Synthesis and infrared spectroscopy of amphiboles along the tremolite-pargasite join

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Abstract: Amphiboles along the tremolite-pargasite join have been hydrothermally synthesized at 900°C, 3 kbar. Run products were characterized by optical and electron microscopy, powder X-ray diffraction and infrared spectroscopy. Under the experimental conditions used, there is complete solid-solution between tremolite and pargasite and the variation of cell parameters is linear as a function of composition. The infrared spectra in the principal OH-stretching region are consistent with the predictions of Hawthorne (1997) on local bond-valence grounds, and show strong short-range order of cations at the octahedral sites and strong coupling between Al at T(1) and Na at A.

Key-words: synthesis, tremolite-pargasite, cell-parameters, infrared spectra, short-range order.

Introduction

Calcic amphiboles are important rock-forming minerals and occur in a wide variety of metamorphic, plutonic and volcanic rocks. From a chemical point of view, calcic amphiboles can be regarded as a complex multicomponent system between tremolite [Tr: Ca₂Mg₅Si₈O₂₂OH₂], edenite [Ed: NaCa₂Mg₅Si₇AlO₂₂OH₂], pargasite [Pa: NaCa₂(Mg₄Al) $(Si_6Al_2)O_{22}OH_2$ and tschermakite [Ts: $Ca_2(Mg_3Al_2)$ $(Si_6Al_2)O_{22}OH_2$]. The stability of end-member compositions in this system has been investigated extensively (Bovd, 1959; Colville et al., 1966; Gilbert, 1969; Holloway, 1973; Jasmund & Schäfer, 1972). Solid solution along the binary join Tr-Ts has been the subject of much work, focused primarily on the definition of a possible miscibility gap between tremolite-actinolite and hornblende (Jasmund & Schäfer, 1972; Oba, 1978; Cao et al., 1986; Jenkins, 1988; Cho & Ernst, 1991; Jenkins, 1994; Smelik et al., 1994). The Tr-Ed join, which is particularly important in relation to the transition from greenshist to amphibolite facies in metabasites, has been studied by Best (1978) using mixtures of (natural) tremolite and albite over the pressure range 3-10 kbar at 600°C, and by Welch *et al.* (1984) at lower P_{H2O} (up to 2 kbar) and higher T (up to 850°C). According to these studies, the P-T stability of edenite + quartz at low pressure is limited, and at higher pressures, amphibole breaks down to two pyroxenes \pm albite \pm liquid \pm vapour. Phase relations along the Tr-Pa join were investigated by

Oba (1980, 1990) in the temperature range 750 to 1150°C at water pressures of 1 to 10 kbar. According to Oba (1980), at 1 kbar up to 800°C, there is a well-defined solvus between tremolite and pargasite. At temperatures above 850°C, the stable assemblage includes clino- and ortho-pyroxene plus quartz, forsterite and plagioclase in addition to amphibole (Oba, 1980). More recently, Sharma (1996) studied the stability of pargasite plus quartz in the system Na₂O-CaO-MgO-Al₂O₃-SiO₂-H₂O, and observed a continuous change in amphibole composition from pargasite to tremolite at 840°C and 1 kbar, suggesting complete solid-solution between these two end-members at these conditions, in apparent contrast with the work of Oba (1980, 1990). All these experimental studies have focused on the definition of the phase relations in the calcic amphibole system. However, structural details of the product amphiboles, such as ordering of cations over non-equivalent structural sites, have not been examined. This point is particularly relevant when using experimental results for thermodynamic analysis of observed phase-relations and for petrological modelling. Although long-range ordering (LRO) patterns of cations in calcic amphiboles are quite well characterized (e.g. Oberti et al., 1995a and 1995b), we know far less about short-range ordering (SRO) patterns. Hawthorne (1997) used bond-valence theory at a local (short-range) level (rather than at the long-range level of the average structure) and showed that only a limited number of cation arrangements are likely to occur, as many of the geometrically possible patterns devi-





Fig. 1. Schematic calcic-amphibole ternary system showing the nominal starting compositions used in the present work (open squares). Tr = tremolite, Ed = edenite, Pa = pargasite, Ts = tschermakite, Hb = magnesiohornblende.

ate considerably from the valence-sum rule, thus providing theoretical indications of short-range order in the structure. Hawthorne *et al.* (1996a, 1997, 2000) and Della Ventura *et al.* (1999) have recently characterized several series of synthetic amphiboles and have shown that the numbers of bands in their infrared spectra correspond closely to the number of local configurations predicted by the valencesum rule. In this paper we report the synthesis and characterization of cation-ordering by infrared methods for amphiboles along the Tr-Pa join (Fig. 1).

