# Long-Range Order in Amphiboles

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# **INTRODUCTION**

Comprehensive knowledge of the order-disorder relations in amphiboles is essential to (1) complete understanding of the crystal chemistry of these minerals, and to (2) the use of amphiboles in thermodynamic calculations (e.g., of temperature and pressure of equilibration) where accurate activity models are critical to the accuracy of such treatments. Moreover, such information is essential to our understanding of phase relations, optical and electrical properties and dehydrogenation mechanisms. As a result, more effort has been expended on characterizing site occupancies in amphiboles than in any other group of minerals. Hawthorne (1983a,b) reviewed in detail all work prior to 1983. Here, we will briefly summarize this work, and focus more on what has been learned since then.

# METHODS OF DERIVING SITE POPULATIONS

We will briefly review the common methods of deriving site populations. It is important that everyone who uses site populations has an appreciation of the methods used to derive this information, as a significant fraction of the data in the literature is wrong, and the user has to be in a position to assess the accuracy and precision of the data that they will use. The most comprehensive method of deriving site populations is crystal-Structure REFinement (SREF), as this method senses every atom (in significant amounts) in a crystal. However, this universality has a negative side. Some atomic species cannot be distinguished as they scatter radiation in a very similar way. Different types of radiation (e.g., X-rays, neutrons) can compensate for this drawback: for example, X-ray scattering cannot easily distinguish between Fe and Mn or Fe and Ti (differences in size of these species can be used for this purpose, but this becomes inaccurate to ineffective in more complicated compositions), whereas neutron scattering can distinguish these species. However, there are many instances where such differentiation is not possible. It is here that spectroscopy can be useful, as many spectroscopic techniques are species sensitive and are not complicated by the presence of other elements in a mineral. Thus Mössbauer spectroscopy can "see" only Fe in a very complicated amphibole, and can easily sense valence-state differences that are not easy to characterize by SREF. Frequently, a much better characterization of site populations can be attained by a combination of techniques that can compensate for each other's inadequacies.

# Single-crystal Structure REFinement

SREF is the method most commonly used to address calculation of site populations and

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thus of cation and anion partitioning in minerals. It can be actually regarded as a method of chemical analysis. X-ray SREF is an electron-counting technique with spatial resolution (Hawthorne and Grice 1990), and neutron scattering yields an aggregate site-scattering length which can be further interpreted with the incorporation of additional chemical information. SREF allows accurate and precise determination of:

- (1) the relative positions, point symmetry and numbers of sites, from which derive the stoichiometric requirements of the formula unit; in addition, the relative positions give accurate interatomic distances and angles which are used extensively for crystal-chemical analysis.
- (2) the relative scattering power at each site; note that some sites are assumed to have fixed scattering power (usually the anion sites), and these serve to scale the relative scattering at those sites considered to have variable scattering in the refinement process.

For X-rays, the refined scattering corresponds to the mean atomic number of all constituents at that site (i.e., averaged over the diffraction volume). When properly scaled, the refined sitescattering values give the total number of electrons per formula unit (epfu) (Hawthorne et al. 1995a) with a precision (depending on how well the scattering curves used in the refinement procedure approach the real site-populations) of  $\sim 0.1 e^{-1}$  in high-quality structure refinements (i.e.,  $R_{obs} \approx 1-2\%$ ). For neutrons, the refined scattering corresponds to the mean scattering length of all constituents at that site. If there is sufficient difference in scattering power of constituents occupying a site, binary site-occupancies can be determined. Where a site is occupied by more than two species (e.g., Mg, Fe, Mn), a single SREF experiment cannot determine site occupancies. One may deal with this issue in two ways: (1) in some circumstances, one may do two SREF experiments with different radiations if there are significant differences in scattering values for different pairs of species with the two radiations. In the example given above, X-ray scattering can distinguish between Mg and (Fe + Mn) but not between Fe and Mn, whereas neutrons can distinguish between Fe and Mn; thus structure refinement on the same material with X-rays and with neutrons will give unique site-occupancies for Mg, Fe and Mn. The problem here is that not all combinations of scattering species have such differences in scattering by X-rays and neutrons. (2) Alternatively, one may assume a site occupancy for one species and leave it as fixed in the refinement process; the other two occupancies can then be refined in the usual way. To do this, one needs (i) an accurate chemical analysis of the crystal, and (ii) knowledge that the species considered as fixed only occupies one site (i.e., it is completely ordered at a specific site). For example, this will work for the refinement of Mg, Fe and Cr over the M(1,2,3) sites where Cr is assumed to occur only at the M(2) site whereas Mg and Fe are partly disordered over the M(1), M(2) and M(3) sites, and here the Cr content is known from microchemical analysis of the crystal. Note that this procedure cannot work where all three constituents are partly disordered (e.g., for Mg, Fe and Mn over the M(1,2,3)sites) as knowing the composition of the crystal does not determine the site occupancies of any of the three constituents.

A major advance in our knowledge of the chemical composition of amphiboles since the last amphibole Short Course (1981) is the common occurrence of *variable* light lithophile elements, specifically H and Li, in amphiboles. The presence of these variable constituents was detected by SREF and subsequent crystal-chemical analysis. A number of convincing examples are now available (Hawthorne et al. 1993; Hawthorne and Oberti 2007), and diagrams suitable to detect and quantify Li and H based on SREF results are reported elsewhere in this volume by Hawthorne and Oberti (2007, Fig. 1) and in a following section. Interestingly, this has promoted the development of SIMS for the analysis of LLE (Light Lithophile Elements) in amphiboles (Ottolini et al. 1993; 1995; Ottolini and Oberti 2000).

*Crystal-chemical constraints.* A lot of work has been focused on improving and validating refinement procedures, and on developing crystal-chemical relations that can be used to confirm or assign site-populations. Some procedures for structure refinement of amphiboles and other rock-forming minerals are described in detail by Ungaretti (1981), and the relevance of particular reflections on the estimation of crystal-chemical parameters has been discussed by Merli et al. (2000, 2001).

The refined model generally has two or three scattering curves assigned to each site, whose relative occupancy is refined under the constraint that the total occupancy is 1.0. The core of the problem is to convert these (possibly) fictive site occupancies into real site-populations which sum directly to give the structural formula. The site population proposed for a particular site *must* be consistent with the refined site-scattering values and mean bond-lengths, as well as with local bond-valence requirements. Furthermore, the sum of all the site populations must sum to a value close to the chemical composition of the crystal as determined by an independent technique (usually electron- and ion-microprobe analysis), and the unit-cell content must be electroneutral.

**Derivation of site populations: general features.** SREF gives the scattering at each site in the crystal, and the issue then is to derive site populations from these values. As noted above, SREF does not directly provide a unique solution to this problem, and other information has to be incorporated into the derivation of site populations, particularly in the case of amphiboles where a site is often occupied by several constituents. Primary scattering information is as follows:

- (1) the sum of the site occupancies is 1.0; note that a site constituent may be a vacancy, and assumptions or external knowledge is required as to whether a vacancy can occur at a specific site.
- (2) the site-scattering values from the SREF procedure.

Additional information is as follows:

- (3) the sum of the unit-cell contents must be electroneutral; note that this is a rigid constraint, as we know that the rule of electroneutrality must be obeyed exactly.
- (4) the observed mean bondlengths and assigned site-populations must be in accord with previously established relations between these quantities.
- (5) the chemical composition of the crystal. This may be (a) observations (i.e., the unit formula derived from a chemical analysis, usually an electron and ion-microprobe analysis possibly supplemented with spectroscopic information giving valence states of some cations), (b) a guesstimate of the composition (e.g., Si, Al, Mg, Fe, Mn, Ca, Na, K, O, F and H only are assumed to be present), or (c) the presence or amount of a constituent (e.g., <sup>B,C</sup>Li, <sup>B</sup>Mg, <sup>M(1)</sup>Ti) as indicated by diagnostic signals from the structure refinement such as anomalous site-scattering values and/or atom-displacement parameters.

Site populations may be derived either by manual solution of a series of simultaneous equations involving equal distribution of error among experimental parameters, or by least-squares minimization of a system of suitable equations relating the full occupancy, the refined site-scattering value, the refined mean bondlength and the overall electroneutrality to the content of the four main cations. Both of these approaches have been used extensively for the assignment of amphibole site-populations.

**Derivation of site populations: a least-squares procedure.** For calcic, sodic-calcic and sodic-amphiboles with  $(OH)_2$  at the O(3) site, a least-squares procedure was applied by Cannillo et al. (1981) to 130 structure refinements of amphiboles, and later optimized by

Cannillo et al. (1986) on a more representative database of around 500 structure refinements. Here, we report for the first time the results of a recent re-examination of the problem with a database of more than 1100 structure refinements comprehensively covering the composition space of monoclinic amphiboles. The resulting program (COMAMPH) will be described in detail in a manuscript in preparation, and is available on request from R. Oberti.

Multiple regression analysis of 440 selected crystals with complete chemical analyses and superior agreement with SREF results gave predictive equations relating the main chemical variables in the crystal-chemical formula [<sup>A</sup>K, <sup>B</sup>Li, <sup>B</sup>Na, <sup>B</sup>Ca, <sup>B</sup>Mg, <sup>B</sup>(Fe<sup>2+</sup>, Mn<sup>2+</sup>), <sup>C</sup>Li, <sup>C</sup>Mg, <sup>C</sup>(Fe<sup>2+</sup> Mn<sup>2+</sup>), <sup>C</sup>Al, <sup>C</sup>(Fe<sup>3+</sup>, Mn<sup>3+</sup>), <sup>C</sup>Ti, <sup>T</sup>Al, <sup>O(3)</sup>F, <sup>O(3)</sup>O<sup>2-</sup>] and the net positive charges at the *A*, *M*(4) and *M*(1,2,3) sites with all the geometric and atomic-displacement parameters of the structure. The equations and their regression parameters are given in Table 1. <sup>T</sup>Si, and <sup>O(3)</sup>OH are calculated by difference to the complete group-site occupancy. For the *A* site, which has variable occupancy, <sup>A</sup>Na is calculated based on the predicted positive charge. <sup>*T*(1)</sup>Al is calculated based on the revised equation

$$T^{(1)}$$
Al (apfu) = [ $< T(1)$ -O> - 1.6193] × 34.2199   
  $R = 0.997 \sigma = 0.048$ 

which has been newly derived based on the whole CNR-IGG database, and which is slightly different from that given by Oberti et al. (1995a) based on a smaller dataset,  $[<T(1)-O> - 1.6187] \times 33.2055$ . As discussed in Hawthorne and Oberti (2007), there is some spreading in <T(1)-O> distances of amphiboles with <sup>T</sup>Al (from EMP analyses) < 0.30 apfu (cf. for instance their Fig. 17 and Fig. 10 in this Chapter). This feature mostly derives from errors in the analysis and in the calculation of the unit formula; however, amphiboles with significant amount of small B cations (namely, Li, Mg, Fe) and Si = 8.0 apfu have <T(1)-O> distances significantly shorter than 1.619 Å. Therefore, caution must be used when dealing with very low <sup>T</sup>Al contents.

The total amounts of the B and C cations are subsequently normalized to the stoichiometric values (2.0 and 5.0 apfu, respectively). At this point, the site populations are optimized by minimizing the differences between the calculated and refined site-scattering values. Lastly, the resulting crystal-chemical formula is optimized to achieve overall electroneutrality using an iterative procedure which changes the cumulative charges of the A, B, C, T and W species

Dependent variable	Number of parameters	R	see	Dependent variable	Number of parameters	R	see
AK	65	0.996	0.021	<sup>C</sup> (Fe,Mn) <sup>2+</sup>	60	0.993	0.096
<sup>B</sup> Na	47	0.998	0.040	<sup>C</sup> Fe <sup>3+</sup>	76	0.984	0.095
вСа	55	0.999	0.039	cLi	50	0.995	0.016
<sup>B</sup> Li	52	0.998	0.021	<sup>T</sup> A1	39	0.998	0.043
<sup>B</sup> Mg	56	0.937	0.029	<sup>O(3)</sup> F	74	0.988	0.073
<sup>B</sup> (Fe,Mn) <sup>2+</sup>	40	0.990	0.028	<sup>O(3)</sup> O <sup>2-</sup>	70	0.985	0.076
<sup>c</sup> Al	57	0.996	0.045	A charge	47	0.996	0.028
<sup>C</sup> Mg	63	0.999	0.055	B charge	52	0.991	0.086
c <sub>Ti</sub>	68	0.989	0.031	C charge	61	0.991	0.086

**Table 1.** The relation between the chemical composition and the amphibole structure.Predictive equations have been obtained by stepwise multiple regression analysis of the<br/>CNR-IGG-PV data base. They are now used in the COMAMPH program.

*R* is the multiple correlation coefficient; see is the standard error of the estimate.

while keeping the corresponding site-scattering values fixed. Starting from the formula obtained with the above procedure, which provides a good estimate of the OH content and of the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio, M(1), M(2) and M(3) site populations can be derived by assigning the cations according to the site preferences discussed in a following section, and checked against the refined site-scattering values.

The accuracy of this method was first tested on a group of ~100 samples for which some chemical information is available, and then used on the whole database. The results show that this method generally produces accurate crystal-chemical formulae. Discrepancies with the available chemical information could be always explained by (1) analytical problems [e.g., (Na+K) or (Si+Al) contents inconsistent with amphibole stoichiometry], (2) erroneous formula recalculation (e.g., underestimation of the oxo component), or (3) incorrect structure refinement (e.g., too high atom-displacement parameters at the *A* sites, which wrongly increases the refined site-scattering value).

Notably, with this procedure, we can obtain reliable estimates of those chemical variables which escape routine EMP analysis, i.e., Li, F,  $^{O(3)}O^{2-}$  (and thus H), Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio, and of cation partitioning between the group sites [e.g., Li, Mg and (Fe + Mn) between B and C sites]. This information is crucial to the correct classification of the sample, and possibly to draw attention to the need of further chemical or spectroscopic analysis.

As shown by multiple regression (Cannillo and Ungaretti 1982) and leverage analysis (Merli et al. 2000, 2001), some reflections from the complete set of diffraction data are particularly sensitive to the variation of structural parameters. Based on this relation, another program has been developed which predicts the crystal-chemical formula based solely on unit-cell parameters and measured structure factors. Because it takes into account all data for common and uncommon C2/m amphibole compositions, this approach is particularly useful in producing an appropriate structure model to begin normal least-squares refinement of the structure. The program is called PREDICT, and is available on request from R. Oberti. In this case, stepwise multiple regression analysis gave a series of equations which estimate the scattering values and the mean bondlengths at each site, together with other geometrical parameters which provide information on the Li, F and O<sup>2-</sup> contents (see Hawthorne and Oberti 2007 for more details). In particular, the site-scattering values at the A, A(m), A(2), M(4) and M(4') sites are treated separately. At the end of an optimization procedure similar to that for COMAMPH, the program provides a highly reliable formula (simplified to major elements, e.g.,  $Fe^{2+} = Fe^{2+} + Mn^{2+}$ ,  $Fe^{3+} = Fe^{3+} + Cr^{3+}$ , ...) and thus a consistent set of scattering factors to be used in the proper proportions in a straightforward structure refinement.

