Computational investigation of Al/Si and Al/Mg ordering in aluminous tremolite amphiboles

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Abstract

The ^[4]Al/Si and ^[6]Al/Mg order-disorder behaviour of minerals in the tremolite-tschermakite solid solution (namely, end-member tschermakite and the 50:50 composition, magnesiohornblende) has been investigated by Monte Carlo simulation, using a model Hamiltonian in which atomic interaction parameters J_i were derived from empirical lattice energy calculations, and chemical potential terms μ_j (to express the preferences of cations for particular crystallographic sites) were derived from *ab initio* methods. The simulations performed were increasingly complex. Firstly, ordering in one tetrahedral double chain with Al:Si = 1:3 (tschermakite) was simulated. Although the low-temperature cation distribution in this system was ordered, there was no phase transition (due to the quasi-one-dimensional nature of the system). Next, interactions between tetrahedral Al:Si = 1:3 double chains were included, and a phase transition was observed, with the cation distribution in one double chain lining up with respect to that in the next. Finally, interactions between tetrahedral and octahedral sites were incorporated, to model the whole unit cell, and compositions corresponding to tschermakite and magnesiohornblende were investigated. The whole-cell simulation results compare favourably with experimental conclusions for magnesiohornblende, in that Al at T1 is preferred over Al at T2, and Al at M2 is favoured over that at M1 and M3, but the significant amount of Al at M1 is at odds with experimental observation.

Introduction

In this paper we present a computer simulation study of the order-disorder behaviour of two compositions in the aluminous tremolite (tremolite-tschermakite) solid solution: the fictive end-member, tschermakite, ${}^{[A]}\square^{[8]}Ca_2{}^{[6]}(Mg_3Al_2){}^{[4]}[Si_6Al_2]O_{22}(OH)_2$ and the 50:50 composition, magnesiohornblende, ${}^{[A]}\square^{[8]}Ca_2{}^{[6]}(Mg_4Al){}^{[4]}[Si_7Al]O_{22}(OH)_2$. This work follows on from our previous simulation studies of cation ordering in minerals, in which we have investigated the effects of both the number of ordering species and the number of types of crystallographic sites across which these species may order. Our work on Al/Si ordering in muscovite (Palin et al., 2001) investigated the behaviour of two types of cations on one type of site. Our study of phengite (Palin et al., 2003a) explored the ordering behaviour of three types of cation across two types of site, namely tetrahedral Al/Si and octahedral Al/Mg ordering, and the nature of the coupling between these ordering processes. Subsequently, we investigated the behaviour of three ordering species across one type of site, in the case of Al/Fe/Mg ordering in the general dioctahedral phyllosilicate sheet (Sainz-Diaz et al., 2003a,b; Palin et al., 2004). Finally, in our work on glaucophane (Palin et al., 2003b), we investigated Al/Mg ordering across three crystallographically-distinct sites.

Though we have previously studied coupled ordering processes (phengite) and ordering across several site types (glaucophane), we have not previously studied both phenomena in one mineral system. The present study addresses this; we explore two ordering processes and a total of five crystallographically-distinct sites taking part in ordering in aluminous tremolites.

The interest in the order-disorder behaviour of tremolite-tschermakite minerals stems from their potential importance in geothermobarometry. If a better understanding could be gained of the thermodynamics governing cation ordering in this system, amphiboles may offer an opportunity to create geothermometers in conditions where other minerals are not appropriate. For example, studies of divalent cation ordering in olivines (Redfern et al., 1997), which have been suggested as potential geothermometers, show that Mg/Mn^{2+} and Mg/Fe^{2+} exchange can be sufficiently fast that high-T cation distributions are not preserved in natural samples, with the result that geothermometers based on olivine may be inaccurate. By contrast, it appears (Raudsepp et al., 1987) that exchange of heterovalent cations is much slower, meaning that crystallisation temperatures could be deduced from e.g. Mg/Al distributions. Clearly, aluminous tremolites, with ^[6]Al/Mg and ^[4]Al/Si, could be appropriate for such an application. This study is not intended to provide conclusive results with respect to geothermobarometry, but the computational approach that we have used yields simulated Mg/Al site occupancies and cation distributions, which may be of use in further investigations.