Materials and methods

Starting materials were prepared as silicate gels according to the method of Hamilton and Henderson (1968). Intermediate compositions were prepared by mixing end-member gels. All syntheses were done at 900°C and 3 kbar P(H₂O) in internally-heated pressure vessels. Step-scan X-ray powder patterns were collected on a Scintag X1 diffractometer operated in the vertical θ - θ configuration with Ni-filtered CuK α radiation and a Si(Li) solid-state detector. Cell dimensions were refined by whole-powder-pattern refinement (Rietveld method) using the DBW3.2 software package (Wiles & Young, 1981). 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 at room temperature on a Nicolet 760 spectrophotometer equipped with a DTGS detector and a KBr beam splitter. The nominal resolution is 2 cm⁻¹; spectra are the average of 64 scans.

The nominal amphibole compositions for the samples studied are given in Table 1. Run compositions are referred by their nominal Pa and Tr components, from $Tr_{80}Pa_{20}$ to

Table 1. Nominal compositions of amphiboles synthesized along the Tr-Pa join.

| Sample | А | M(4) | M(1,2,3) | T(1,2) | Tot Al |
|-------------------|-----------------------------------|-----------------|--------------------|-------------------------------------|--------|
| Tr ₁₀₀ | $\square_{1,0}$ | Ca ₂ | Mg ₅ | Si ₈ | 0.00 |
| $Tr_{80}Pa_{20}$ | $\square_{0.8}$ Na _{0.2} | Ca_2 | $Mg_{4.8}Al_{0.2}$ | Si _{7.6} Al _{0.4} | 0.60 |
| $Tr_{60}Pa_{40}$ | $\square_{0.6}$ Na _{0.4} | Ca ₂ | $Mg_{4.6}Al_{0.4}$ | Si _{7.2} Al _{0.8} | 1.20 |
| $Tr_{50}Pa_{50}$ | $\square_{0.5}$ Na _{0.5} | Ca ₂ | $Mg_{4.5}Al_{0.5}$ | Si _{7.0} Al _{1.0} | 1.50 |
| $Tr_{40}Pa_{60}$ | $\square_{0.4}$ Na _{0.6} | Ca_2 | $Mg_{4,4}Al_{0,6}$ | Si _{6.8} Al _{1.2} | 1.80 |
| $Tr_{20}Pa_{80}$ | $\square_{0.2}$ Na _{0.8} | Ca_2 | $Mg_{4,2}Al_{0,8}$ | $Si_{6.4}Al_{1.6}$ | 2.40 |
| Pa ₁₀₀ | Na _{1.0} | Ca ₂ | $Mg_{4.0}Al_{1.0}$ | Si _{6.0} Al _{2.0} | 3.00 |

 Pa_{100} . As shown in Table 1, the M(4) composition remains constant along the join, while the (A)-site, octahedral (M) and tetrahedral (T) compositions vary systematically according to the exchange reaction

 ${}^{[A]}\Box + {}^{[6]}Mg + 2{}^{[4]}Si = {}^{[A]}Na + {}^{[6]}Al + 2{}^{[4]}Al.$

This reaction can be resolved into two independent exchange rections:

- (i) the tschermak-type substitution: $\begin{bmatrix} 6 \\ 1 \end{bmatrix} A = \begin{bmatrix} 4 \\ 1 \end{bmatrix} \begin{bmatrix} 6 \\ 1 \end{bmatrix} A = \begin{bmatrix} 7 \\ 1 \end{bmatrix}$
 - ${}^{[6]}Mg + {}^{[4]}Si = {}^{[6]}Al + {}^{[4]}Al, and$
- (ii) the edenite-type substitution: $^{[A]}\Box + ^{[4]}Si = ^{[A]}Na + ^{[4]}Al$.

Run powders were characterized by powder XRD, SEM and optical microscopy, and consist of monophase amphibole solid-solution, in the limit of resolution of these techniques.

Results

X-ray diffraction

The refined cell parameters are given in Table 2 and their variation as a function of amphibole composition is shown in Fig. 2. All cell edges vary linearly with Pa content; in particular, for increasing Pa component, there is a significant increase of the *a* parameter and a decrease of *b*. The *c* parameter remains almost constant, even if the data points are somewhat scattered and seem to show a slight positive deviation from linearity. A marked increase also occurs for the β angle. The strong increase of the *a* parameter clearly reflects the increase of Na at the (A)-site. The cell volume decreases slightly as a function of composition (Fig. 3).