## Mössbauer spectroscopy

The Mössbauer effect involves the recoil-free emission and absorption of  $\gamma$ -rays by a specific atomic nucleus. The emission of a  $\gamma$ -ray during a nuclear transition normally causes a recoil of the emitting atom; this recoil energy dissipates by transfer to the phonon spectrum of the structure. As the phonon spectrum is quantized, this transfer must occur in integral multiples of the phonon energy and the probability exists that no energy is transferred. The effective line-width of the zero-phonon (recoil-free) process is that of the  $\gamma$ -ray; this is extremely small (Wertheim 1964, Chap. 4, Fig. 1) in relation to the characteristic energies of interaction between the nucleus and its surrounding electrons. If the zero-phonon  $\gamma$ -ray encounters another nucleus, its energy may be absorbed by raising that nucleus to an excited state, provided the transition energies of the emission and absorption events are equal to within the line-width of the  $\gamma$ -ray. As the linewidth of the  $\gamma$ -ray is much smaller than the characteristic interaction energies between nuclei and electrons, a change in structural environment is generally sufficient to bring the two nuclei out of resonance. However, the energy of the  $\gamma$ -ray may be modulated by applying a Doppler shift to bring the system into resonance. In this way, nuclear transition energies may be compared in different environments.

A change in the s-electron density at the nucleus of an atom will result in a shift in the nuclear energy levels. Where such a variation occurs between emitter and absorber, the processes are separated in the energy spectrum by an amount known as the Isomer Shift (IS) or Chemical Shift (CS). This quantity is thus a measure of the relative s-electron density at the nucleus. Two factors are principally responsible for variations in isomer shift. Screening of s-electrons from the nucleus by valence electrons is strongly affected by valence state and degree of covalent bonding. Thus isomer shift may be used to characterize valence state and coordination number. If the nucleus does not have a uniform charge density, a quadrupole moment arises which can interact with the electric field gradient (EFG) at the nucleus to lift the degeneracy of the nuclear states. The splitting of the nuclear energy levels gives rise to a series of possible transitions between the ground and excited states of the nucleus, the number of which depends on the nuclear spin quantum number. For  ${}^{57}$ Fe (I = 1/2) in paramagnetic materials, the ground state is not split and the first excited state (I = 3/2) is split into two levels; the two allowable transitions give rise to a doublet in the energy spectrum; the separation of the two components is known as the Quadrupole Splitting (QS) and is thus a measure of the EFG at the nucleus. Principal factors affecting the EFG at the nucleus are the non-spherical electron distribution in the atom itself, a function of valence state, and the nonspherical component of the crystal field. Thus quadrupole splitting may be used to characterize valence state and variations in structural environment. More detailed discussions of the Mössbauer effect in Mineralogy are given by Bancroft (1973), Hawthorne (1988), Murad and Cashion (2004) and Dyar et al. (2006), and Hawthorne (1983c) considers issues associated with the derivation of site occupancies and their attendant standard deviations in detail.

Site-occupancy derivation. There are thirty or so isotopes that are sensitive to the Mössbauer effect, but only <sup>57</sup>Fe is of interest to amphibole crystal chemistry. An experimental Mössbauer spectrum is shown in Figure 1. The counts at the margins of the spectrum represent the background counts and are approximately constant. Toward the center of the spectrum, the counts decrease due to the resonant absorption of  $\gamma$ -rays of this specific energy by the sample,



Figure 1. The Mössbauer spectrum of ferrotschermakite, showing the absorption of  $\gamma$ -rays as a function of energy (velocity). Each data point is shown by a broken line, the length of which is 2 standard deviations (based on counting statistics). The spectrum is fitted to component pairs of bands (doublets) that correspond to Fe of a particular valence state and at a particular site (marked above the spectrum). (Modified from Hawthorne 1983a).

and the observed spectrum consists of a series of peaks, the number and characteristics of which are a function of the valence(s) of Fe in the sample, the number of sites occupied by Fe, and the occupancies of those sites. Unfolding the observed envelope into its component peaks is done by least-squares refinement.

Inspection of Figure 1 shows that peaks in the spectrum can overlap strongly, causing problems in the least-squares process. These problems may be alleviated somewhat by incorporating into the model additional information that is external to the spectral data itself. There are two types of constraints that are widely used: (1) *Width constraints:* Mössbauer spectral examination of many end-member compounds suggests that the peak widths corresponding to Fe<sup>2+</sup> in various sites are equal in a specified sample. Thus in the spectrum refinement procedure, the width of all the peaks can be constrained to be equal, with a considerable improvement in both the convergence rate and standard deviations. (2) *Area constraints:* Experimental evidence suggests that the individual peaks of a quadrupole-split doublet should have approximately equal intensity. This is another very powerful constraint that is frequently used in spectral refinement. This constraint may not be strictly correct as preferred orientation in a sample can give rise to intensity asymmetry in quadrupole-split doublets. In complex, poorly-resolved spectra, the final solution is only as good as the constraints which were used in the fitting procedure. If the constraints are true, then the fitted parameters are valid; however, if the constraints are wrong (or inappropriate) then the solution will be wrong.

**Precision.** Least-squares refinement is a widely used method in Science. The reason for this is that once convergence has been attained, some kind of precision (a standard deviation) can easily be assigned to the variable parameters of the model. However, many Mössbauer studies in the literature do not report standard deviations for their assigned site-population. These values are of little use without some estimation (a minimum estimation in the case of least-squares modeling) of their precision. For an extensive discussion on precision in spectral fitting, see Hawthorne (1988) and Hawthorne and Waychunas (1988).

## Infrared spectroscopy

Vibrational spectroscopy involves the interaction between electro-magnetic radiation and the vibrational modes of a crystal. A vibrational mode in a crystal will absorb electromagnetic radiation if the frequencies of the vibration and the radiation are coincident and if the excited vibration results in a change in the dipole moment of the crystal; this gives rise to *infrared absorption spectroscopy*. Infrared spectroscopy in the principal (OH)-stretching region (3800-3600 cm<sup>-1</sup> in amphiboles) is a powerful method for characterizing order in amphiboles.

A fragment in many common hydroxyl-bearing minerals is the trimer of edge-sharing octahedra  $[M_3\phi_{12}(OH)]$  ( $\phi$  = unspecified anion) (see Hawthorne and Della Ventura 2007, Figure 3a); this trimer is embedded for instance in the structures of the humites, the amphiboles, the micas, talcs and chlorites. The exact position (energy) of the fundamental band of the corresponding OH stretching vibration is a function of the nature of the next-nearest and nextnext-nearest neighbor cations [at 2 M(1), M(3), M(4) and A] and of the strength of hydrogen bonding [involving O(7) in amphiboles, Hawthorne and Della Ventura 2007, Fig. 3b]; stronger hydrogen bonds are associated with lower wavenumbers (values in  $cm^{-1}$ ). Amphiboles with a completely ordered arrangement of cations in this cluster [i.e., M(1)M(1)M(3) = MgMgMg] show a single sharp band in this region. However, this band in minerals of intermediate composition shows considerable fine structure. Strens (1966) and Burns and Strens (1966) interpreted the fine-structure bands in amphiboles in terms of cation disorder over the octahedrally coordinated sites in the structure, and used the relative intensity of the various bands to derive the frequency of occurrence of the different possible combinations of cations and the cation ordering over the non-equivalent sites in the structure (e.g., Burns and Greaves 1971). This issue is discussed in some detail by Hawthorne (1983a), Hawthorne et al. (2005) and Hawthorne and Della Ventura (2007).

**Other considerations.** The derivation of site-occupancies from band intensities assumes that the band intensity for a specific configuration is related to the frequency of occurrence of that configuration in the same way that all other bands are related to their corresponding configurations. Thus the transition moment of the OH vibration should be independent of the type of configuration. However, weak hydrogen bonding may significantly affect the transition moment of the OH band, whether or not the strength of the hydrogen bonding is related to the cation configuration at the coordinating M sites. In older work on the derivation of site populations (see surveys by Strens 1974 and Hawthorne 1981, 1983c), it was implicitly assumed that the molar absorptivity of all fundamental OH-stretching bands is the same. However, Skogby and Rossman (1991) showed that this is not the case for polarized single-crystal absorption spectra of amphiboles, where the molar absorptivity ( $\epsilon$ ) of OH-stretching bands can increase strongly with decreasing absorption frequency (Fig. 2).

Della Ventura et al. (1997) measured the powder infrared spectra of (magnesium, nickel)and (magnesium, cobalt)-potassic-richterite solid-solutions (Fig. 3) and showed that the molar absorptivities of the four OH-stretching bands are the same in a single powder sample (Fig. 4), and hence the method can be used to derive long-range site-populations when dealing just with disorder of divalent cations over the M(1), M(2) and M(3) sites, and where there are no changes in the formal charges of the next-nearest and next-next-nearest neighbor cations. Thus the situation regarding variation in molar absorptivity as a function of band frequency in amphiboles is currently unclear. However, it is clear that we must consider possible variations in molar absorptivity in relating band intensities to structural and chemical features.

Another problem that can arise in natural amphiboles involves the effects of anion variations. In many amphiboles, the O(3) site may be occupied by F, Cl (and  $O^{2-}$ ) in addition to the OH group. In order to apply infrared spectroscopy to calculate site populations, it is necessary to assume that there is random mixing of OH groups and F, Cl anions with no segregation at specific cation configurations. Unfortunately, this does not appear to be the case, as Fe<sup>2+</sup> tends to avoid F-coordinated sites (Rosenberg and Foit 1977). In addition, stretching frequencies are sensitive to coupling of OH-OH or OH-F(Cl) through the *A* site (Robert et al. 2000 and references therein). Despite these problems, infrared spectroscopy can be a very useful method where used in the appropriate circumstances and on well characterized samples.



Figure 2. The variation in integrated molar absorptivity as a function of absorption frequency (data from Skogby and Rossman 1991). Band frequencies for synthetic (Ni,Mg,Co)-richterite solidsolutions are shown by the letters A, B, C, D corresponding the local arrangements M(1)M(1)M(3) = MgMgMg,MgM<sup>2+</sup>M<sup>2+</sup>, MgMgM<sup>2+</sup>,  $M^{2+}M^{2+}M^{2+}$ ; the lengths of the vertical lines are relative measures of the integrated molar absorptivities at the corresponding absorption frequencies. (Modified from Della Ventura et al. 1996).



Absorbance





Figure 4. Variation in Ni (squares) and Co (circles) content of the M(1) and M(3) sites in synthetic (Ni,Mg)- and synthetic (Co,Mg)richterite solid-solutions calculated from the band intensities of the infrared spectra (Fig. 3) versus the corresponding values measured by Rietveld refinement. The hollow symbols were calculated using the integrated molar absorptivities indicated by Fig. 2, and the filled symbols were calculated using an integrated molar absorptivity of 1.0 for all bands (from Della Ventura et al. 1996).



# Other spectroscopic methods

Other methods have not been used extensively to derive quantitative site-occupancies in amphiboles. Of course, there are important examples of site-occupancy information being derived for amphiboles where the standard methods of SREF or Mössbauer spectroscopy are not effective. However, they are sufficiently infrequent that descriptions of these methods are not warranted here. Of interest in this regard are Magic-Angle-Spinning Nuclear Magnetic Resonance (MAS NMR), electron paramagnetic (spin) resonance (EPR, ESR), electronic absorption spectroscopy and X-ray absorption spectroscopy (XAS). The reader is referred to other sources for an introduction to these techniques.

# SITE PREFERENCES OF THE MOST COMMON CATIONS

A detailed discussion of cation distribution in amphiboles was given by Hawthorne (1983a). In the last twenty five years, much work has been done on both natural and synthetic amphiboles to understand cation site preference and partitioning. As a result, our understanding has improved substantially. The principal advances generally involve

- (1) unusual site preferences under peculiar chemical or pressure/temperature conditions;
- (2) patterns of order for the A cations as a function of bulk composition and short-range order;
- (3) patterns of orders for Al and Ti between and within the T(1,2) and M(2,3) sites as a function of composition and *P*,*T*,  $f_{H_2O}$  conditions of crystallization;
- (4) crystal-chemical mechanisms affecting the incorporation of Li at the M(3) site and its partitioning between the M(3) and M(4) sites;
- (5) detection of the oxo component and our understanding of the crystal-chemical mechanisms controlling primary incorporation of O<sup>(3)</sup>O<sup>2-</sup> and secondary dehydrogenation [O<sup>2-</sup><sub>1</sub>(OH)<sub>-1</sub>] at O(3).

The present knowledge on site-preference is discussed below for the major cations arranged in alphabetic order. Details are given only for monoclinic amphiboles, because recent work on the ordering of C and T cations in *Pnma* amphiboles has been discussed in Hawthorne and Oberti (2007). The oxo-component is discussed in a separate section. Information on longrange order of trace elements is given in Tiepolo et al. (2007).

# Aluminum

Aluminum is a T and a C cation (Warren 1930). There is presently a general consensus that <sup>C</sup>Al is preferred in high-*P* environments and <sup>T</sup>Al is preferred in high-*T* environments.

<sup>*C*</sup>*Al.* Semet (1973) provided incontrovertible IR evidence [Fig. 5, spectrum (c)] that <sup>*C*</sup>Al (and Fe<sup>3+</sup>) occur at more than one of the M(1,2,3) sites in synthetic magnesiohastingsite. Despite this evidence, early structure work continued to assign <sup>*C*</sup>Al to M(2). Raudsepp et al. (1987a,b, 1991) confirmed this behavior for <sup>*C*</sup>Al and showed that this disorder of trivalent cations also occurs for Cr<sup>3+</sup>, V<sup>3+</sup> and Ga in synthetic pargasites.

Oberti et al. (1995b) first documented by SREF that <sup>C</sup>Al is partly disordered over the M(2) and M(3) sites in pargasites from the peridotites at Finero (Ivrea Verbano, Italy); they also showed that <sup>M(3)</sup>Al is higher in samples with high Mg content (which also crystallized at the higher *T*). Figure 6 shows the <M(1)-O> and <M(3)-O> distances in calcic amphiboles (without significant oxo component) in the CNR-IGG-PV database. The samples mentioned above have anomalously small <M(3)-O> distances, and the departure from the general trend is maximal for the highest-Mg compositions (with the smallest <M(1,3)-O> distances for the group identified by black triangles). Similar behavior has since been found in mantle pargasites and kaersutites



**Figure 5.** Infrared spectra in the principal (OH)-stretching region for synthetic (a,e) Cr-pargasite (b,f) Ga-pargasite, (c) magnesiohastingsite (Semet 1973), (d) pargasite, (g) Sc-pargasite (from Raudsepp et al. 1987a, Fig 3 and 4).



**Figure 6.** The variation in  $\langle M(3) - O \rangle$  versus  $\langle M(1) - O \rangle$  in calcic amphiboles with 2 (OH,F,Cl) pfu. Note that  $\langle M(3) - O \rangle$  is always shorter than  $\langle M(1) - O \rangle$  when Mg  $\rangle >$  Fe<sup>2+</sup>. Even shorter  $\langle M(3) - O \rangle$  distances indicate Al occupancy of the M(3) site, which occurs in Mg-rich pargasite and solid-solutions between pargasite and edenite.

from world-wide occurrences, e.g., in hornblendite veins and peridotites at Lherz, Eastern Pyrenees, France (Zanetti et al. 1996), in megacrysts in basalt and in composite mantle xenoliths from the Carpatho-Pannonian Region (Zanetti et al. 1995), in peridotites and pyroxenites at Zabargad Island, Red Sea (Zanetti et al. 2000), and also in pargasite from metamorphic rocks, e.g., marbles along the Soper river, Baffin Island (Tait et al. 2001).

