<i>M</i> (4)	Α	<i>T</i> (1)*	T(2)	Σ	
O(1)	0.33 ^{x2} ↓	0.20 ^{x2} ↓	0.50 ^{x4} !			1.00		2.03	
O(2)	0.33 ^{x2} 1	0.40 ^{x2} ↓		0.28 ^{x2} i			1.00	2.01	
O(3)	0.34 ^{x2} ↓-	•	0.50 ^{x2} 1					1.18	
O(4)		0.40 ^{x2} ↓		0.45 ^{x2} ↓			1.10	1.95	
O(5)				0.14 ^{x2} ↓	-	1.00	0.95	2.09	
O(6)				0.13 ^{x2} ↓	-	1.00	0.95	2.08	
O(7)						1.00/0.75	5	1.75	
Σ	2.00	2.00	3.00	2.00	-	4.00	4.00		

* O(7) is bonded to two T(1) cations. In some local arrangements (and always in long-range arrangements), these two T(1) cations are identical and the bond-valence sum at O(7) involves a x2- symbol. In other local arrangements, the two T(1) cations are different, and the bond-valence sum involves two different contributions from the T(1) site [e.g., 0.75/1.00 for pargasite arrangement (1)]. However, the bond-valence sum at the T(1) site for a specific local arrangement involves only one of the two bond-valence entries for the T(1)-O(7) bond. In these tables, the first of the two entries [e.g., 0.75 for pargasite arrangement (1)] is the value that contributes to the sum at the T(1) site.

** The arrows indicate the direction of the bond multiplicity indicated by the superscript.



Fig. 9. Possible coupling between Al and Si occupancy of T(1) and Al and Mg occupancy of M(2) in pargasite such that $T^{(1)}Al$ links to O(1) bonded to $M^{(2)}Al$ and $T^{(1)}Si$ links to O(1) bonded to $M^{(2)}Mg$.

duces the overall charge in the structure, it must be accompanied by a substitution that increases the charge in the structure: $^{T(1)}Si \rightarrow ^{T(1)}Al$. Is there significant $^{M(4)}Na \rightarrow ^{M(4)}Ca$ substitution in this compositional range? If there were the corresponding amount of $^{M(4)}Na \rightarrow ^{M(4)}Ca$ and $^{T(1)}Si \rightarrow$ T(1)Al substitutions to move the composition linearly from Pa(100) toward Pa(0), one would expect the cell volume to be linear between the two end-members over this range [Pa(100)–Pa(80)]. However, it is not. Between Pa(100) and Pa(80), the cell volume increases more rapidly than simple solid-solution between the end-member components suggests, indicating that the M(2)Mg \rightarrow M⁽²⁾Al substitution is greater than the M⁽⁴⁾Na \rightarrow M(4)Ca substitution.

Short-range order in pargasite

The original crystal-structure work on pargasite (Robinson *et al.*, 1973) was interpreted in terms of all ^[6]Al ordered at M(2). This caused a problem in the interpretation of the infrared spectrum of pargasite in the principal OH-stretching region as this indicated Al at the M(1) and/or M(3) sites (Raud-sepp *et al.*, 1987). However, recent results of crystal-structure refinement have definitely established the pattern of LRO in pargasite: ^[4]Al is completely ordered at T(1) (Oberti *et al.*, 1995a) except at high temperature (Oberti *et al.*, 1995b), ^ANa is ordered at A(2) (Hawthorne *et al.*, 1996c), and ^[6]Al is disordered over M(2) and M(3) (Oberti et al., 1995a). These are important results with regard to deriving patterns of SRO, as they provide constraints on possible short-range arrangements. Hawthorne (1997) has argued that local structural arrangements that obey the valence-sum rule (Brown, 1981) should be more stable, and hence more favoured, than local structural arrangements that depart significantly from the valence-sum rule. This hypothesis can be used to derive the most probable schemes of SRO in amphiboles. The results for pargasite are shown in Table 8. Arrangements (1) and (2) combine to give the ordered structure shown in Fig. 9. This arrangement can propagate to form a completely short-range ordered structure with the maximum possible long-range order (*i.e.*, $T(1) = Si_2Al_2$, $T(2) = Si_4$, $M(1) = Mg_2, M(2) = MgAl, M(3) = Mg, M(4) =$ Ca₂, $A(2) = Na\Box$). This would give rise to an infrared spectrum with a single narrow peak; however, the infrared spectrum shows that this is not the case. There is also Al at the M(3) site (Oberti et al., 1995a), something that Hawthorne (1995) has interpreted in terms of entropy-driven disorder. This will give rise to other patterns of SRO, as indicated in Table 8, and these patterns may combine in different ways to give different shortrange environments around the OH group occupying the O(3) site. As shown here, infrared spectroscopy in the principal OH-stretching region can provide a sensitive probe for characterizing such patterns of SRO, provided the details of the patterns of LRO are completely understood.

Summary and conclusions

(1) Amphiboles synthesized with nominal compositions along the join richterite-pargasite always coexist with additional phases except for endmember compositions which consist of >98%amphibole.

(2) These synthetic amphiboles are free of chainmultiplicity faults.

(3) The amphiboles show very non-linear variation in cell parameters as a function of nominal composition.

(4) The infrared spectra of these amphiboles in the principal OH-stretching region can be resolved into eight bands, not all of which are present in each spectrum.

(5) As established by previous work, the spectrum of end-member richterite consists of two bands at 3734 and 3674 cm⁻¹ due to local configurations MgMgMg–OH–^ANa and MgMgMg–OH–^A, respectively.

(6) The spectrum of end-member pargasite consists of six bands due to variations in NN (nearestneighbour) and NNN (next-nearest-neigbour) configurations around the OH anion.

(7) The MgMgMg-OH-ANa band in pargasite is shifted to lower frequency (3705 cm⁻¹) relative to the same band in richterite, as the latter is associated with an Si-O(7)-Si configuration whereas the former is associated with an Al-O(7)-Si configuration, these two configurations producing different band frequencies via different strengths of H-bonding from the OH group to the O(7) anion. (8) The band intensities indicate extensive SRO in the amphiboles synthesized here, in accord with the arguments of Hawthorne (1997).

(9) From the variation in band intensities across the series, it is apparent that the amphibole compositions do not lie along the richterite-pargasite join, but extend from both end-member compositions toward edenite, $NaCa_2Mg_5Si_7AIO_{22}(OH)_2$, with intermediate compositions not being stable.

(10) The non-linear variation in cell dimensions along the series is completely conformable with (9) and with the long-range order indicated by the infrared spectra.

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