Table 2. Cell-dimensions and volumes of amphiboles synthesized along the tremolite-pargasite join.

| Sample | a (Å) | <i>b</i> (Å) | <i>c</i> (Å) | β (°) | $V(\text{\AA}^3)$ |
|-------------------------|-----------|--------------|--------------|------------|-------------------|
| Tr(23-5)* | 9.807(2) | 18.054(3) | 5.276(1) | 104.56(1) | 904.20 |
| $\Gamma r_{80} Pa_{20}$ | 9.8202(6) | 18.042(1) | 5.2786(4) | 104.753(5) | 904.44 |
| $\Gamma r_{60} Pa_{40}$ | 9.8321(5) | 18.015(1) | 5.2792(4) | 104.934(4) | 903.53 |
| $\Gamma r_{50} Pa_{50}$ | 9.8450(6) | 17.994(1) | 5.2781(4) | 105.083(4) | 902.84 |
| $\Gamma r_{40} Pa_{60}$ | 9.8598(6) | 17.990(1) | 5.2794(4) | 105.176(4) | 903.81 |
| $\Gamma r_{20} Pa_{80}$ | 9.881(1) | 17.961(3) | 5.2760(8) | 105.33(1) | 903.11 |
| Pa ₁₀₀ ** | 9.890(9) | 17.940(5) | 5.274(2) | 105.54(4) | 901.5 |

* from Hawthorne et al. (1997)

** from Della Ventura et al. (1999)



Fig. 2. Variation in refined cell-dimensions of amphiboles synthesized along the Tr-Pa join. Standard deviations are less than the size of the symbols.

According to Sharma (1996), the amphibole composition in terms of pargasite mol% component along the studied join can be approximated using the 2 θ separation between the X-ray powder peak-positions of the (151) and ($\overline{3}31$) reflections [$\Delta 2\theta$ (151- $\overline{3}31$)]. Fig. 4 shows that the measured angular separations of these two peaks define a linear trend as a function of nominal composition. The equation of the regression line is y = 5.18x + 0.22 with R² = 0.97.



Fig. 3. Variation in refined cell-volumes of amphiboles synthesized along the Tr-Pa join. Standard deviations are less than the size of the used symbols.



Fig. 4. Relation between the Pa content (mol%) and the $\Delta 2\theta$ (151– 331) for the amphibole synthesized along the Tr-Pa join.

Infrared spectra

The IR spectra for the synthesized amphiboles are shown in Fig. 5. Taking the spectrum of tremolite (Fig. 5a) as a reference point, with increasing Pa component in the amphibole, several additional bands appear in the OH-spectrum at both higher and lower frequencies relative to the sharp band of tremolite centered at 3675 cm^{-1} . This behaviour is substantially different from that observed along the tremolite-magnesiohornblende join (Hawthorne *et al.*, 2000). For the latter samples, several additional bands appear with increasing AI content in the amphibole (Ts component), but only toward the lower-frequency side of the tremolite band. In the series



Fig. 5. Infrared spectra in the principal OH-stretching region of amphiboles synthesized along the Tr-Pa join.

examined here, there is a new factor to take into account in understanding the pattern of bands in Fig. 5: the progressive filling of the A-site with increasing Pa component.

Referring to Fig. 5, which also gives the band nomenclature used throughout this paper, we observe several interesting features in the evolution of the IR spectra as a function of composition:

(i) The appearence of a prominent and broad band (band A) at 3710 cm⁻¹ which grows in intensity as a function of increasing Pa content of the amphibole;

(ii) the appearence of two components (B and D) on either side of the tremolite (C) band which are well visible in the intermediate samples. Both components, centered at 3688 and 3671 cm⁻¹, respectively, increase in intensity along the join and finally give a broad absorption centered at 3680 cm⁻¹;

(iii) the appearence of several additional shoulder at frequencies < 3650 cm⁻¹ (E, F, G and H). These latter bands are prominent in the spectrum of Fig. 5c. They can be grouped into two pairs: E-F and G-H; the former pair (E-F) shows strong asymmetry toward the low-frequency side of the low-frequency band of pargasite (Fig. 5g), whereas the latter pair (G-H) constitutes the very broad band centered around 3625 cm⁻¹ in all samples from $Tr_{60}Pa_{40}$ to $Tr_{20}Pa_{80}$ (Fig. 5b to 5f). Note that this broad band at 3625 cm⁻¹ is not present in Pa_{100} .