The effect of divalent cations on the ordering of Al over M(2) and M(3) was further elucidated by Della Ventura et al. (1998) who showed that while <sup>C</sup>Al is almost completely disordered over M(2)and M(3) in synthetic pargasite, <sup>C</sup>Al is completely ordered at M(2) in the Co<sup>2+</sup> analogue of pargasite, <sup>A</sup>Na <sup>B</sup>Ca<sub>2</sub> <sup>C</sup>( $\dot{Co^{2+}}_4Al$ ) <sup>T</sup>( $\dot{Si_6Al_2}$ )  $O_{22}$  <sup>W</sup>( $\dot{OH}$ )<sub>2</sub> (Fig. 7). The spectrum of synthetic pargasite shows two prominent components at ~ 3710 and 3678  $cm^{-1}$ , assigned to MgMgMg-(OH) and MgMgAl-(OH), indicating that Al is almost completely disordered over M(2) and M(1,3) [note that the spectroscopic evidence indicates only that Al occurs at M(2) and M(1,3); it cannot tell us whether Al occurs at M(1)or M(3) or both]. In contrast, the OH-stretching spectrum of Co-substituted pargasite consists of a single band at 3656 cm<sup>-1</sup>. This band is assigned to a local  $M^{(1)}Co^{M(1)}Co^{M(3)}Co$  configuration (Della Ventura et al. 1998), and indicates complete order of Al at the M(2) site in this sample, which is also supported by Rietveld structure refinement of site occupancies (Della Ventura et al. 1998). Figure 7 also shows the OH-stretching spectrum of a Mgrich pargasite from Finero (sample 229-18 in Oberti et al. 1995b); note the similarity to the spectrum of



Figure 7. OH-stretching FTIR spectra of pargasite from Finero (top), synthetic pargasite (from Della Ventura et al. 1999, middle) and synthetic Co-substituted pargasite (from Della Ventura et al. 1998, bottom).

synthetic pargasite: both show two prominent bands in the OH-stretching spectrum, which are assigned to OH-groups bonded to  ${}^{M(1)}Mg^{M(1)}Mg^{M(3)}Mg$  and  ${}^{M(1)}Mg^{M(3)}Mg^{M(3)}Al$ , respectively.

Further work on synthetic (Della Ventura et al. 1999, 2003; Welch et al. 1994; Welch and Knight 1999; Najorka and Gottschalk 2003; Jenkins et al. 2003) and natural amphiboles (Bellatreccia et al. in prep.) confirm that disorder of <sup>C</sup>Al is a common feature of Mg-rich calcic amphiboles. Welch et al. (1994) and Hawthorne et al. (2000) further confirmed by MAS NMR that <sup>C</sup>Al occurs at both the M(2) and M(1,3) sites. Figure 8 shows the triple-quantum MAS NMR <sup>27</sup>Al spectrum of synthetic pargasite. There are three distinct signals, one due to <sup>T</sup>Al and two due to <sup>C</sup>Al; Hawthorne et al. (2000) argue that if Al occurred at the M(1), M(2) and M(3) sites, three signals should be observed. If this is the case, the results are in accord with those of Oberti et al. (1995b), although they do not indicate which of the M(1) or M(3) sites are occupied by Al. Welch and Knight (1999) studied a synthetic end-member pargasite crystallized at 932 °C by Rietveld refinement of data collected by neutron diffraction on powders, FTIR and <sup>1</sup>H MAS NMR spectroscopy. They concluded that <sup>C</sup>Al disorder is higher [50% at M(3) and 50% at M(2)] than in natural samples, where the maximum disorder detected is statistical [34% at M(3) and 66% at the two M(2) sites pfu (Oberti et al. 1995b)]. Actually, the refined natural samples contain significant amounts of larger cations (down to 1.25 <sup>C</sup>Fe<sup>2+</sup> apfu), thus confirming their effect on ordering.



Figure 8. Triple-quantum (3Q) MAS NMR spectrum of a synthetic amphibole approximately on the tremolite–aluminohornblende join. Three distinct signals are observed, and their assignments are indicated on the figure; see text for discussion (from Hawthorne et al. 2000).

Palin et al. (2003, 2005) did Monte Carlo simulations of Al-Mg and Al-Si non-convergent ordering in glaucophane and along the tremolite–tschermakite solid-solution at different *T*. The goal was to check for their potential use in geothermobarometry under *X*, *T* conditions where other minerals are not stable. Indeed, the ordering process of homovalent cations is relatively fast, and their high-*T* distribution can thus be easily reset. In contrast, ordering of heterovalent cations is much slower and can register accurately crystallization temperatures. Palin et al. (2003) predicted complete Al ordering at the M(2) site in glaucophane even at *T* above 1000 K, a result confirmed by OH-stretching IR spectroscopy on the synthetic samples synthesized by Pawley (1992). A very different situation was obtained in calcic amphiboles, where simulations considered both Al/Si and Al/Mg ordering and obtained only a marked preference of Al for the T(1) and the M(2) sites, respectively (Palin et al. 2005). In magnesiohornblende, Al at T(2) was found to reach 20% but Al at M(2) was higher than 55% at *T* around 1500 K. Admittedly, Monte Carlo simulation give high Al occupancy at M(1), even higher than at M(3), a result conflicting with experimental evidence on natural and synthetic amphiboles.

Both structure refinement and FTIR show that high F contents hinder Al disorder over the M(1,2,3) sites. In fluoro-amphiboles, <sup>C</sup>Al behaves exactly as the other highly charged C cations, and is always ordered at the M(2) site (Oberti et al. 1998). Accordingly, calcic fluoro-amphiboles plot closer to the dotted line in Figure 6.

*TAL*. Ordering of Al over the T(1) and the T(2) sites is a bit more complicated. Aluminum is commonly strongly ordered at the T(1) site in C2/m amphiboles, where the local bond-valence requirements can be satisfied by incorporation of (1) highly charged cations at the M(2) site, (2) A cations, (3) divalent cations at the M(4) site (in sodic amphiboles).

The occurrence of <sup>T</sup>Al beyond 2.0 apfu was first reported by Adams and Harrington (1896) in a sample from the Hasting County, Ontario. Admittedly, these authors reported Si = 5.75 apfu, but with a total cation excess of 0.7 apfu. Appleyard (1975) provided modern analyses of "sub-silicic hastingsite" (to be presently named ferri-ferrosadanagaite) from metasomatic alkaline gneisses at Wolfe, Ontario; he recorded Al up to 2.73 apfu, but did not propose any scheme for Al ordering over the T(1) and T(2) sites. The latter was provided based on structure refinement by Hawthorne and Grundy (1977a), who concluded that all the Al in excess of

2.0 apfu is incorporated at the T(2) site. Hawthorne et al. (1996a) reported the discovery and characterization of fluorocannilloite with 2.40 <sup>T</sup>Al apfu ordered at the T(1) site and the *A* sites slightly over half-filled by Ca. Oberti et al. (1995c) refined the structure of synthetic fluoropargasite with 0.30 Ca apfu at the *A* sites and 2.20 Al at the T(1) site. Sadanagaite was reported by Sawaki (1989), and Sokolova et al. (2000) and Banno et al. (2004) reported structure refinements of sadanagaite in which nearly all <sup>T</sup>A beyond 2.0 apfu is incorporated at the T(2)site. From this work, it became apparent that the order-disorder of Al over T(1) and T(2) is significantly affected by amphibole composition.

Oberti et al. (1995a) reported crystal-structure refinements for a suite of magnesiohornblendes and pargasites from a leucogabbro from Punta Falcone (Sardinia, Italy), in which the <sup>T</sup>Al contents range from 1.0 to 1.7 apfu. They showed that <sup>T</sup>Al is partly disordered over the T(1)and the T(2) sites in the amphiboles from Punta Falcone, and found different degrees of Al disorder in amphiboles equilibrated under different temperatures (Fig. 9), indicating that increasing disorder of <sup>T</sup>Al is related to higher-T (magmatic) equilibration conditions. The maximum degree of disorder observed is 25% in pargasites with 1.60-1.69 <sup>T</sup>Al apfu, for which the estimated crystallization temperature was around 1000 °C. In agreement with these results, Welch and Knight (1999) reported 15% long-range disorder of <sup>T</sup>Al in a synthetic pargasite crystallized at 932 °C at 1 kbar with 1.71 <sup>T</sup>Al apfu.

Bond-valence calculations show that Al-O(7)-Al linkages between adjacent T(1) sites are unfavorable in amphiboles with vacancy or monovalent cations at the *A* site (Hawthorne 1978b, 1997), whereas they can occur where divalent cations are (locally) present at the *A* site. Thus a general scheme of ordering for <sup>T</sup>Al implies incorporation of Al at the T(1) site up to 2.0 apfu, followed by incorporation of Al at the T(2) site. Aluminum contents at T(1) beyond 2.0 apfu should be allowed solely in the presence of a cannilloite component, whereas <sup>T</sup>Al disorder between the T(1) and T(2) sites below 2.0 apfu is a signal of high-*T* crystallization.



**Figure 9**. The variation of <T(1)-O> is strongly correlated only with the Al content at T(1), whereas <T(2)-O> is sensitive to a number of substitutions at different sites. Deviations above the band limited by the broken lines implies substitution at the T(2) site: Ti (black stars), Ti and Al (stars), Al beyond 2.0 apfu <sup>T</sup>Al (circles), Al below 2.0 apfu <sup>T</sup>Al (triangles, disorder). The half black dots identify sadanagaites (vertical cut) and volcanic amphiboles with high Fe<sup>3+</sup> content (horizontal cut).

Figure 9 shows the relative variation of  $\langle T(1) - O \rangle$  and  $\langle T(2) - O \rangle$  in the CNR-IGG-PV amphibole database. Consideration of their crystal-chemical formulae suggests that nearly all the samples within the broken lines have T(2) occupied only by Si. The data above the upper broken line have Ti and/or Al at the T(2) site; those below the lower broken line have significant amounts of Li at the M(4) site. Figure 10 shows the relation between < T(1)-O> and the <sup>T</sup>Al content; the line represents the (updated) equation relating T(1)Al and T(1)-O> obtained by regression analysis and discussed in a previous section, namely  $T^{(1)}Al$  (apfu) = [< T(1)-O > - $1.6193 \times 34.2199$  (R = 0.997,  $\sigma = 0.048$ ). It is clear that the majority of amphiboles have <sup>T</sup>Al ordered at the T(1) site, and that < T(1)-O> has a limit around 1.680 Å (which should correspond to T(1)Al = 2.08 ± 0.05 apfu). The only amphiboles with  $\langle T(1) - O \rangle$  clearly beyond that limit, besides the ferri-ferrosadanagaite of Hawthorne and Grundy (1977a) with 1.681 Å, are the fluorocannilloites of Hawthorne et al. (1996a), and the synthetic fluoropargasites of Oberti et al. (1995c), for which the bond-valence requirements of the Al-O(7)-Al linkages are fulfilled by the occurrence of Ca at the A(2) site. Notably, the  $\langle T(1) - O \rangle$  value of 1.69(1) Å given by Sokolova et al. (2000) derives from Rietveld refinement, and is most probably overestimated. If we take into account the reported standard deviation, it is compatible with 2.08 Al apfu at T(1)and 0.59 Al apfu at T(2), which would bring this sample closer to the trend in Figure 11.

Figure 11 shows the relation between the refined  $\langle T(2)-O \rangle$  distance and  $T^{(2)}Al$  obtained by subtracting  $T^{(1)}Al$  from <sup>T</sup>Al (estimated by COMAMPH). Negative  $T^{(2)}Al$  values are an artifact due to the esd of the method, and are limited to 0.10 Al apfu (i.e., 0.025 Al per site). There is a clear positive trend, which is compared to that modeled for the T(1) site (broken line). However, the variance is large, and no simple linear equation can be used to evaluate  $T^{(2)}Al$  from the refined  $\langle T(2)-O \rangle$  value.

A stepwise multiple regression analysis was done on the 413 samples with no <sup>T</sup>Ti to relate the  $\langle T(2)-O \rangle$  distance with the chemical composition of the groups of sites. The resulting



**Figure 10.** Total <sup>T</sup>Al as a function of <T(1)-O>. The solid line represents the regression equation <sup>T(1)</sup>Al (apfu) = [<T(1)-O> – 1.6193] × 34.2199, which was calculated for amphiboles with no Al at the *T*(2) site in the CNR-IGG-PV database. <T(1)-O> values longer than 1.678 Å correspond to Al at the *T*(1) site beyond 2.0 apfu.



**Figure 11.** Relation between the Al content at T(2) (expressed as the difference between <sup>T</sup>Al calculated by COMAMPH and <sup>T(1)</sup>Al calculated by the regression equation of Fig. 10) and the refined < T(2)-O> bond length. For the potassic-ferrisadanagaite reported by Sokolova et al. (2000), <sup>T(1)</sup>Al is calculated based on < T(1)-O> = 1.680 Å (see text for discussion).

polynomial equation has 14 terms, the most critical of which is  $^{T(2)}Al$  (calculated as  $^{T}Al - ^{T(1)}Al$ ); *R* is 0.956 and the standard error of the estimate (see) is 0.001. Similar results were obtained using the compositions obtained by COMAMPH for all the database (1092 samples; R = 0.927 and see = 0.002). Hence, the < T(2)-O> distance is strongly dependent on all the compositional changes in the various sites, the least important being those of the A cations. The same approach was used for the 316 samples with complete Si occupancy at the T(2) site (those falling below the upper broken line in Fig. 9); the resulting polynomial equation has 13 terms, R = 0.899 and see = 0.001.

Oberti et al. (1995a) provided an equation which relates the  $^{T(2)}$ Al content with the difference between the refined < T(2)-O> value and that calculated based on the composition of the *A*, *M*(4), *M*(1,2,3) and *T*(1) sites by means of an equation similar to that described in the previous paragraph. The proposed equation [ $^{T(2)}$ Al =  $\Delta < T(2)$ -O> × 35.2592, *R* = 0.985] worked well for magnesiohornblendes and pargasites crystallized under high-*T* conditions at Punta Falcone, Sardinia. Since then, the equation gave reasonable results for pargasites, but failed for Mg-rich pargasites and sadanagaites (Sokolova et al. 2000). We have seen above that the calculated value of the < T(2)-O> distance in the absence of  $^{T(2)}$ Al is not well constrained. This is probably the reason why a further attempt to relate  $\Delta < T(2)$ -O> with  $^{T(2)}$ Al within the database could not provide a relation of general use. Therefore, we cannot presently provide a simple procedure to evaluate  $^{T(2)}$ Al based on structure refinement.

# Beryllium

The only occurrence of Be in amphiboles is in the P2/a amphibole joesmithite, <sup>A</sup>Pb <sup>B</sup>Ca<sub>2</sub> <sup>C</sup>(Mg<sub>3</sub>Fe<sup>3+</sup><sub>2</sub>) <sup>T</sup>(Si<sub>6</sub>Be<sub>2</sub>) O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub>, where Be orders at the *T*(1)B site, and both electroneutrality and local bond-valence requirements are satisfied by the occurrence of Pb<sup>2+</sup> at the *A* site in a strongly asymmetric coordination (Moore 1969; Moore et al. 1993).

#### Boron

Boron has been reported so far only as a very minor constituent in amphiboles (maximum value = 0.06 apfu in the IGG-CNR-PV database). However, synthesis of a B-rich fluoroedenite (Kohn and Comeforo 1955) with 0.92 B apfu, shows that B can be a major element in amphiboles. No information is available on the site preference, but analogy with Al and Be suggests that it should order at the T(1) site.