A further motivation for study is that the tschermakite end-member is not known to exist in nature — tschermakitic bulk compositions yield Al-rich amphibole and other phases such as chlorite, spinel and forsterite (Jenkins, 1994). However, tschermakite remains interesting with reference to comparative studies across the solid solution. Moreover, solid solutions at the tremolite-rich end of the series do occur naturally, and also can be synthesised; the most tschermakite-rich composition that can be synthesised along the tremolitetschermakite join is usually considered to be magnesiohornblende. A computational study of this system could provide a new perspective on the reasons for the compositional limits of stability in this series.

Structure of tremolite-tschermakite amphiboles

The amphibole structure is shown in Figure 1. The sites which are relevant in this study are the two distinct tetrahedral (T) sites, T1 and T2, and the three distinct octahedral (M) sites, M1, M2 and M3. The tetrahedral sites are corner-linked to form a tetrahedral double chain (so named by analogy with the single-chain structure of pyroxenes), with T1 sites occurring along the centres of the double chains and T2 sites along the edges, giving a T1:T2 ratio of 1:1, and eight T sites per formula unit. The octahedral sites are edge-linked to form ribbons, with M3 sites running down the centre, M2 sites along the edges and M1 sites between the two, such that the ratio of numbers of M sites is M1:M2:M3 = 2:2:1, and there are five M sites per formula unit. One octahedral ribbon is sandwiched between two tetrahedral ribbons, to produce the familiar "I-beam" structural unit. The other sites shown in the diagram are the distorted, highly-coordinated M4 site (important in defining the major amphibole groups — calcic, sodic-calcic, alkali) and the A site, situated between adjacent I-beams.

Tremolite and tschermakite end-member components are related by the Tschermak substitution ^[6]Mg^[4]Si \Rightarrow ^[6]Al^[4]Al, and so we must consider Al both on the octahedral and the tetrahedral sites, and the possibility of coupling between octahedral and tetrahedral ordering schemes. Many experimental studies have been undertaken in order to determine the ordering behaviour of Al in aluminous tremolites (e.g. Hawthorne et al., 2000; Jenkins et al., 1997), and on other closely-related minerals such as pargasite and pargasitic hornblendes (e.g. Raudsepp et al., 1987; Welch et al., 1994). Pargasite, ^[A]Na^[8]Ca₂^[6](Mg₄Al)^[4][Si₆Al₂]O₂₂(OH)₂, is relevant to this study as it has the same octahedral cation ratio as magnesiohornblende, and the same tetrahedral cation ratio as tschermakite.

To date, the following deductions have been made for ordering across octahedral sites. Hawthorne (1981; 1983) argued from bond-valence considerations that in these minerals ^[6]Al should occur at M2. Raudsepp et al. (1987) concluded from IR, MAS-NMR and structure refinement studies that $^{[6]}$ Al should occur at M2 and M1/M3, a finding which was later supported by MAS-NMR and IR investigations by Welch et al. (1994). Later studies by X-ray structure refinement (Oberti et al., 1995a), neutron diffraction (Welch and Knight, 1999), IR spectroscopy (Ventura et al., 1999), IR and triple-quantum NMR (Hawthorne et al., 2000) revised this to M2 and M3, but not M1. For the tetrahedral cation behaviour, bond-valence calculations (Hawthorne, 1981, 1983, 1997) suggest that Al should order preferentially at T1. This proposition was corroborated by ²⁹Si MAS NMR studies (Welch et al., 1998). It was also concluded by Oberti et al. (1995b) that an Al content of more than two tetrahedral Al atoms per formula unit leads to Al at T2, but that less Alrich compositions had Al at T1. Additionally, a recent computational/experimental study (Najorka and Gottschalk, 2003) of both tetrahedral and octahedral order in tremolitetschermakite assumed that ^[4]Al was located at T1, and then used Monte Carlo simulations to infer octahedral occupancies from IR spectroscopy data. The two occupancy models used by these authors had Al at M2 and Al at M2 and M3; simulations gave better agreement for the latter. These diverse and sometimes contrasting results for both the octahedral and tetrahedral sites highlight the need for further investigation of this system.