Band assignment

The configuration notation used throughout the following discussion was introduced by Della Ventura et al. (1999) and Hawthorne et al. (2000). It includes in a single notation all possible cation arrangements at the NN (nearest-neighbour) and NNN (next-nearest-neighbour) sites around the OH group. In the amphibole structure, the OH group is bonded to two M(1) and one M(3) cations, and the H atom projects into the A-site cavity, which can be vacant or occupied. This NN configuration can be represented as M(1)M(1)M(3)-OH-^[A]A. The M(1)M(1)M(3) cluster is surrounded by two M(2) and one M(3) cations in the octahedral sheet and by two T(1) tetrahedra in the tetrahedral double-chain. Introducing these NNN sites in the notation above gives the general symbol M(1)M(1)M(3)-OH-[A]A:T(1)T(1)-M(2)M(2)M(3). For ideally ordered endmember tremolite and pargasite, the configuration symbols are MgMgMg-OH-^[A] :SiSi-MgMgMg and MgMgMg-OH-^[A]Na:SiAl-MgAlMg, respectively.

The spectra of the end-members along the Tr-Pa series are well-known. The spectrum of tremolite (Fig. 5a) consists of a single very sharp absorption band at 3675 cm^{-1} , assigned to the MgMgMg-OH-^[A]:SiSi-MgMgMg configuration (Hawthorne *et al.*, 1996a, 1997, 2000). The spectrum of pargasite (Fig. 5g) shows two very broad absorptions of almost equal intensity, centered at 3709 and 3678 cm⁻¹. These are assigned to the NN MgMgMg-OH-^[A]Na and MgMgAl-OH-^[A]Na configurations, respectively (Della Ventura *et al.*, 1999).

Assignment of the bands in the high-frequency, 3800-3650 cm⁻¹ region can be based on the data of Della Ventura

Table 3. Possible configurations around the OH group in synthetic amphiboles along the Tr-Pa series, together with the assigned bands and observed band frequencies.

| | Confi | guration | Frequency (cm ⁻¹) | Band | |
|--------------|-------|----------|----------------------------------|------|---|
| M(1)M(1)M(3) | А | T(1)T(1) | M(2)M(2)M | (3) | |
| MgMgMg | Na | SiAl | MgMgMg | 3710 | А |
| MgMgAl | Na | SiAl | MgMgMg | 3688 | В |
| MgMgMg | | SiSi | MgMgMg | 3675 | С |
| MgMgAl | Na | SiAl | MgMgAl | 3671 | D |
| MgMgMg | | SiAl | MgMgMg | 3655 | Е |
| MgMgMg | | SiAl | MgMgAl | 3642 | F |
| MgMgAl | | SiSi | MgMgMg | 3642 | F |
| MgMgAl | | SiSi | MgMgAl | 3625 | G |
| MgMgAl | | SiAl | MgMgMg | 3625 | G |
| MgMgAl | | SiAl | MgMgAl | 3608 | Н |

et al. (1999) on the spectra of amphiboles along the richterite-pargasite join. Accordingly, the A band is due to the MgMgMg-^[A]Na-SiAl configuration and the B and D bands can be assigned to the MgMgAl-^[A]Na-SiAl configuration. The assignment of the bands present in the lower-frequency, 3650-3500 cm⁻¹ region can be based on the data of Hawthorne *et al.* (2000) on the spectra of amphiboles along the tremolitemagnesiohornblende join. Accordingly, the E-F doublet can be assigned to the MgMgMg- \Box -SiAl configuration, and the G-H doublet to the MgMgAl- \Box -SiAl configuration. Within each doublet, the component bands are due to the Al/Mg distribution at the NNN M(2)M(3)M(2) trimers. The resultant band assignments are summarized in Table 3.