# Calcium

Calcium is generally a B cation in amphiboles. However, Ca is the dominant A cation in fluorocannilloite (Hawthorne et al. 1996a), and is significant in natural and synthetic fluoropargasites (Oberti et al. 1995c), where it orders at the A(2) site. In all these samples, <sup>A</sup>Ca is presumed to locally couple with Al at the two adjacent T(1) sites.

#### Cobalt and nickel

Della Ventura et al. (1993a, 1996, 1997) showed that both Ni and Co preferentially enter the M(1,3) sites in synthetic richterite and potassic-richterite, with a slight preference for the M(3) site. The partition coefficients calculated on the basis of the Rietveld-derived sitepopulations [defined as  $K_d^{M2+} = (M^{2+})$  $Mg)_{M(1,3)}/(M^{2+}/Mg)_{M(2)}$ , with  $M^{2+} = Ni^{2+}$  or  $Co^{2+}$ ] are  $K_d^{Ni} = 2.98 \pm 0.37$  and  $K_d^{Co} =$  $1.34 \pm 0.31$ , and  $K_d^{\text{Ni}} = 4.26 \pm 0.56$  and  $K_d^{Co} = 1.92 \pm 0.29$  for the K and Na series, respectively (Fig. 12). This evidence confirms that electronic structure has a significant effect on long-range ordering of cations in the amphibole structure. Ni<sup>2+</sup> is smaller than Mg, whereas Co<sup>2+</sup> is larger than Mg; if long-range ordering of cations were controlled solely by their size, then the  $K_d$  value for Ni<sup>2+</sup>-Mg ordering should be > 1.0, whereas that for  $Co^{2+}$ -Mg



**Figure 12.** Relation between the refined Ni-Mg and Co-Mg occupancies at the M(1,3) and M(2) sites. Circles: the Ni,Mg series; squares; the Co-Mg series (from Della Ventura et al. 1993a).

ordering should be < 1.0, which is not the case for these amphiboles (Fig. 12). Both Rietveld site-occupancy refinement and FTIR spectroscopy shows that Co and Ni are not incorporated at the M(4) site in these synthetic amphiboles (Della Ventura et al. 1993b, 1996, 1997). Stoichiometric Co-pargasite was synthesized by Della Ventura et al. (1998), who showed that Co is ordered at the M(1) and M(3) sites (see Oberti et al. 2007 and Hawthorne and Della Ventura 2007 for more details).

# Chromium, vanadium, scandium and indium

All these lithophile transition-elements are known to occur in limited amounts in monoclinic amphiboles. Chromium rarely exceeds 0.15 apfu; 0.38 Cr apfu was reported for glaucophane in jadeitite from Burma (Mével and Kienast 1986), and 0.35 Cr apfu for pargasite in a lherzolite xenolith from Nunivak, Alaska (Francis 1976). The highest reported V content in amphibole is 0.64 apfu in potassic-leakeite from pegmatite-like veinlets that cut a Mn orebody in the Tanohata mine, Iwate Prefecture, Japan (Matsubara et al. 2002).

Systematic work on synthetic analogues has shown that Sc, In and  $Cr^{3+}$  can be major components in calcic (pargasite: Raudsepp et al. 1987a, 1991; Oberti et al. 1998), sodic-calcic (katophorite: Oberti et al. 1998) and sodic amphiboles (eckermannite, nyböite: Raudsepp et al.

1987b, 1991; Oberti et al. 1999). Therefore,  $Cr^{3+}$  incorporation is probably controlled solely by its geochemical availability. Structure refinement shows that in OH-amphiboles, these elements are disordered between the M(2) and M(3) sites; accordingly, OH-stretching FTIR spectroscopy shows absorption bands which can be ascribed to transition elements at the M(1)and M(3) sites (Raudsepp et al. 1987a; Fialips-Guédon et al. 2000) (Fig. 5; see Hawthorne and Della Ventura 2007 for more details). In the F analogues, the transition metals are ordered at the M(2) site (Raudsepp et al. 1987a,b; Oberti et al. 1998, 1999). Oberti et al. (1999) first noted that the electronic properties of the transition element have a major control on their incorporation into the amphibole structure, and that the nature of the O(3) anion (OH<sup>-</sup>, F<sup>-</sup>) has a strong control on cation ordering within the M(1,2,3) sites.

## Gallium

The behavior of Ga is analogous to that of Al. Gallium is both a C and a T cation in synthetic pargasites and magnesiokatophorites, with a significant preference for [4]-coordination. <sup>C</sup>Ga can partition between M(2) and M(3) in pargasite (e.g., Raudsepp et al. 1987a), but is ordered at the M(2) site in fluoropargasite (Oberti et al. 1998; Jenkins and Hawthorne 1995). <sup>T</sup>Ga generally orders at the T(1) sites, but incorporation at the T(2) site has been detected in Gabearing fluoropargasite (Jenkins and Hawthorne 1995; Oberti et al. 1998). Similar to Al, Ga partitioning between the M(2,3) and T(1,2) sites depends on the conditions of crystallization; however, Pavlovich and Jenkins (2003) reported a correlation between Ga at the M(2) site and Na at the M(4) site in synthetic magnesiokatophorites crystallized at fixed T and P conditions of 900 °C and 1.5 GPa. Incorporation of <sup>T</sup>Ga can be easily detected by a strong progressive increase in the refined site-scattering values coupled with a decrease in the O(5)-O(6)-O(5) angle, a measure of the kinking of the double-chain of tetrahedra. Figure 13 shows the effects of incorporating larger trivalent (Al and Ga, with ionic radii 0.39 and 0.47 Å, respectively) and tetravalent cations (Ti and Ge, with ionic radii 0.42 and 0.39 Å, respectively) on the kinking



Figure 13. Variation in the O(5)-O(6)-O(5) angle as a function of the amount of Al (i.r. = 0.39 Å), Ti<sup>4+</sup> (0.42 Å), Ga (0.47 Å) or Ge (0.39 Å) substituting for Si (0.26 Å) at the *T*(1,2) sites.

of the double chain of tetrahedra. Papers relevant to this issue are Raudsepp et al. (1987a,b), Oberti et al. (1998), Jenkins and Hawthorne (1995), Jenkins et al. (2002), Pavlovich and Jenkins (2003), Hawthorne and Della Ventura (2007).

In geochemical modeling of the partition coefficients for transition elements, only the fraction of Ga occurring at the M(2,3) sites should be compared with amounts of the other trivalent C cations.

# Germanium

Synthesis of Ge-bearing amphiboles was reported by Wiecek et al. (1992), but no information on site occupancy is provided. Senda et al. (2005) showed that Ge can substitute completely for Si in synthetic richterite. Rietveld refinement of X-ray powder data shows that along the <sup>A</sup>Na <sup>B</sup>(NaCa) <sup>C</sup>Mg<sub>5</sub> <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> – <sup>A</sup>Na <sup>B</sup>(NaCa) <sup>C</sup>Mg<sub>5</sub> <sup>T</sup>Ge<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> join, Ge has a marked preference for *T*(2) over *T*(1). Increasing Ge correlates linearly with an increase in both <T(1)-O> and <T(2)-O>, and in the kinking of the double chain of tetrahedra (measured by the O(5)-O(6)-O(5) angle, Fig. 13).

# **Ferrous iron**

Similar to Mg and Mn<sup>2+</sup>, Fe<sup>2+</sup> can be both a B and a C cation. The C site-preference is usually M(3) > M(1) >> M(2); random partitioning between the M(1) and M(3) sites is however observed at high-*T* conditions of crystallization or during annealing. In cummingtonites, the presence of Fe<sup>2+</sup> at the M(4) site lowers the transition temperature to the *C*2/*m* structure (see Welch et al. 2007).

There have been numerous measurements of site populations of  $Fe^{2+}$  in amphiboles by SREF, Mössbauer and infrared spectroscopies. SREF can have problems with amphiboles of particularly complicated compositions due to the large number of scattering species and possible variations in valence state of Fe. Mössbauer spectroscopy has the advantage of "see-

ing" only Fe (in amphiboles), but spectra are often poorly resolved (allowing only partial interpretation, as in the spectra of the Mg-Fe-Mn-Li amphiboles), and do not address the other components of the structure. The same issues affect infrared spectroscopy, with the added complication that it "sees" all components of the structure and can have such poor resolution that spectra cannot be interpreted at all. This being said, all methods have produced useful information on ordering of Fe<sup>2+</sup>.

Figure 14 shows the distribution of Fe<sup>2+</sup> over the M(1) and M(3)sites in amphiboles of the glaucophane–ferroglaucophane–magnesioriebeckite–riebeckite series (•) and nyboite (•) (data from Ungaretti et al. 1978). There is strong site-preference for M(3) and very regular behavior as a function of bulk composition. Note the posi-



**Figure 14.** The distribution of Fe<sup>2+</sup> over the M(1) and M(3) sites in amphiboles of the glaucophane–ferroglaucophane–magnesioriebeckite–riebeckite series ( $\bullet$ ) and nyboite ( $\blacksquare$ ), data from Ungaretti et al. (1978). The star indicates riebeckite containing <sup>C</sup>Li (from Hawthorne 1983a).

tion of the Li-bearing riebeckites indicated by the stars in Figure 14; the deviation from the general trend for these amphiboles is caused by the presence of Li at the M(3) site. Figure 15 shows the distribution of  $Fe^{2+}$  over the M(1), M(2) and M(3) sites in amphiboles of the tremolite-ferro-actinolite series (Yang and Evans 1996; Evans and Yang 1998). Here we see very different behavior: the distribution of  $Fe^{2+}$  over the M(1) and M(3) sites is now very similar (Fig. 15b); there is no longer any strong site-preference of  $Fe^{2+}$  for the M(3) site. Almost the same behavior is seen in the amphiboles of the cummingtonite-grunerite series (Fig. 16; Hirschman et al. 1994); Figure 16b shows the slightest suggestion of a preference of Fe<sup>2+</sup> for the M(1) site. Amphiboles of the tremolite-ferro-actinolite and cummingtonite-grunerite series are significantly different from the amphiboles of the glaucophane-ferroglaucophane-magnesioriebeckite-riebeckite series in that they have divalent cations (primarily Mg and  $Fe^{2+}$ ) dominant at the M(2) site. In tremolite-ferro-actinolite, Fe<sup>2+</sup> is equally distributed over M(1) and M(2) (Fig. 15a) and M(2) and M(3) (Fig. 15c), whereas in cummingtonite-grunerite, Fe<sup>2+</sup> shows a distinct preference for M(1) relative to M(2) (Fig. 16c). The strong preference of Fe<sup>2+</sup> for M(3) relative to M(1) in glaucophane–ferroglaucophane–magnesioriebeckite–riebeckite amphiboles and the lack of such preference in tremolite-ferro-actinolite and cummingtonite-grunerite amphiboles is in accord with the observation of Hawthorne (1983a) that the degree of ordering of  $Fe^{2+}$  at M(3) relative to M(1) is strongly an inverse function of the aggregate size of the M(2) cations.

In Mg-Fe-Mn amphiboles, the M(4) site is occupied by Mg, Fe<sup>2+</sup> and Mn<sup>2+</sup>. Extensive Mössbauer spectroscopy showed that  $Fe^{2+}$  is strongly ordered at M(4) relative to M(1), M(2)and M(3) (e.g., Bancroft 1967; Hafner and Ghose 1971; Ghose and Weidner 1972). Figure 17 shows the spectra of cummingtonite and grunerite; the inner doublet is due to Fe<sup>2+</sup> at M(4)and the outer doublet is due to  $Fe^{2+}$  at M(1,2,3) combined. In cummingtonite close to nominal composition (Fig. 17a), the amount of  $Fe^{2+}$  is very small and most of it occurs at the M(4) site; in grunerite (Fig. 17b), the amount of  $Fe^{2+}$  is large, and although the site occupancy is higher at M(4) and lower at M(1,2,3), the fact that there are two M(4) sites and five M(1,2,3) sites in the structural formula means that the total amount of Fe<sup>2+</sup> is higher at M(1,2,3) than at M(4), and hence the outer doublet is more intense than the inner doublet (compare Figs. 17b and 17a). Hirschmann et al. (1994) showed that (1) this site-preference of Fe<sup>2+</sup> for M(4) extends across the complete cummingtonite-grunerite series, and (2) it is much stronger than any other site preference of  $Fe^{2+}$  in this series (Fig. 16). Also apparent from Figure 16a is the fact that the degree of order of Fe<sup>2+</sup> at M(4) relative to M(1) [or M(2) or M(3)] is strongly sensitive to the temperature of equilibration. Similar results have been obtained for the orthorhombic Mg-Fe-Mn amphiboles (e.g., Bancroft et al. 1966; Law 1981; Seifert 1977, 1978).

In calcic amphiboles, it is common to have C cations in excess of 5.0 apfu, implying that some of the C cations occur at the M(4) site. The first direct evidence of this is shown in Figure 18 (Goldman and Rossman 1977; Goldman 1979). The Mössbauer spectrum of tremolite containing 1.9 wt% FeO (Fig. 18a) is very similar to the Mössbauer spectrum of grunerite containing 37.0 wt% FeO (Fig. 18b); in both cases, the inner doublet was assigned to Fe<sup>2+</sup> at the M(4) site and the outer doublet was assigned to Fe<sup>2+</sup> at the (overlapped) M(1,2,3) sites. Can we be sure of this assignment? Figures 18c and 18d show the electronic absorption spectra of the same two amphiboles. Both spectra show an intense band at 1030 nm in the  $\beta$  polarization, a band that is absent in the spectrum of a pargasite (Goldman and Rossman 1977) that contains no "excess" (Mg, Fe<sup>2+</sup>, Mn<sup>2+</sup>) to assign to M(4). The intensity of an absorption is a function of the probability of that transition. The transition probability is governed by the Laporte selection rule (King 1964) which forbids transitions between 3d orbitals. When a transition metal occupies a site without a center of symmetry, mixing between the 3d and 4p orbitals allows a transition, the intensity of which is a function of the degree of mixing which, in turn, is related to the deviation of the cation environment from centrosymmetry. Thus when a transition-metal cation occurs at more than one site in a crystal, the intensities of the *d*-*d* bands are a function of both the cation site-populations and the deviation of the cation environment from centrosymmetry. For Fe<sup>2+</sup> in the amphibole structure, the M(4) site occupies a far less centrosymmetric environment than the



**Figure 15.** The distribution of  $Fe^{2+}$  over the M(1), M(2) and M(3) sites in amphiboles of the tremolite–ferro-actinolite series; (a) M(2) vs. M(1); (b) M(3) vs. M(1); (c) M(2) vs. M(3) (from Evans and Yang 1998).

**Figure 16.** The distribution of Fe<sup>2+</sup> over the M(1), M(2), M(3) and M(4) sites in amphiboles of the cummingtonite–grunerite series; (a) M(4) vs. M(1); (b) M(3) vs. M(1); (c) M(2) vs. M(1) (from Hirschmann et al. 1994).



Figure 17. Mössbauer spectra of (a) magnesiocummingtonite, and (b) grunerite (modified from Hafner and Ghose 1971).

M(1,2,3) sites, and hence any Fe<sup>2+</sup> at M(4) will absorb far more strongly than Fe<sup>2+</sup> at M(1,2,3), accounting for the relative intensity of the 1030 nm band in the spectrum of grunerite (Fig. 18d). However, this band is also observed in the spectrum of tremolite containing 1.9 wt% FeO (Fig. 18c), indicating that this band may be assigned to Fe<sup>2+</sup> at the M(4) site.