It has been suggested that coupling between M and T sites is an important control on ordering in certain amphiboles. Hawthorne (1997) suggested that coupling occurs between Al at M2 and T1 on the grounds that if Al rather than Si is at T1, a more favourable bond-valence sum is incident at the O1 atom. This theory is supported by the experimental results of Jenkins (1994), who studied a series of tremolite-tschermakite amphiboles and found that agreement between his experiment and activity-composition models was best for a model involving coupling between Al at M2 and T1. Subsequently, Welch et al. (1998) proposed that coupling between Al at M2 and T2 was a significant factor in controlling the long-range order behaviour of Al and Si in the tetrahedral sites. The simulation method we have employed in this work is capable of accounting for possible coupling terms, by including interactions between the tetrahedral and octahedral sites (T–O), as well as T–T and O–O interactions.

Methods

The method we employed in this work is identical to that previously employed in our study of glaucophane (Palin et al., 2003b). The general approach is described in detail elsewhere (Bosenick et al., 2001; Warren et al., 2001), here we simply note that it comprises two stages: firstly, lattice energy minimisation methods are used to compute values for atomic interaction parameters and chemical potentials; and secondly, these values are used in Monte Carlo simulations of ordering. In this work, as for glaucophane, the atomic interaction parameters were determined using an empirical method, and a quantum mechanical approach was used to calculate the chemical potentials.

The general expression for the ordering energy is

$$E = E_0 + \sum_i N^i_{\text{Al}-\text{Al}} J_i + \sum_j \mu_j x^j_{\text{Al}}$$
(1)

where E denotes the energy of a particular configuration of cations, E_0 denotes an energy constant subsuming all energy terms not involved in the ordering process, J_i indicates the *i*th pair interaction parameter, and N_{Al-Al}^i denotes the number of Al–Al linkages corresponding to J_i (the choice of atom type here is arbitrary, any of the atom types involved in ordering could be chosen). Where there is more than one type of site (e.g. tetrahedral vs. octahedral), a chemical potential μ_j can be included to express the preference of a cation for a particular site type j (again we have chosen to compute chemical potentials with respect to Al; the value of the chemical potential is multiplied by x_{Al} , the fraction of sites of type j which are occupied by Al). Equation 1 is simply a multilinear regression problem; given a set of N_{Al-Al}^{i} and E values, computer algorithms can be used to solve for E_{0} and a set of J values (and μ values, if used). The E values are obtained by constructing a set of model configurations in which the cations of interest are randomly located across the sites which take part in ordering; each of these configurations is optimised using the lattice energy minimisation program GULP to yield an E value. For each configuration, the N_{Al-Al}^{i} values are determined by a spreadsheet method. The specific procedure is discussed below.

Interatomic potentials and model testing

The tschermakite model consists of two parts: structural data (cell parameters and atomic coordinates), and a series of empirical interatomic potentials to model the interactions between the atoms. The parameters used in the interatomic potentials for the tschermakite model are given in Table 1. Four types of potential are employed, and two types of oxygen atom are considered: "O1" is used to denote oxygen atoms forming part of a hydroxyl group, and "O2" is used for all other oxygen atoms.

Buckingham potentials are used to model short-range interactions such as Si–O and K–O:

$$E(r) = A \exp(-r/\rho) - Cr^{-6}$$
(2)

where A, ρ and C are adjustable parameters. When C = 0, as is the case for all shortrange interactions except for Si–O2 and O–O, the functional form is that of the Born-Mayer potential.

The Morse potential is used to model the hydroxyl group (i.e. bonding between O1 and

H):

$$E(r) = D\left[(1 - \exp\left[-a(r - r_0) \right])^2 - 1 \right]$$
(3)

where D, a, r and r_0 are adjustable parameters. The polarisability of the oxygen atom is modelled via the core-shell potential, in which each oxygen atom is considered as a core consisting of the nucleus and inner electrons, and a massless shell consisting of the outer electrons. The core and shell are linked by an harmonic interaction, related to the displacement of the core with respect to the centre of the shell, d:

$$E\left(d\right) = \frac{1}{2}Kd^2\tag{4}$$

where K is an adjustable parameter. Atoms comprising polyhedral units (MgO₆ and AlO₆ octahedra, and AlO₄ and SiO₄ tetrahedra) are held together by three-body potentials, which act against unrealistic distortions of the polyhedra, and are of the form

$$E\left(\theta\right) = \frac{1}{2}k\left(\theta - \theta_{0}\right)^{2} \tag{5}$$

where k is an adjustable parameter, and θ_0 is taken to be the ideal angle at the centre of the polyhedron (i.e. 90° for octahedral coordination and 109.47° for tetrahedral coordination).