Interpretation of the spectra

To simplify the interpretation of the spectra in Fig. 5, it is convenient to divide the recorded spectral range (3800-3500 cm⁻¹) into two regions on either side of the tremolite band: region (1), at higher frequency, is the region of A-site-filled local configurations; region (2), at lower frequency, is the region of A-site-vacant local configurations. The two regions are shown in Fig. 6 where it can be seen that the OHspectra of different end-member amphiboles are very different from each other, reflecting the extreme sensitivity of the O-H bond to the nearest-neighbour and next-nearest-neighbour cation environments. It is apparent that the infrared spectra contain significant structural (both long-range and short-range) information if properly interpreted. For example, both tremolite and richterite have the same NN environment around O(3) (MgMgMg-OH-SiSi); however, tremolite (Fig. 6d) shows a single very sharp (FWHM full-width at half maximum height = 3-4 cm⁻¹) band at 3675 cm⁻¹, whereas richterite (Fig. 6a) shows a single broad (FWHM = 17 cm⁻¹) band at 3730 cm⁻¹. These spectra differ substantially in both (i) the frequency of the main band and (ii) in the band width. The reason for the significant difference in band position (55-60 cm⁻¹) is related to the presence of Na at the A-site in richterite. The occupancy of the A-site in amphiboles has a major effect on the OH-spectrum; this feature was recognized in the pioneering work of Rowbotham &



Fig. 6. Comparison of OH-stretching spectra of selected synthetic amphibole end-members. The richterite spectrum is from Robert *et al.* (1989), the magnesiohornblende spectrum is from Hawthorne *et al.* (2000).

Farmer (1974), and has been well-characterized in several later works (Della Ventura & Robert, 1990; Della Ventura, 1992; Hawthorne *et al.*, 1996a). Note that, in the above discussion, only bands due to the main cationic environments in the structure have been discussed, for simplicity. In fact, the richterite spectrum (Fig. 6a) shows a minor band at 3670 cm⁻¹, in addition to the main one, and tremolite (Fig. 6d) shows a well-defined minor component at 3666 cm⁻¹, on the right of the sharp and very intense peak. These features are related to minor departures of the amphibole stoichiometries from the nominal ones, and have been fully discussed in several previous papers (*e.g.* Della Ventura, 1992; Haw-

thorne *et al.*, 1966a, 1997), therefore will not be considered here.

The reason for the difference in band width is related to short-range cation ordering. Tremolite is a completely ordered amphibole (Hawthorne, 1997) and shows a very sharp band. However richterite, despite being locally very similar to tremolite around the (OH) group, has positional disorder of Na at A-site (Hawthorne *et al.*, 1996b), and Na and Ca at the (M4) site. This disorder is translated into larger band widths in the IR spectrum of richterite compared to tremolite (Hawthorne *et al.*, 1996a, 1997). This effect is also known as "substitutional broadening" (Strens, 1974).

Pargasite (Fig. 6b) and richterite (Fig. 6a) are both A-site filled amphiboles, but their spectra differ markedly in band multiplicity, band position and band width. In contrast to richterite, the spectrum of pargasite shows two bands due to the presence of two different NN octahedral configurations, MgMgMg and MgMgAl, around O(3). This assignment is supported by the equal intensity of these two bands (Fig. 6b) which is consistent with the octahedral Mg/Al distribution of synthetic pargasite (Welch & Knight, 1999). The downward shift ($\Delta_{\nu} = 30-35$ cm⁻¹) in the frequency of the MgMgAl-OH band relative to the MgMgMg-OH band, is due to the presence of Al at M(3) (e.g. Robert, 1981; Raudsepp et al., 1987; Della Ventura et al., 1998, 1999). This is a prominent effect in the OH spectrum of amphiboles, and is due to the significant increase of incident bond-valence at O(3) because of the occurrence of a trivalent cation at M(3).

Why the MgMgMg-OH-^[A]A band of richterite has a higher frequency with respect to the corresponding band in pargasite (3730 cm⁻¹ vs 3709 cm⁻¹)? According to Della Ventura et al. (1999), this is due to the presence, in pargasite, of Al at the NNN T(1) site. In the amphibole structure, the O(7) atom acts as a hydrogen bond acceptor for the OH group at the adjacent O(3) site. Where the O(7) atom occurs as an Si-O(7)-Si linkage, the H...O(7) hydrogen bond is weak; when O(7) is involved in an Si-O(7)-Al linkage, the hydrogen bond is stronger (and consequently the O(3)-H bond is weak), hence the principal stretching band shifts to lower wavenumbers. In pargasite, all T-O(7)-T linkages are of the Si-O(7)-Al type, and hence all OH groups are involved in significant O-H...O(7) hydrogen bonds, therefore the IR bands in pargasite are of lower frequency (wavenumber) than in richterite (Della Ventura et al., 1999).