As with the amphiboles of the cummingtonite–grunerite series, the distribution of Fe<sup>2+</sup> between *M*(4) and *M*(1,2,3) shows a strong temperature dependence in amphiboles of the tremolite–actinolite series (Skogby and Annersten 1985; Skogby 1987; Evans and Yang 1998; Skogby and Ferrow 1989; Driscall et al. 2005). Figure 19 (from Driscall et al. 2005) is a composite plot of data from several sources showing the distribution of Fe<sup>2+</sup> over *M*(4) and *M*(1,2,3) together with the temperatures of equilibration and the isotherms calculated for  $\Delta G^{\circ}$  (1073 K) = 20 kJ (broken lines), and  $\Delta G^{\circ}$  (298 K) = 62 kJ and  $\Delta S^{\circ}$  (298 K) = 54 kJ/K (broken lines).

Where considering equilibration of cations over different sites in a structure, it is important to know the kinetics of the process such that one can estimate (1) whether equilibrium has been achieved in laboratory experiments, and (2) whether it is possible to quench cation distributions in natural processes. Skogby and Annersten (1985) and Skogby (1987) examined this issue in Fe-bearing tremolite; Figure 20 shows that equilibrium is achieved after about 5 hours at 650 and 750 °C.

An important factor in the occurrence of  $(Mg,Fe^{2+},Mn^{2+})$  at the M(4) site is whether the  $(Mg,Fe^{2+},Mn^{2+})$  at M(4) resides in exsolved Mg-Fe-Mn amphibole in a calcic host (i.e., shows extreme short-range order) or is truly a component of the calcic amphibole. Skogby and Ferrow (1989) and Driscall et al. (2005) examined their samples in the tremolite–actinolite join [in which they characterized Fe<sup>2+</sup> at M(4)] and did not report any exsolution structures (just a small % of chain-multiplicity faults), indicating that  ${}^{B}(Mg,Fe^{2+},Mn^{2+})$  is a true component of the calcic amphibole, at least at concentrations significant but usually < 0.50 apfu. However, these cations order at a position [namely, M(4')] closer to the strip of octahedra, and assume a coordination more similar to [6]-fold.

## Ferric iron

Trivalent iron is always ordered at the M(2) site in amphiboles with W = (OH,F,Cl)<sub>2</sub>, but can occur at all the M(1,2,3) sites in the presence of the oxo component. The oxidation of iron at the M(1) and M(3) sites is the principal mechanism to achieve local bond-valence satisfaction during post-crystallization dehydrogenation processes (and experimental annealing). More details on the dehydrogenation process are given in a following section of this chapter.



**Figure 18.** Mössbauer spectra of (a) low-Fe tremolite, and (b) Fe-rich grunerite; electronic absorption spectra of (c) low-Fe tremolite, and (d) Fe-rich grunerite [modified from Goldman and Rossman (1978) and Goldman (1979)].

One significant issue is the lack of  $Fe^{3+}$  as a T cation. There are chemical analyses in the literature in which Si + Al + Ti < 8.0 apfu. However, we have investigated several of these amphiboles over the past 30 years, and all showed the same result: either Mössbauer spectroscopy or SREF showed no evidence of <sup>[4]</sup>Fe<sup>3+</sup>, and re-analysis of the amphibole resulted in formulae with Si + Al + Ti > 8.0 apfu. Hawthorne and Grundy (1977b) reported 0.04 <sup>[4]</sup>Fe<sup>3+</sup> apfu based on Mössbauer spectroscopy, but inspection of the spectrum shows that the relevant doublet is a result of overfitting the spectrum (i.e., fitting an additional doublet



**Figure 19.** The distribution of Fe<sup>2+</sup> over M(4) and M(1,2,3), together with the temperatures of equilibration and the isotherms calculated for  $\Delta G^{\circ}$  (1073 K) = 20 kJ (broken lines), and  $\Delta G^{\circ}$  (298 K) = 62 kJ and  $\Delta S^{\circ}$ (298 K) = 54 kJ/K (broken lines) (from Driscall et al. 2005).

to compensate for orientational asymmetry in the spectrum). The reason why <sup>[4]</sup>Fe<sup>3+</sup> is not present in amphiboles is not clear. <sup>[4]</sup>Fe<sup>3+</sup> is present in pyroxene (e.g., Mössbauer: Huckenholz et al. 1969; Hafner and Huckenholz 1971; Virgo 1972; SREF: Cellai et al. 1994) and in mica (e.g., Mössbauer: Rancourt et al. 1992; SREF: Brigatti et al. 1996), and the similarity between these structures would seem to suggest that <sup>[4]</sup>Fe<sup>3+</sup> should occur in amphiboles. However, (1) this does not seem to be the case, and (2) the reason why <sup>[4]</sup>Fe<sup>3+</sup> does not occur in amphiboles is not understood. The behavior of Fe<sup>3+</sup> in amphibole will be described more extensively in the section on the oxo component below.

# Lithium

Until 1992, Li was considered exclusively a B cation in amphiboles, and thus confined to Mg-Fe-Mn-Li amphiboles (e.g., Ginzburg 1965; Litvin et al. 1975). The occurrence of <sup>C</sup>Li in minor amounts in sodic amphiboles was indicated by chemical analyses (e.g., Borley 1963; Hawthorne 1978a) and by anomalously low scattering at the *M*(3) site (Hawthorne 1978a; Ungaretti et al. 1978). However, the discovery of leakeite, <sup>A</sup>Na <sup>B</sup>Na<sub>2</sub> <sup>C</sup>(Mg<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Hawthorne et al. 1992), kornite, <sup>A</sup>K <sup>B</sup>Na<sub>2</sub> <sup>C</sup>(Mg<sub>2</sub>Mn<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Hawthorne et al. 1992), kornite, <sup>A</sup>K <sup>B</sup>Na<sub>2</sub> <sup>C</sup>(Mg<sub>2</sub>Mn<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Hawthorne et al. 1996c), potassic-leakeite, <sup>A</sup>Na <sup>B</sup>Na<sub>2</sub> <sup>C</sup>(Hg<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Matsubara et al. 2002), and dellaventuraite, <sup>A</sup>Na <sup>B</sup>Na<sub>2</sub> <sup>C</sup>(MgMn<sup>3+</sup><sub>2</sub>Ti<sup>4+</sup>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>O<sub>2</sub> (Tait et al. 2005), showed that <sup>C</sup>Li can be a major constituent in amphiboles in manganiferous metasediments, and Hawthorne et al. (1993, 1994, 1996c, 2001) went on to show that <sup>C</sup>Li is a not-uncommon major constituent in sodic amphiboles from Si-saturated peralkaline granites.



**Figure 20.** Kinetic experiments on Fe-bearing tremolite in the presence of  $H_2O$ : (a) disordering at 650 °C; (b) ordering at 650 °C; (c) disordering at 750 °C (modified from Skogby 1987).

Crystal-structure refinement has shown that <sup>C</sup>Li is restricted to the M(3) site (Hawthorne et al. 1993, 1994), and is easily apparent from the anomalously low site-scattering observed at the M(3) site (Hawthorne and Oberti 2007, Fig. 1). The introduction of Li at the M(3) site must be accompanied by additional substitutions at adjacent sites to satisfy the bond-valence requirements at the anions bonded to  $^{M(3)}$ Li. Hawthorne et al. (1994) showed that this involves incorporation of trivalent cations (usually Fe<sup>3+</sup>) at the M(2) site. In all the <sup>C</sup>Li amphiboles studied, <sup>A</sup>Na  $\geq$  <sup>C</sup>Li and is usually ordered at a particularly off-centred A(m) site, showing that <sup>A</sup>Na helps to satisfy bond-strength requirements; the proposed mechanism involves changes in individual T(1)-O distances, T(1)-O(1) being always very short in <sup>C</sup>Li-bearing amphiboles (Oberti et al. 2003a). This conceptual mechanism may be written as

$${}^{M(3)}\text{Li} + {}^{M(2)}\text{Fe}^{3+} \leftrightarrow {}^{M(3)}\text{Fe}^{2+} + {}^{M(3)}\text{Fe}^{2+}$$
 (1)

$${}^{M(3)}\text{Li} + {}^{A}\text{Na} \leftrightarrow {}^{M(3)}\text{Fe}^{2+} + {}^{A}\square$$
(2)

where (2) might occur in amphiboles with vacant A sites (e.g., riebeckite).

Li has long been known as a B cation in amphiboles, specifically in the *Pnma* amphibole holmquistite, ideally  $^{A}\square ^{B}Li_{2} ^{C}(Mg_{3}Al_{2}) ^{T}Si_{8} O_{22} ^{W}(OH)_{2}$ . However, the discovery of several monoclinic amphiboles with essential <sup>B</sup>Li has greatly expanded the compositional and structural range of <sup>B</sup>Li-bearing amphiboles: clino-ferriholmquistite, <sup>A</sup> <sup>B</sup>Li<sub>2</sub> <sup>C</sup>(Fe<sup>2+</sup><sub>3</sub>Fe<sup>3+</sup><sub>2</sub>) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Caballero et al. 1998), sodic-ferripedrizite, <sup>A</sup>Na <sup>B</sup>Li<sub>2</sub> <sup>C</sup>(Mg<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Oberti et al. 2000a; note that sodic-ferripedrizite was originally defined by Oberti et al. 2000a with B = (NaLi), but was redefined by Leake et al. 2003 with B = Li<sub>2</sub>), ferripedrizite, <sup>A</sup>Na <sup>B</sup>Li<sub>2</sub> <sup>C</sup>(Mg<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Caballero et al. 2002), sodic-ferri-ferropedrizite, <sup>A</sup>Na <sup>B</sup>Li<sub>2</sub> <sup>C</sup>(Fe<sup>2+</sup><sub>2</sub>Fe<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Oberti et al. 2003b), clino-ferri-ferroholmquistite, <sup>A</sup> <sup>B</sup>Li<sub>2</sub>  $^{C}(Fe^{2+}_{3}Fe^{3+}_{2})$   $^{T}Si_{8}$  O<sub>22</sub>  $^{W}(OH)_{2}$  (Oberti et al. 2003b), ferri-ottoliniite,  $^{A}\square$   $^{B}(LiNa)$   $^{C}(Mg_{3}Fe^{3+}_{2})$ <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>(OH)<sub>2</sub> (Oberti et al. 2004), and ferriwhittakerite, <sup>A</sup>Na <sup>B</sup>(LiNa) <sup>C</sup>(Mg<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>Li) <sup>T</sup>Si<sub>8</sub>  $O_{22}$  <sup>W</sup>(OH)<sub>2</sub> (Oberti et al. 2004). Of great importance was the observation that there is Li  $\leftrightarrow$ Na solid-solution at the M(4) site, and Oberti et al. (2004) showed that this solid solution is complete (Fig. 21) (more details are given in Oberti et al. 2007). Full occupancy of Li at the M(4) site in naturally occurring amphiboles has been reported only in *Pnma* holmquistite (with no Li at M(3), see Cámara and Oberti 2005), in clino-ferri-ferroholmquistite, and in C2/m sodic-pedrizite with up to 0.90 Li apfu at the M(3) site. In the compositional space of clinoholmquistite, only Fe-rich varieties have been characterized so far (Oberti et al. 2005). Note that amphiboles with mixed  $^{B}(Na,Li)$  occupancy always have significant Li at M(3).

The parageneses of relevance are metamorphosed episyenites and alkali ultramafic diatremes (cf. Oberti et al. 2003a and Cámara and Oberti 2005 for comprehensive reviews). The incorporation of Li into the amphibole structure is strongly related to the geochemistry of the coexisting fluid. In addition, analysis of Mg-Fe-Mn-Li and Na-Ca-Mg-Fe-Mn-Li amphiboles in episyenites from the Pedriza Massif, Sierra de Guadarrama, Spain (Oberti et al. 2003a) shows that high-*T* of crystallization favors incorporation of Li at the M(3) site, which is consistent with the occurrence of only <sup>C</sup>Li in peralkaline granites and the absence of <sup>B</sup>Li in amphiboles from low-*T* Mn-rich metasediments.



**Figure 21.** Li partitioning between the M(3) and M(4) sites in amphiboles from various geochemical and petrogenic environments. The data available in the literature have been combined with the CNR-IGG-PV database. This plot does not show homovalent substitutions such as  $Mg_{-1} Fe^{2+}_{1}$  or  $Al_{-1} (Fe^{3+}, Mn^{3+})_{1}$ .

There is spectroscopic evidence of  $\sim 0.20$  Li apfu at the *A* site in a synthetic clinoferriholmquistite (Iezzi et al. 2004). Therefore, Li must be considered a frequent and important element in amphibole crystal-chemistry, as is apparent by the rapid evolution of amphibole classification at this time (Leake et al. 1997, 2003).

#### Magnesium

Magnesium is one of the major constituents of amphiboles. The composition  $^{A}\square {}^{B}Mg_{2} {}^{C}Mg_{5} {}^{T}Si_{8} O_{22} {}^{W}(OH)_{2}$  (cummingtonite) is used as the starting point for classification of Mg-Fe-Mn-Li amphiboles, and  $^{A}\square {}^{B}Ca_{2} {}^{C}Mg_{5} {}^{T}Si_{8} O_{22} {}^{W}(OH)_{2}$  (tremolite) as the starting point for the classification of calcic, sodic-calcic and sodic amphiboles.

The only significant recent improvement in our understanding of Mg crystal-chemistry in amphiboles concerns the detection and characterization of mixed Na, Ca and Mg occupancy at the M(4) site. Due to their different ionic radii and preferred coordination, the occurrence of large and small cations at the M(4) site is represented in the long-range perspective by a non-spherical distribution of electron density, indicative of two distinct sub-sites [M(4) and M(4')] in the structure (Fig. 22). Smaller cations order closer to the wall of octahedra [at the M(4') site], and tend to assume [6]-coordination.

The presence of a significant  ${}^{B}(Mg,Fe)^{2+}$  component (up to 0.35 apfu) is common in amphiboles crystallized under high-*T*, *P* conditions, such as mantle environments. It is also common in synthetic amphiboles (Oberti et al. 1999). Amphiboles with high  ${}^{B}(Mg,Fe)^{2+}$  components have anomalously low values of the  $\beta$  angle, smaller unit-cell volumes, and slightly more kinked chains of tetrahedra [as measured by the O(5)-O(6)-O(5) angle]. A peculiar series of synthetic amphiboles with B = (NaMg) (i.e., with the charge arrangement of richterite) was studied in detail because of its relevance to phase-transitions in amphiboles. In fact, this particular composition at the *M*(4) site implies crystallization in the space group *P*2<sub>1</sub>/*m* (Oberti et al. 2007; Welch et al. 2007).

#### Manganese

Similar to Mg,  $Mn^{2+}$  can be incorporated at the M(4') and at the M(1,2,3) sites.  $Mn^{2+}$  is preferentially ordered at the M(4') site (e.g., Oberti et al. 1993b, 2006), suggesting that its site preference is controlled by ionic radius, and at the M(1) or M(3) site, depending on the overall amphibole composition. In synthetic manganoan fluoro-edenite and fluoropargasite, where the presence of F strongly decreases the size of the M(1) and M(3) sites (cf. the paragraph on fluorine) and the M(3) is particularly small (cf. the paragraph on Al), the site preference is M(4) >> M(2) >> M(3) (Oberti et al. 1997). Mn disorder during annealing has been studied



**Figure 22.** The electron density at the M(4) site in parvowinchite with  $M(4) = Na_{0.87}Ca_{0.39}Mn_{0.57}Mg_{0.17}$  (Oberti and Ghose 1993); the black square marks the M(4') site. Contours show steps of 5  $e^{-1}$ Å from 0.0.

in detail with reference to the phase-transition behavior (Reece et al. 2000, 2002; as reported in Welch et al. 2007).