Before proceeding with the calculation of any J parameters, it is first necessary to create a disordered model of the system, from which a data set of configurations (and hence values for E and $N_{\rm Al-Al}$) can then be generated. Disorder is represented by assigning to each site available for ordering a virtual occupancy corresponding to the statisticallydisordered (high-temperature) case; this is known as the "virtual crystal approximation" (VCA). In the case of tschermakite, this means that all the tetrahedral sites are occupied by 0.25 Al and 0.75 Si, and all octahedral sites by 0.4 Al and 0.6 Mg. Since tschermakite is not a naturally-occurring mineral, no cell parameters were available for the initial model. Instead, the cell parameters were extrapolated back from experimental cell parameters for tremolite (Hawthorne et al., 1997) and magnesiohornblende (Jenkins et al., 1997), assuming a linear relationship between compositions (Vegard's Law). The initial atomic coordinates used were those for glaucophane. The model was optimised with GULP at constant pressure (i.e. allowing the cell parameters to change), using the potential parameters in Table 1. Whilst in this study the optimised structure cannot be compared with an experimentally-determined one, its cell parameters were sensible for calcic amphiboles, and visual inspection of the structure with Cerius² showed that the atoms were in feasible positions with correct coordinations.

Calculation of J values and chemical potentials

As already specified above, this study investigates the effect of coupled ordering schemes (Al/Mg in the octahedra vs. Al/Si in the tetrahedra), and of the possible preference of Al for a particular type of site (T1/2, M1/2/3). It was thus necessary to use three sets of J values — namely for T–T, O–O and T–O interactions. The first stage of the process was to calculate a set of T–T interactions. Rather than calculating new O–O interactions, the values determined for glaucophane were used (Palin et al., 2003b); these are reproduced in Table 2. The second stage was to combine these O–O interactions with the calculated T–T interactions to enable the evaluation of the T–O interactions. Chemical potentials were also determined; as discussed below.

The ordering behaviour of tremolite-tschermakite was examined by beginning from a model of end-member tschermakite, despite the fact that it does not occur naturally. The reason for this is that compositions in the naturally-occurring part of the solid solution cannot be used for this purpose — tremolite because all sites are occupied by one species only, giving no capacity for cation ordering; and magnesiohornblende because the tetra-hedral occupancy is very dilute (Al:Si = 1:7), and would not result in a sufficient N_{Al-Al}^{i}

database from which to calculate the J_{T-T} parameters.

Calculation of T-T Js and chemical potential

To calculate the T–T interactions, the optimised VCA model of tschermakite was used to generate a data set of 90 configurations, each with Al and Si atoms randomly located on the tetrahedral sites and the VCA employed for the octahedral sites, since the behaviour of the octahedral cations was not known. These configurations were each then optimised with GULP.

The T–T interaction parameters were assigned by visual inspection of the tschermakite model using Cerius². Interactions within the same double chain were considered; examples of these are shown in Figure 2. In addition, interactions between sites in different double chains were included; these have been grouped according to the difference in the fractional x-coordinates of two interacting sites, here labelled w. Figure 3 illustrates the groupings: interactions with w = 0.59 operate between tetrahedral sites in the same I-beam, across the octahedral ribbon; w = 0.41 denotes interactions which operate between tetrahedra in Ibeams adjacent along x, and w = 0.09 shows interactions which operate between tetrahedra in I-beams adjacent along y. Examples of the assigned Js for inter-chain interactions are shown in Figures 4 and 5.