Finally, Della Ventura *et al.* (1999) and Hawthorne *et al.* (2000) have shown that variation in NNN octahedral occupancy also has a significant effect on the OH-stretching frequency and may produce band splitting of the order of 12-15 cm⁻¹. Due to severe band overlap, this splitting is not easily resolved and gives rise to the evident broadening (FWHM = 25 cm^{-1}) of the pargasite bands. For this reason, the IR spectrum of pargasite is much more complex than the two-band model would suggest, and can be resolved into six components which are related to SRO in the structure involving Mg and Al at the M(3) site, Si and Al at T(1), and Mg and Al at the M(2) site (Della Ventura *et al.*, 1999).

Pargasite (Fig. 6b) and magnesiohornblende (Fig. 6c) have similar composition, but magnesiohornblende has an empty A-site. Thus the principal difference between the band positions in the spectra of pargasite and magnesio-

hornblende is largely due to the effect of the A-site cation. Accordingly, the double-band spectral pattern of pargasite is shifted downward by 55-60 cm⁻¹. In addition the spectrum of magnesiohornblende shows an intense component at high frequency (3670 cm⁻¹). It is due to OH groups involved in weak H...O(7) hydrogen bridges: in magnesiohornblende, because of the (Si₇Al) composition, some of the T-O(7)-T arrangements must be of the Si-O(7)-Si type (Fig. 6c).

Ordering of cations along the tremolitepargasite join

General patterns of LRO of ^[4]Al/^[4]Si and ^[6]Al/^[6]Mg in calcic amphiboles have been recently discussed by Hawthorne (1997) and Hawthorne *et al.* (2000). Tetrahedrally coordinated Al is completely ordered at T(1), except in high-temperature igneous occurrences (Oberti *et al.*, 1995b); octahedral Al is ordered at M(2) and M(3) in both natural (Oberti *et al.*, 1995a) and synthetic (Welch & Knight, 1999) pargasite.

It is now accepted that, in OH-bearing minerals, information on SRO can be obtained by infrared spectroscopy in the OH-stretching region, provided that we can assign all spectral features to specific local configurations. The band assignments given in Table 3 are based on a large amount of data collected in the last decade on several series of synthetic amphiboles, and the infrared spectra of Fig. 5 can be used to derive information on ordering patterns of tetrahedral and octahedral cations along the studied join. Due to accidental band degeneracy and to lack of data on possible variation in absorption coefficients among the bands (Skogby & Rossman, 1991), we cannot calculate accurate site-populations from the measured band intensities (Hawthorne *et al.*, 2000). However, there are a couple of qualitative conclusions to be made from the spectra of Fig. 5.

The low-frequency A-site-vacant region (region 2, Fig. 6), has been discussed in Hawthorne *et al.* (2000). In this range, the FTIR spectra show a fine structure due to NNN interactions. In amphiboles along the tremolite-hornblende join, several combinations of NNN configurations involving Al at T(1) and Al/Mg at both M(2) and M(3) are possible; however, only a limited number of combinations satisfy the valence-sum rule (Hawthorne, 1997) and these combinations closely correspond to the number of bands observed in the infrared spectra. In the amphiboles considered here, the low-frequency region shows the same fine structure and band multiplicity as observed in aluminous tremolites by Hawthorne *et al.* (2000), indicating that the same strong short-range order is present in the samples described here.

As shown in Table 3, the A band is due to a local configuration involving Na at the A-site and Al at the T-sites. Comparing Fig. 5 with Fig. 6 we observe the complete absence in the spectra of Fig. 5 of a band at 3730 cm⁻¹, (a band that is due to a richterite-like configuration, Fig. 6a, *i.e.* to a configuration with only Mg at the octahedral strip, only Si at the T-sites, and a fully occupied A-site). This observation suggests that in amphiboles along the tremolite-pargasite series, there is strong coupling between Na at the A-site and Al at the T-sites, in accordance with the prediction of Hawthorne (1997) based on local bond-valence considerations. Acknowledgements: Financial support to GDV was provided by MURST 1999 "Cristallochimica delle specie minerali: uso di tecniche avanzate per una moderna sistematica". FCH was supported by a Canada Research Chair and Research and Equipment Grants from the Natural Sciences and Engineering Research Council of Canada. Thanks are due to Annibale Mottana and Ciriaco Giampaolo for allowing use of the IR, SEM-EDAX and powder XRD facilities at the University of Roma Tre. Sergio Lomastro assisted with X-ray powder-pattern diffraction. Positive criticism of H. Skogby and an anonymous referee is also acknowledged.

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Received 31 October 2001 Modified version received 5 May 2002 Accepted 12 June 2002