 $Mn^{3+}$  is normally ordered at the M(2) site (Ghose et al. 1986; Oberti et al. 1993b). However, in ungarettiite, <sup>A</sup>Na <sup>B</sup>Na<sub>2</sub> <sup>C</sup>(Mn<sup>2+</sup><sub>2</sub> Mn<sup>3+</sup><sub>3</sub>) <sup>T</sup>Si<sub>8</sub> O<sub>22</sub> <sup>W</sup>O (Hawthorne et al. 1995b; Kawachi et al. 2002), Mn<sup>3+</sup> orders at M(1) and M(3) and Mn<sup>2+</sup> orders at M(2), i.e., inverse to that expected in the amphibole structure. This unusual order results from cooperative interaction of three factors: (1) the typical Jahn-Teller distortion of (Mn<sup>3+</sup>O<sub>6</sub>) octahedra, (2) the occurrence of O<sup>2-</sup> at the O(3) site, and (3) the bond-valence requirements of O<sup>2-</sup> at O(3). The result is extremely short Mn<sup>3+</sup>-O(3) distances, very strong Mn<sup>3+</sup>-O(3) bonds, and satisfaction of bond-valence requirements at O(3) (Hawthorne et al. 1995b).

# Potassium

Potassium can be a major A cation in calcic, sodic-calcic and sodic amphiboles, and is generally ordered at the A(m) site. In contrast, K is generally very low (< 0.05 apfu) in Mg-Fe-Mn-Li amphiboles. Coupling of K and Fe is expected for both geochemical and structural reasons. However, K can be dominant at the *A* site also in Mg-rich compositions, and even in F-rich Mg-rich compositions (e.g., potassic-fluororichterite), showing that there is no structural constraint to complete solid-solution with Na. For a recent review on the occurrence and paragenesis of K-dominant amphiboles, see Mazdab (2003).

A series of high-*P* experiments produced richterites with K up to 1.95 apfu, and showed a correlation between excess K and pressure (Sudo and Tatsumi 1990; Luth 1997; Inoue et al. 1998; Konzett et al. 1997). Yang et al. (1999) provided a single-crystal structure refinement of a sample with B = (KCa). The main structural variations due to the incorporation of K at *M*(4) are discussed by Oberti et al. (2007). Here we note the high values measured for the *a* and *b* edges and the  $\beta$  angle (10.193 and 18.121 Å and 105.51°, respectively; cf. Hawthorne and Oberti 2007, Fig. 35).

#### Sodium

Sodium can be an A and B cation in amphiboles in all compositional groups. The only significant advance since Hawthorne (1983a) is the understanding of the reasons for Na ordering within the A cavity. Analysis of the experimental Fourier maps (Hawthorne and Oberti 2007, Fig. 30) and bond-strength considerations confirmed that Na orders at the A(m) site in fluoro-amphiboles, and distributes between the A(m) and A(2) sites in OH-dominant amphiboles. The preferred local arrangements are  ${}^{M(4)}Ca-{}^{O(3)}OH-{}^{A(2)}Na$  and  ${}^{M(4)}Na-{}^{O(3)}OH-{}^{A(m)}Na$  (Hawthorne et al. 1996b; Hawthorne and Oberti 2007; Hawthorne and Della Ventura 2007). Other studies showed that the presence of Li at the M(3) site implies a further shift of the A(m) site toward the chain of tetrahedra (Oberti et al. 2003a).

# Strontium

Strontium is incorporated at the M(4) site, replacing Ca in synthetic richterite (Della Ventura and Robert 1990), potassic-richterite (Robert et al. 1993) and tremolite (Gottschalk et al. 1998). In potassic-richterite with increasing Sr content, Rietveld refinement shows a linear increase in  $\langle M(4) - O \rangle$  with increasing aggregate ionic radius at the M(4) site ( ${}^{[8]}Sr^{2+} = 1.26$  Å). Careful analysis of the X-ray diffraction patterns indicated no evidence of violation of C2/m symmetry, excluding the possibility of long-range Na-Sr order at M(4) in these amphiboles (Robert et al. 1993). Analysis of the FTIR Si-O, Si-O-Si and O-Si-O lattice modes (1400-600 cm<sup>-1</sup>) of synthetic tremolites with increasing Sr content shows no evidence of short-range order of Ca-Sr at M(4) (Andrut et al. 2000).

# Titanium

The ordering of Ti over the various sites of the amphibole structure has been the subject of much work in the last twenty years, and is briefly summarized here. There is no evidence of Ti<sup>3+</sup>

in amphiboles, and all Ti is assumed to be tetravalent.  $Ti^{4+}$  is a C cation except in richterite and its homovalent analogues where it can occur both as a C and a T cation.

Partitioning of Ti over the M(1,2,3) and T(1,2) sites in potassic-richterites was originally suggested by numerous chemical analyses of amphiboles from lamproites (e.g., Wagner and Velde 1986) and confirmed structurally by Oberti et al. (1992) for natural amphiboles and by Della Ventura et al. (1991, 1993a, 1994, 1996) and Tiepolo et al. (2003) for synthetic amphiboles. <sup>T</sup>Ti is completely ordered at the T(2) site (Oberti et al. 1992) and is easily detected by the high values of the refined site-scattering at T(2) and the high angular variance of the T(2)tetrahedron. This latter feature suggests a reason for the ordering of  $^{T}Ti^{4+}$  at the T(2) site; in fact, the T(2) tetrahedron is generally more distorted than the T(1) tetrahedron in amphiboles, which fits better with the electronic configuration of Ti<sup>4+</sup>. The occurrence of <sup>T</sup>Ti significantly lengthens both  $\langle T(2) - O \rangle$  and the c unit-cell edge. The occurrence of <sup>T</sup>Ti only in richteritic compositions can be explained by the matching requirements of the various structural units in potassic-richterite, which has only divalent C cations and nearly stoichiometric amounts of the largest A cation. Experimental work shows that the solubility of <sup>T</sup>Ti in richterite increases with T up to ~ 0.7 apfu at T = 800 °C but decreases rapidly from 0.60 to 0.16 apfu with increasing F in the system (Della Ventura et al. 1993a). The inverse correlation between F and <sup>T</sup>Ti confirms the critical role of the relative dimensions of the octahedra. Because it crystallizes in Al-free environments, richterite generally has low amounts of highly charged cations, and M(2) is even the largest of the M octahedra. Ti can be an exception to this rule in ultrapotassic magmatic rocks (silica-rich lamproites) and in rare types of mantle xenoliths [metasomatically altered peridotites, MARID (Mica-Amphibole-Rutile-Ilmenite-Diopside; Dawson and Smith, 1977) and cumulate xenoliths; Tiepolo et al. 2003 and references therein]. Kushiro and Erlank (1970) synthesized potassic-richterites at 3 GPa from a starting material similar in composition to the samples investigated by Oberti et al. (1992), and found very limited TiO<sub>2</sub> contents (~0.5%, to be compared with 3.6-4%), showing that the incorporation of <sup>T</sup>Ti is unfavorable at high *P*. Konzett (1997) characterized the stability and composition of Ti-bearing potassic-richterite in MARIDtype rocks (in the range 0.5 < P < 8 GPa, 900 < T < 1400 °C, and concluded that amphibole is stable up to 1300 °C at 8 GPa, that Ti is almost completely incorporated at the T sites, and that its amount significantly increases with T (e.g., from 0.8 apfu at 900 °C to 0.28 apfu at 1200 °C at 4 GPa) and decreases with P (e.g., from 0.23 apfu at 3 GPa to 0.05 apfu at 8 GPa at 1100 °C).

The distribution of Ti over the M(1,2,3) sites is controlled by two different mechanisms. Titanium at M(1) provides local electroneutrality to the oxo component at the O(3) site *via* local ordering  ${}^{M(1)}\text{Ti}^{4+O(3)}\text{O}^{2-}_2$ . In contrast, Ti at the M(2) and M(3) sites is involved in the exchange  ${}^{M(2),M(3)}\text{Ti}^{4+T(1),T(2)}\text{Al}_2^{3+M(2),M(3)}(\text{Mg},\text{Fe})^{2+}_{-1}$   ${}^{T(1),T(2)}\text{Si}^{4+}_{-2}$  (for a detailed discussion, see Tiepolo et al. 1999). The occurrence of Ti at the M(3) site was first inferred by neutron diffraction by Kitamura et al. (1975). However, analysis of the CNR-IGG-PV database showed that it is rather rare (8 out of the 250 Ti-bearing amphiboles), and is restricted to compositions with low amounts of <sup>C</sup>Al. The most striking case is a sample from a gabbro from the type locality of kaersutite (Kaersut, Greenland). This samples couples one of the highest Ti contents ever reported in nature for amphiboles (0.72 apfu) with a relatively low oxo-component (0.96  ${}^{O(3)}$ O apfu); the residual, 0.24 Ti apfu are nearly equally partitioned between the M(2) and M(3) sites, because SREF provides evidence of  $\approx 0.10$  Ti apfu at the M(3) site. In this sample, <sup>C</sup>Al is 0.17 apfu; therefore, <sup>C</sup>Ti seems to play the same role as  ${}^{M(3)}$ Al whenever the composition of the system is depleted in Al or when the high *T* of crystallization increases Al preference for tetrahedral coordination.

A decrease in the  $^{Amph/L}D_{Ti}$  with increasing *P* was observed in sodic-calcic (richterites) and calcic amphiboles (titanian pargasites) synthesized by Sweeney et al. (1992) and Adam and Green (1994, 2003) in carbonatitic and basaltic systems, respectively. The data by Sweeney et al. (1992) show a clear negative correlation between  $^{Amph/L}D_{Ti}$  and H<sub>2</sub>O content, suggesting that the role of Ti in mantle amphiboles is related mainly to the oxo component.

Titanium at M(1) occupies a position different from that of Mg, Fe<sup>2+</sup> and Fe<sup>3+</sup>. From a long-range perspective, static disorder implies first an increase in the M(1) atom-displacement factor, and (at higher Ti contents) non-spherical electron density within the M(1) octahedron, which must be modeled by two sites [M(1) and M(1')] during structure refinement (Fig. 23a). Shortening of the M(1)-O(3) distance couples with a shortening of the O(3)-O(3) edge, which reaches 2.62 Å (the sum of the ionic radii) in the most dehydrogenated amphiboles. At the M(3) site, where the two O(3) oxygen atoms are in a *trans* configuration, the occurrence of Ti increases the atom-displacement parameter in the O(3)-O(3) direction (Fig. 23b), and shortens all the M(3)-O(1,3) distances. Therefore, SREF allows straightforward detection of the Ti distribution over the M(1,2,3) sites *via* analysis of the atom-displacement parameters and individual M-O distances (Tiepolo et al. 1999). In particular, Ti at M(3) implies shorter M(3)-O(1) and longer M(3)-O(3) distances than expected in the presence of  $^{M(3)}$ Fe<sup>3+</sup> balancing dehydrogenation.



**Figure 23.** Long-range effects of the incorporation of Ti at the M(1) and M(3) sites. Two projections of the local environment of Ti, showing positional disorder (a) along *b* at the M(1) site, and (b) approximately along the line joining the two O(3) sites at the M(3) site. The O(3)-O(3) edge shortens significantly in amphiboles with Ti ordered at the M(1) site. Ellipsoids drawn at 98% probability.

# Zinc

Zinc is a rare constituent in amphiboles. Zinc contents up to 1.22 apfu have been reported in Mg-Fe-Mn-Li amphiboles from Franklin, New Jersey (Klein and Ito 1968), and structure refinement of samples with 0.76 Zn apfu showed the following site preference: M(1) > M(3)>> M(2) (Hawthorne and Grundy 1977b). More recently, low Zn contents (up to 0.10 apfu) in Li-bearing fluoro-arfvedsonites were assigned to the M(2) site based on refined bondlengths and site-scattering values (Hawthorne et al. 1993, 1996c). Higher Zn contents (up to 0.48 apfu) have also been found in amphiboles from episyenites at the Pedriza Massif (Sierra de Guadarrama, Spain). The site-preference proposed for these amphiboles is M(2) >> M(1).

#### Zirconium

Chemical analysis shows that amphiboles from nepheline syenites and peralkaline granites (e.g., Jones and Peckett 1980; Pearce 1989; Preston et al. 2000) can contain up to several wt% ZrO<sub>2</sub>. Hawthorne et al. (2001) assigned Zr to the M(2) site in a series of arfvedsonitic amphiboles from Strange Lake, Quebec, Canada. The absence of Mg from these amphiboles allowed assignment of Zr via the refined site-scattering values, showing that Zr occurs at the M(2) site. On the basis of EXAFS data, Farges et al. (1994) showed that Zr is [6]-coordinated in arfvedsonite from a phonolite from the Rumoi Hill, Cameroon, and further showed that

Zr occurs at the M(2) site. At the trace-element level, Oberti et al. (2000b) compared refined mean bondlengths and lattice-strain models and concluded that Zr is ordered at the M(2) site in synthetic pargasite and kaersuite from alkali basalts and basanites, and at the M(1) site in strongly dehydrogenated synthetic richterite from lamproites. Hence, the behavior of Zr strongly resembles that of Ti, despite the significant different in their size.

#### ANION INCORPORATION IN AMPHIBOLES

O(3) is the only anion site in the amphibole structure where chemical substitution is possible. This site can host either the homovalent constituents OH<sup>-</sup>, F and Cl, or O<sup>2-</sup>. In the latter case, extra positive charge is provided by high-charge C cations, and the occurrence of the oxo component may eventually lead to oxo amphiboles.

# Chlorine

Only two amphibole compositions with Cl dominant at the O(3) site have been formally recognized so far: chloro-potassicpargasite (Chukanov et al. 2002) and chloro-potassichastingsite (formerly "dashkesanite"; Pekov et al. 2005). These amphiboles may contain nearly stoichiometric amounts of Cl (Deer et al. 1997), and occur in the granulite complex of Sal'nye Tundry Massif (Kola Peninsula) and in magnetite orebodies at Dashkesan (Transcaucasia, Azerbaijan), respectively. Other reported but not formally recognized compositions are: "chloro-potassic-ferro-edenite" with Cl = 1.38 apfu in a calc silicate rock from Willroy Mine (Ontario, Canada; Pan and Fleet 1992); "chloro-potassic-ferropargasite" with Cl up to 1.16 apfu from marbles in the Sesia Lanzo Zone (Italian Western Alps; Castelli 1998); potassian "chloro-ferrosadanagaite" with Cl up to 1.5 apfu from Nusfjord (Lofoten, Norway; Kullerud and Erambert 1999); chloro-potassic-hastingsite with Cl = 1.15 apfu from a granodioritic charnockite (Airport Hill, Visakhapatnam, India; Kamineni et al. 1982). In general, Cl-rich amphiboles are rich in Fe<sup>2+</sup> and K (e.g., Dick and Robinson 1979; Morrison 1991; McCormick and McDonald 1999), indicating the effect of increasing Fe<sup>2+</sup> in increasing the dimensions of the strip of octahedra, and increasing K in promoting the bonding between K at the A(m)site and Cl at the O(3) site. For a detailed review on the occurrence of Cl in amphiboles, refer to Deer et al. (1997), pages 280-284, and for the association of Cl with K in alkali-chloride metasomatism, refer to Mazdab (2003).

There is general consensus on (1) the dependence of the Cl content on the composition of the mineral-forming fluid; (2) the positive correlation between Cl,  $Fe^{2+}$  and <sup>T</sup>Al, which has been explained by the need to enlarge both the strip of octahedra and the double-chain of tetrahedra in order to allow incorporation of Cl at the O(3) site. However, the incorporation of  $Fe^{2+}$  does not by itself produce more room for a larger anion.

Oberti et al. (1993a) examined chlorian amphiboles from the Sesia-Lanzo marbles (Castelli 1998), and compared these results with the structure refinement of a similar Clfree composition. The results they obtained have been later confirmed by many structure refinements of Cl-bearing amphiboles done at CNR-IGG-PV and one by Rastsvetaeva et al. (1996) on chloro-potassic-hastingsite with 1.31 Cl apfu.

Even very low Cl contents significantly increase the atom-displacement parameters of the O(3) site, particularly the component along [100]. At higher Cl content, the shape of the electron density changes significantly, and the best-fit model has two distinct positions for the oxygen atom and the chlorine atom, the second becoming dominant at Cl > 0.60 apfu (Fig. 24a). The distance between the two sites is around 0.5 Å in samples with 0.98 Cl apfu (as measured with a data set collected within  $\theta_{max} = 40^{\circ}$ ). Rastsvetaeva et al. (1996) gave an O(3)-O(3') distance of 0.76 Å when working on 485 independent reflections collected up to  $\theta_{max} = 30^{\circ}$ ; however, inspection of their model shows that the position of the weaker O(3) site is



**Figure 24.** Long-range effects of the incorporation of Cl at the O(3') site: (a) The electron density at the normal O(3) site occupied by O (square) and at the split site O(3) occupied by Cl (dot) in (1) an OH-dominant amphibole, and in chlorian potassic-ferropargasites, with 0.56 (2) and 0.98 (3) Cl apfu, respectively. The diamond indicates the position occupied by the proton (contours at steps of 5 *e*/Å starting from 0.0) (modified from Oberti et al. 1993a). (b) The local environment of Cl, which protrudes from the strip of octahedra toward K at the A(m) site. Also visible is the static disorder at the adjacent M(1) sites, which confirms the local relaxation resulting from the incorporation of Cl. Ellipsoids drawn at 98% probability.

poorly determined and too close to the M(3) site. With increasing amounts of Cl at the O(3) site, the M(1) and M(3) sites become enriched in Fe<sup>2+</sup>. The distances between the M(1,3) cations and the O(1,2) oxygen atoms do not change much (and thus these bonds become relatively stronger than in Cl-free amphiboles). We thus conclude that Cl protrudes out of the strip of octahedra in the direction of the A cavity (Fig. 24b), and that the presence of large M(1,3) cations allows bonding with Cl. However, Cl receives less than 1 vu from the M(1,2,3) cations (see above), and thus interaction with the A cation is important; in fact, the refined A(m)-Cl distance is particularly short (2.93 Å in Oberti et al. 1993a, 2.96 Å in Rastsvetaeva et al. 1996), even shorter than the K-Cl distances in sylvite and other inorganic compounds (> 3.15 Å). In contrast, the OH bond is somewhat bent away from the **a** direction, to avoid interaction of the proton with the A cation. In Cl-bearing amphiboles, however, the proton is masked by the electron density of Cl, and cannot be detected.

The incorporation of Cl in amphiboles also implies an expansion of the strip of octahedra in the (011) plane, which can be monitored with the M(1)-M(1) distance, always larger than expected based on the M(1) site population. Analysis of the atom-displacement parameters at the M(1) site also confirms significant relaxation close to Cl (Fig. 24b). The increase in the unit-cell edges is  $b \sim c > a$ , confirming that Cl protrudes significantly into the A cavity, avoiding lengthening of the *a* edge.

# Fluorine

The incorporation of F in amphiboles is a very widespread phenomenon in all except the Mg-Fe-Mn-Li amphiboles. The F content seems to depend primarily on its geochemical availability and not on structural constraints. The only observed inverse correlation is with the Fe<sup>2+</sup> content, which is in agreement with the well-known criterion of  $Fe^{2+}$ -F avoidance in silicates (Rosenberg and Foit 1977), a result of the smaller crystal-field stabilization energy provided by F.

The fact that the local environment of F implies Mg at the adjacent M(1) and M(3) sites has been confirmed by FTIR analysis. Detailed spectroscopic work has shown that the substitution of F for OH in the amphibole structure is strongly controlled by the bond-valence sum at the O(3) site. In local configurations involving  $^{M(3)}$ Al in pargasite (Robert et al. 2000) or in the pargasite–richterite solid solution (Della Ventura et al. 2001), the bond-valence contribution from the C cations incident to O(3) is > 1.0 vu. Hence, the hydroxyl proton contributes less than 1.0 vu, and can be involved in significant hydrogen bonding with the surrounding oxygen atoms, especially O(7). This feature is confirmed by the lower stretching frequency observed in the FTIR spectrum. In such a case, the hydroxyl group is less easily replaced by F (Della Ventura et al. 2001).

The occurrence of F at the O(3) site causes significant shortening of the M(1)-O(3) and M(3)-O(3) distances, which reduces  $\langle M(1)$ -O,OH,F> and  $\langle M(1)$ -O,OH,F> (Hawthorne 1983a). An attempt to quantitatively evaluate this effect was done by Oberti et al. (1993b) in a series of richterites with variable F content. The resulting regression equations [ $\langle^{M(1)}Mg$ -O> = 2.0769-0.0130 F apfu and  $\langle^{M(3)}Mg$ -O> = 2.0696-0.0128 F apfu, with R = 0.994 and 0.978, respectively] confirm that incorporation of F affects the two sites almost equally [the *cis* and *trans* arrangements of the O(3) site being thus irrelevant], and that the shortening is roughly proportional to the difference in the ionic radii of [<sup>3</sup>]OH<sup>-</sup> and [<sup>3</sup>]F<sup>-</sup> (1.34 and 1.30 Å, respectively). However, the fictive  $\langle$ Mg-O> values vary considerably among the various (Mg,Al) amphibole end-members, and thus only the shortening coefficient can be transferred to other amphibole compositions.

As discussed above, the incorporation of F also has a strong ordering effect on the distribution of Al and all transition metals over the M(2) and M(3) site. These cations disorder over the M(2) and M(3) sites in Mg-rich compositions (see above discussions for Al, Fe<sup>3+</sup>, V<sup>3+</sup> and Cr<sup>3+</sup>), whereas they are always fully ordered at M(2) in fluoro-amphiboles.

# Hydrogen (as OH-)

The observed OH<sup>-</sup> content in amphibole can vary from 0 to 3 pfu. In monoclinic and orthorhombic amphiboles, only the O(3) site is commonly available for OH<sup>-</sup>, which results in 2.0 (OH) pfu. Values lower than 2.0 (OH) pfu are related either to substitution of (OH) by F or Cl (the effects of which have been discussed above), or by O<sup>2-</sup> (the oxo component), which implies either crystallization under low  $f_{\rm H_{2O}}$  conditions and/or high-*T*, or loss of H during post-crystallization oxidation processes. Values higher than 2.0 (OH) pfu are still a matter of debate, and has been incontrovertibly proven only in a triclinic sample with a tripling of the *b* edge (Witte et al. 1969; Liu et al. 1996; Cámara et al. 2004). The issues of the oxo component and of excess (OH) will be discussed separately in the next two sections.

The O-H bond points in the direction of the A cavity, and thus repulsive interactions are possible between the proton and the A cations, especially when ordered at the closest A(m) site. In contrast, incorporation of F and Cl allows cation-anion interactions, and thus favor the ordering of K and Na at the A(m) site. More details on the local environment of the proton are given in Hawthorne and Oberti (2007) and Hawthorne and Della Ventura (2007).

# THE OXO COMPONENT: A DETAILED DISCUSSION

Rather ironically, amphiboles were long considered as anhydrous minerals, similar to pyroxenes (for a survey, see Cipriani 2007). Notwithstanding the generally low total of the oxide wt%, Schaller (1916) was the first to consider  $H_2O$  as an essential constituent of amphiboles, and the definitive confirmation came from the structure refinement of tremolite done by Warren (1930). However, the first attempt to investigate dehydrogenation in amphiboles by heating experiments was done by Posnjak and Bowen (1931).

Oxburgh (1964) first noted the role that amphibole could have in mantle processes. Saxena and Ekström (1970) discussed the statistical relevance of the oxo component  $[^{O(3)}O^{2-}]$  in calcic amphiboles, stressed its positive correlation with the Ti content, and did not find any significant correlation with the Fe<sup>3+</sup> content. From the 70s, many experimental studies were done to determine amphibole stability as a function of pressure, temperature, composition and volatile content under mantle conditions and in meteorites (for comprehensive references, see

Popp et al. 1995a,b and King et al. 1999), but they could not *in situ* measure the H content. Incidentally, evaluation of the H<sub>2</sub>O content by difference to 100% oxides is not reliable for mantle amphiboles if independent estimates of the Fe<sup>3+</sup> contents are not available. However, the volatile content of amphiboles was used to estimate water activity ( $a_{H_2O}$ ) of the melt from which the amphibole crystallized, as well as the hydrogen fugacity ( $f_{H_2O}$ ) of the melt.

The first modern and comprehensive study of dehydrogenation in calcic amphiboles was published by King et al. (1999, 2000) who examined major elements and H analyses (by SIMS) for 38 natural and synthetic Ti-rich calcic amphiboles crystallized at mantle conditions. They concluded that the high Ti contents derive from crystallization from mafic-ultramatic melts at low to moderate pressure ( $\leq 1.0$  GPa), high temperature (> 950 °C) and low to moderate oxygen fugacity ( $f_{O_2}$ ), and that iron oxidation state in amphiboles is affected by  $f_{O_2}$  and  $f_{H_2}$  in the melt. The oxo component and the Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios are a function of both initial crystallization conditions and dehydrogenation, with variations occurring due to different pressure-temperature- $f_{H_2}$ -time paths. Amphibole dehydrogenation likely occurs at the surface or en route to the surface where  $f_{H_2}$  is low, cooling is slow, or grain attributes tend to favor rapid H diffusion. A schematic representation of the stability of calcic amphibole in hydrous volcanic systems and of the factors affecting the oxo component is shown in Figure 25.

As discussed in Oberti et al. (2007), much evidence has been found in the last 15 years that all amphibole compositions can crystallize with low (OH,F,Cl) (i.e., volatile element) contents under different *P*, *T*, *X*,  $f_{\rm H_2O}$  conditions. In the CNR-IGG-PV amphibole database, around 25% of the 1150 entries have volatile contents significantly less than 2.0 pfu. For almost 90% of them, petrologic analysis suggests that this deficiency in volatile components is a feature of primary crystallization. Commonly, low volatile contents occur in magmatic amphiboles (from both intrusive and extrusive rocks), and are very frequent in high-grade metamorphic environments. Most calcic amphiboles with volatile-element contents between 0 and 0.8 pfu are volcanic in



Temperature

**Figure 25.** Schematic pressure vs. temperature diagram showing amphibole stability and some factors possibly affecting the oxo component in calcic amphiboles from hydrous volcanic systems. Initial crystallization conditions control both the oxo component and the incorporation of C cations. The final amount of the oxo component depends on the ascent rate and  $f_{H_2}$  gradient. [Used by permission of Elsevier, from King et al. (1999), *Geochimica et Cosmochimica Acta*, 63, Fig. 8, p. 3647.]

origin, and for many of them, the low volatile content is related to post-crystallization oxidation processes (dehydrogenation). Thus detection of the oxo component, and understanding the mechanisms that satisfy local bond-valence requirements are of major and general interest to amphibole crystal-chemistry. Notably, investigation of amphiboles in mantle and volcanic-arc environments is presently considered by some as an issue of great relevance in petrogenetic and geochemical studies. In this regard, the detection and quantification of the oxo component is critical for the correct calculation of the unit formulae to be used either for thermodynamic modeling or for the interpretation of trace-element behavior (Tiepolo et al. 2007).

Electron-microprobe analysis of F in minerals is still difficult to do accurately because of second-order peak interferences from Mg and Al, and first-order *L*-lines from Fe and other transition elements, and because peak shape is strongly affected by matrix effects (including orientation effects in the standards; Stormer et al. 1993; Ottolini et al. 2000).

SIMS analysis is the only method available to detect and quantify the H content *in situ* (on  $\mu$ m-scale areas), a requirement that is extremely important for (1) small and rare crystals, and (2) compositionally zoned crystals. Although reasonable accuracy can now be achieved ( $\pm$  10% rel., although the precision and accuracy still need to be improved significantly), the use of proper calibration curves is still crucial, because matrix effects (non-linear ion yields of hydrogen due to changes in bulk chemistry) severely affect hydrogen quantification (Ottolini et al. 1995). The ability to detect and quantify the oxo component directly from the results of structure refinement will complement SIMS analysis, and agreement will further validate each method and allow a rigorous evaluation of accuracy.

The oxo component at the O(3) site can be locally balanced by two different crystalchemical mechanisms:

$${}^{M(1)}\text{Ti}^{4+}{}_{1}{}^{O(3)}\text{O}^{2-}{}_{2}{}^{M(1)}(\text{Mg},\text{Fe})^{2+}{}_{-1}{}^{O(3)}(\text{OH})^{-}{}_{-2}, \text{ with a cation:}\text{O}^{2-} \text{ ratio 1:}2$$
 (3)

$$M^{(1,3)}(\text{Fe},\text{Mn})^{3+1} O^{(3)}O^{2-1} M^{(1,3)}(\text{Fe},\text{Mn})^{2+} O^{(3)}(OH)^{-}_{-1}$$
, with a cation:  $O^{2-}$  ratio 1:1 (4)

Mechanism (3) has been discussed in detail in the section dealing with Ti. Mechanism (4) has been examined in a series of experimental studies after the pioneering works on hornblende (Barnes 1930) and crocidolite (Addison et al. 1962a,b). Ernst and Wai (1970) annealed iron-bearing sodic amphiboles in air at ~700 °C, and found that hydrogen loss couples with oxidation of Fe<sup>2+</sup> at the M(1) and M(3) sites. In fact, complete dehydrogenation was reached within one h in riebeckite, whereas in magnesioriebeckite and in glaucophane, the bands of the IR spectrum assigned to local configurations involving at least one Fe<sup>2+</sup> cation disappear after one hour but those assigned to [MgMgMg]-OH persist after 95 hours of annealing.

A more quantitative model for mechanism (4) was provided by the work of Popp et al. (1995a,b; 2006a,b) who did heating experiments under controlled P, T and  $f_{\rm H_2}$  conditions on three titanian pargasites and kaersutites, and monitored the dehydrogenation-protonation process via variation in the Fe<sup>3+</sup>/Fe<sub>tot</sub> content measured by Mössbauer spectroscopy. They concluded that high Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios observed in most natural kaersutitic amphiboles can result from P-T- $f_{H_2}$  conditions characteristic of the upper mantle, rather than from oxidation during ascent or eruption, and that closed-system cooling favors reduction, not oxidation, of amphibole. With the intent of estimating  $f_{\rm H_2}$  of the system from amphibole composition, Popp et al. (2006a,b) expressed the equilibrium constant (K) of the dehydrogenation-protonation reaction as  $K = K_x \Phi$ , where  $K_x$  is the thermodynamic mole fraction (which includes  $f_{H_2}$ ), and  $\Phi$  is the activity coefficient. Variations in  $K_x$  were quantified experimentally as a function of *P*, *T*,  $f_{\rm H_2}$  and composition, and allow evaluation of the equilibrium log  $f_{\rm H_2}$  within 0.3 log units. The main problem with this work is the lack of crystal-chemical control of the assumptions. While monitoring only mechanism (4), Popp et al. (2006a,b) estimated the oxo component as  $2.0 - Fe^{3+} - {}^{Ti}O^{2-} - F - Cl$  (apfu), where  ${}^{Ti}O^{2-}$  is the Ti content accommodated by the Ti oxo substitution expressed as  $Ti^{4+}_{1}O^{2-}_{1}(R^{n+})_{-1}(OH^{-})_{-1}$ . As shown above (and even better shown below), this mechanism is incorrect, because  $Ti^{4+}$  at the M(1) site is not related to postcrystallization dehydrogenation, but solely to the primary oxo component with a cation: $O^{2-}$ ratio 1:2. Also, Popp et al. (2006a,b) considered the overall Ti content of the amphibole, not just the fraction related to the oxo component, and the overall Fe<sup>3+</sup> content and not just the fraction occurring at the M(1) and M(3) sites. This issue is particularly relevant because one of the three samples is the kaersutite from Kaersut, Greenland, whose unusual Ti distribution is described in the paragraph on Ti site-partitioning. Moreover, the equations were derived based on a random mixing model for the C cations, which is certainly inappropriate, given the strong site preferences discussed above.

The statistical analysis of King et al. (1999, 2000) showed that the overall (OH) content correlates well with the  $^{C}(Al,Ti,Fe^{3+})$  content, and provides a way to calculate the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio for the samples where SIMS quantification of H is available and better evaluate the oxosubstitution mechanisms. Again, their model is biased by an incorrect evaluation of the role played by the different highly charged species, and the equation fails for some compositions.

Systematic work combining structure refinement and complete (EMP+SIMS) microanalysis of 75 natural and synthetic calcic amphiboles (some of which are in common with the database of King et al. 1999) has been recently done at CNR-IGG-PV. The amphiboles either belong to ultramafic mantle associations or occur as megacrysts in basaltic lavas, and are representative of the P-T- $f_{H_{2}O}$  conditions of crystallization observed for the upper-mantle/deepcrust in the subcontinental region. The constraints of the structure refinement (in particular the site-scattering values refined at the A, A(m), A(2), M(4), M(1), M(2) and M(3) sites and the accurate determination of <sup>T</sup>Al based on the refined bondlength) allowed calculation of reliable crystal-chemical formulae. Mechanism (3) is definitely dominant at least for  $O^{(3)}O^{2-}$  contents up to 1.0 apfu. Beyond that limit (and solely in volcanic environments), the oxidation of Fe<sup>2+</sup> (rarely of Mn) becomes the prevailing mechanism for incorporation of <sup>O(3)</sup>O<sup>2-</sup>. Figure 26 shows the chemical correlations observed for calcic amphiboles from different petrologic environments, and confirms the stoichiometry and relative importance of mechanisms (3) and (4). Figure 27 shows the concomitant variations observed for the M(1)-O(3) and M(3)-O(3) distances normalized over the aggregate mean bondlength in order to cancel the effect of changes in composition, and confirms that the substitutions occurring at M(1) are more important, the M(3) site becoming active only at  $O^{(3)}O^{2-}$  contents higher than 1.2 apfu. Figure 28 provides a simple way to detect the nature of the highly charged cation that is incorporated at the M(1)site to balance the oxo component. In fact, the occurrence of Ti does not significantly affect the parameter  $\Delta (\Sigma_{i=1.6}[((M-O)_i - \langle M-O \rangle)/\langle M-O \rangle]^2 /6 \times 10^4$ ; Brown and Shannon 1973), which is on the contrary very sensitive to the occurrence of  $Fe^{3+}$ . Based on these observations and on Mössbauer analysis of a subset of selected samples, site populations were derived and related to the observed geometrical changes. A good linear correlation was obtained between O(3)O<sup>2-</sup> (in apfu) and the M(1)-M(2) distance. The M(2) site is not directly involved in the charge balance of the oxo component. However, its geometry is strongly affected by the oxo component, because the O-O edges shared with M(1) and M(3) [O(1)-O(2) and O(1)-O(1), respectively] shorten, whereas the M-M distances lengthen. Therefore, the correlation between the oxo component and the M(1)-M(2) distance must be interpreted as a mechanism of structural relaxation via octahedron distortion, which minimizes repulsion between highly charged cations. Obviously, the M(1)-M(2) distance also depends on the bulk chemistry (see above for a discussion on the variation in <Mg-O> in amphiboles) and thus different regression equations must be used for different subsets of amphiboles.

Statistical analysis of the amphibole database provided two different regression equations that can be reliably used to quantify the oxo component in terms of solid-solution between pargasite-hastingsite and kaersutite, and in Ti-bearing richterites from mantle environments. The trends and the equations are shown in Figure 29. Further work is in progress in order to obtain more general relations which take into account the overall chemistry, as discussed above



**Figure 26.** The relation between the oxo component  $[^{O(3)}O^{2-}]$  and Ti<sup>4+</sup> (a) and Fe<sup>3+</sup> (b) contents in the 75 calcic amphiboles in the CNR-IGG-PV database for which SIMS analyses for H are available. Dots: amphiboles from upper-mantle metamorphic lithologies; diamonds: amphiboles from magmatic lithologies; triangle: the sample from a gabbro at Kaersut discussed in the paragraph on titanium; squares: synthetic Fe-free samples with Ti at M(2) and M(3) (Tiepolo et al. 1999). The arrow joins two phenocrysts found in a pyroclastic deposit at Stromboli (Sicily), which share the same major-element composition but have different oxo components (post-crystallization oxidation).



**Figure 27.** The variation in *M*-O(3) distances in the calcic amphiboles of Figure 26. In order to remove the effects of compositional variation, the measured distances have been normalized to the average of the other distances. Legend as in Figure 26.



3.20 3.18 0.051x + 3.120  $R^2 = 0.95$ 3.16 richterite M(1)-M(2) (Å) 3.14 0.054x + 3.076  $R^2 = 0.99$ 3.12 3.10 gasite-kaersutite-hastingsite 3.08 3.06 0.2 0.4 0.6 1.6 1.8 2.0 0.0 0.8 1.0 1.2 1.4 <sup>O(3)</sup>O<sup>2-</sup> (apfu)

**Figure 28.** Octahedron distortion  $\Delta^{M(1)}$  as a function of oxo component in amphiboles.

Figure 29. The relation between the M(1)-M(2) distance and the oxo component in amphiboles.

when dealing with the program COMAMPH. In order to test the reliability of this method, the oxo component was calculated for all the calcic and sodic-calcic amphiboles with possible (OH) deficiency for which SIMS analyses were not available. Fixing the oxo component allowed calculation of crystal-chemical formulae which obey all the constraints of amphibole stoichiometry and are in excellent agreement with the results of the structure refinement. A detailed discussion of these results, of the amphibole compositions considered, and of the trends discussed in Figures 26-29 will be given in a manuscript in preparation.

# **HYDROGEN IN EXCESS OF 2.0 APFU**

The possible occurrence of (OH) in amphiboles beyond the stoichiometric limit of 2.0 pfu has been debated for many years. In his review of the available amphibole analysis, Leake (1968) reported some "superior" analyses with (OH,F,Cl) values up to 2.99 pfu. Kemp and Leake (1975) reported analyses of two alumino-tschermakites enriched in (OH) (2.60 pfu), and concluded that the (OH) excess was related to the large amounts of Al substituting for Si. However, the samples reported by Kemp and Leake (1975) were re-investigated at CNR-IGG-PV (courtesy of Bernard Leake), and no evidence was found of excess H.

Using Mössbauer and IR spectroscopy, Semet (1973) characterized a series of magnesiohastingsites synthesized at different  $f_{O_2}$  conditions, and suggested that: (1) excess H may balance reduction from Fe<sup>3+</sup> to Fe<sup>2+</sup>; (2) the reaction is reversible; (3) the most likely anion site candidate for protonation is O(4). The main evidence for excess (OH) in the specimen synthesized or reduced to low  $f_{O_2}$  conditions was the growth of a broad absorption band between 3640 and 3540 cm<sup>-1</sup> in the infrared spectra. However, Mössbauer analysis showed Fe<sup>3+</sup> to be ordered primarily at the M(2) site, but occurring also at the M(1) and M(3) sites, which is in favor of the occurrence of an oxo component.

Kuroda et al. (1975) reported increasing H<sub>2</sub>O contents (up to 3 wt%, as determined by hydrogen extraction) in richterite<sub>50</sub> tremolite<sub>50</sub> solid-solutions synthesized at increasing  $f_{\rm H_2O}$  at *P* from 5 to 20 kbar, but did not speculate on the crystal-chemical significance of their results.

Witte et al. (1969) synthesized in the system  $Na_2O-MgO-SiO_2-H_2O$  (NMSH) amphiboles tending to the unusual formula <sup>A</sup>Na <sup>B</sup>Na<sub>2</sub> <sup>C</sup>Mg<sub>5</sub> <sup>T</sup>Si<sub>8</sub> O<sub>21</sub> (OH)<sub>3</sub>. Further syntheses and characterization (Maresch et al. 1991; Liu et al. 1996) suggested triclinic symmetry, which converts to monoclinic symmetry by annealing as shown by infrared and MAS NMR spectroscopy. A broad band peaking at 3430 cm<sup>-1</sup> was also observed in all the run products, which could recently be ascribed to the excess proton based on structure refinement (Cámara et al. 2004).

Several hypotheses have been made on the possible location of the excess proton in the amphibole structure, among them H<sub>2</sub>O occupancy at the *A* site or the presence of an (OH) group (tentatively proposed at the O(4) site) in the double-chain of tetrahedra (Zussman 1955). Recently, Cámara et al. (2004) refined the crystal structure of triclinic <sup>A</sup>Na <sup>B</sup>Na<sub>2</sub> <sup>C</sup>Mg<sub>5</sub> <sup>T</sup>Si<sub>8</sub> O<sub>21</sub> (OH)<sub>3</sub>, and found that it has a  $C\overline{1}$  symmetry and a unit cell with a tripled *b* edge. Interpretation of previous FTIR and MAS NMR results based on structure refinement showed that excess protons are bonded to the O(4) oxygen atoms [O(4)A, O(4)A2, O(4)B1] farthest from the *M*(4) cation, and weakly interact with the adjacent O(2) oxygen atoms [O(2)A, O(2)A2, O(2)B1]. Consideration of site multiplicities gives a maximum excess H content of 1 apfu. Notably, in this very peculiar sample the presence of excess H is sterically allowed by the shift of the <sup>B</sup>Na atoms away from the diad, a feature which is possible only in the triclinic symmetry (more detail in Hawthorne and Oberti 2007). The broad band at around 3430 cm<sup>-1</sup> in the FTIR spectrum of this sample could be unambiguously assigned to the excess proton. The question now is whether excess hydrogen can occur also in monoclinic amphiboles, and what is its possible location.

Acicular amphiboles with significant excess H (measured by vacuum extraction followed by manometric measurements and coulometric titration) were synthesized in the seventies in Bochum (Germany) during a thorough study of the system Na<sub>2</sub>O-Li<sub>2</sub>O-MgO-SiO<sub>2</sub>-H<sub>2</sub>O (LNMSH) (W. Maresch, pers. com.). This sample has been re-examined recently in Pavia and Rome by structure refinement, EMP and SIMS analysis, and FTIR spectroscopy. Combination of chemical analyses and refined site-scattering values gives the formula <sup>A</sup>Na<sub>1,00</sub> <sup>B</sup>(Mg<sub>1,00</sub> Li<sub>0,27</sub>  $H_{0,12} \operatorname{Na}_{0,61} \operatorname{^{C}Mg_5}^{T} \operatorname{Si}_8 \operatorname{O}_{22} \operatorname{^{W}}(OH)_2$ ; the space group is  $P2_1/m$ , and the crystal undergoes a  $P2_1/m$  $\rightarrow$  C2/m transition at around 260 °C. Again, FTIR analysis shows a broad band around 3400 cm<sup>-1</sup>. Albeit the excess H is within the analytical error, there is independent evidence suggesting excess protons ordered at M(4). The shape of the electron density at M(4) is very irregular (as expected from the complex site-population), and studies at low temperature will hopefully give some information on the H coordination. All evidence discussed above seems to indicate that there is no room for an excess proton in the C2/m amphibole structure, and that this anomalous component is sterically tolerated only when (1) the lowering of symmetry allows an anomalous distribution of the B cations which are strongly off-centered and displaced off the diad; (2) the bulk chemistry is very peculiar (and would not otherwise allow for electroneutrality, as is the case of the triclinic sample) or is deficient in B cations.

# FACTORS AFFECTING ORDERING OF CATIONS IN THE AMPHIBOLE STRUCTURE

Although much effort has been expended on characterizing the state of order of cations in the amphibole structure, not much work has been done on the reasons why such order occurs. This is obviously an area for future work.

Whittaker (1949) explained the preferential occupancy of the M(2) site by trivalent cations in "crocidolite" as a result of the "lower electrostatic potential" at M(2) that results from occupancy of the adjacent M(4) site by a monovalent cation. Ghose (1965) also suggested local charge-balance as one of the factors controlling cation order at both the M and T sites in the amphibole structure. Whittaker (1971) did the first quantitative work on this issue. He calculated the Madelung energies and electrostatic site-potentials in a variety of cation arrangements and showed that the results are compatible with the cation arrangements in glaucophane, riebeckite and pargasite. However, the patterns of order predicted for tschermakite and aluminohornblende do not agree with those subsequently observed in crystal-structure refinements. Hawthorne (1978b) calculated the RMS (Root Mean Square) deviation from exact agreement with Pauling's second rule (Pauling 1929) for all possible charge arrangements of the twelve most common amphibole stoichiometries, and showed that the observed patterns of order are those with the lowest RMS deviation from Pauling's second rule for each stoichiometry. Thus Pauling's second rule seemed to be the principal factor controlling the ordering of polyvalent cations in the amphibole structure.

Hawthorne (1997) proposed that bond-valence theory (Brown 1981, 2002) is applicable also at the local (short-range) scale, and showed that certain short-range arrangements of cations are much more stable according to the valence-sum rule than other arrangements also consonant with the overall stoichiometry of the amphibole under consideration. This approach has been very successful in understanding short-range effects in amphiboles and aiding assignment of fine-structure bands in the infrared spectra in the principal (OH)-stretching region (Hawthorne and Della Ventura 2007). As the long-range order is the sum of all of the short-range-order configurations in the structure, it is apparent that the local (short-range) constraint of the valence-sum rule affects the long-range order in the structure. Similar results have been obtained for glaucophane (Palin et al. 2003) and compositions along the tremolite–magnesiohornblende join (Palin et al. 2005) by Monte Carlo simulation as a function of temperature.

Thus the valence-sum rule (Brown 1981, 2002; Hawthorne 1994, 1997) provides a fairly comprehensive explanation for the observed order of heterovalent cations in amphiboles. It is apparent from both observed ordering patterns that some (e.g., Al completely ordered at M(2) in glaucophane) are independent of temperature or pressure, whereas others (e.g., order of Al over T(1) and T(2) in pargasite) are dependent on temperature and/or pressure. The next step is to investigate these effects of temperature and pressure on the ordering of heterovalent cations.

Little quantitative work has been done on the factors that affect ordering of homovalent cations in the amphibole structure(s). This is an area waiting for work to be done.

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