The distances over which all the T–T interactions operate are given in Table 3. Initially, the T1 and T2 sites were considered separately; the interaction parameters calculated are given in Table 4(a). However, as this Table shows, the separate values for J_1 T1–T1/ J_1 T1– T2, J_2 T1–T1/ J_2 T1–T2, J_3 T1–T1/ J_3 T2–T2 and J_4 T1–T2/ J_4 T2–T2 were within error of one another. Hence, these values were considered together, and a new fit performed (J_2 T2–T2 was not within error of the other J_2 values, so it was still considered separately). The J values resulting from this new fit are given in Table 4(b).

The quality of the fit is shown in Figure 6, the R^2 values are 0.956 for the initial model

and 0.953 for the simplified model. This shows that the simplification does not affect the quality of the fit, so the second set of Js, from the simpler model, were used in all subsequent investigations. Additionally, both the sign and the magnitude of $\mu(T1)$ are approximately the same in both fits.

Calculation of T–O Js and chemical potentials

Having the calculated T-T interaction parameters, the next stage of the process was to calculate the T–O Js, so that a complete model of tschermakite could be constructed (using the O–O Js from glaucophane). The set of T–O interactions (Table 5) was chosen so that it includes the nearest- and next-nearest T–O neighbours for all possible types of T–O interaction (i.e. all permutations between T1/T2 and M1/M2/M3). Nearest-neighbour T–O interactions are labelled J_{1a} , J_{1b} etc.; next-nearest neighbour T–O interactions are labelled $J_{\rm b}$, $J_{\rm c}$ etc. Again, this encompasses interactions between sites in the same I-beam, and between sites in different I-beams (see Figures 7 and 8). The chemical potentials were chosen to be $\mu(M1)$, $\mu(M2)$ and $\mu(T1)$; only three chemical potentials are required. In general, if there are n types of site across which ordering can occur, there are n-1independent chemical potentials. In tschermakite, there are five site types, but there are three chemical potentials, not four: exchange of Si and Mg between the tetrahedral and octahedral sites is not expected in amphiboles, and this effectively adds a further constraint to the chemical potentials. To put it another way, there are three octahedral site types, leading to two independent octahedral chemical potentials, and two tetrahedral site types, leading to one independent tetrahedral chemical potential.

For the calculation of the T–O Js, a new data set of 90 configurations was generated, with Al and Si randomly located across the tetrahedral sites and Al and Mg randomly located across the octahedral sites. The VCA can no longer be used for the octahedral sites since interactions are now being counted between octahedra and tetrahedra; the octahedral occupancy did not affect the previous count of interactions between tetrahedra only. The inclusion of a new set of configurations also effectively increases the size of the overall data set used, since overall there is a large number of fitted parameters and the number of configurations should be considerably larger than the number of parameters. The fit included all the T–T Js (using the simplified set from Table 4(b)), all the O–O Js from glaucophane, and the T–O Js shown in Figures 7 and 8. Although all parameters were included in the fit, only the T–O interactions and the chemical potentials were allowed to vary (as well as the E_0 value).

The set of T–O Js and chemical potentials obtained by this fitting procedure is given in Table 6, and the R^2 value for this fit was 0.83. The nearest-neighbour interactions are all large and negative, implying favourable Al–Al interactions across such distances.

SIESTA calculations

In our previous study of glaucophane, we found that there was a discrepancy between the chemical potentials that were calculated via the empirical method (GULP) and those calculated using the *ab initio* code SIESTA. In some respects this was a little surprising, because we had anticipated that the empirical models would be capable of handling the energetics of ordering between chemically similar sites (unlike the case where cations order between sites of different coordination number). Therefore, in the present study we tested our empirical models on this point by calculating chemical potentials for the tschermakite system using both empirical and *ab initio* methods following the approach used in our study of glaucophane.

For the SIESTA calculations, eight ordered configurations were produced, and optimised. As was the case with glaucophane, the configurations were chosen so that they were significantly different from one another in an attempt to compensate for the small number of configurations. Four of them had Al on T1, and four had Al on T2; for each set of four, the octahedral Al was incorporated on either M1, M2, $\frac{1}{2}M2 + M3$, or $\frac{1}{2}M1 + M3$. The pseudopotentials used were produced for other systems: Mg from MgO and Si from solid silicon (Anglada et al., 2002), Al from alumina, Ca from calcite, and O and H from water simulations (all unpublished data). The basis sets were DZP in each case, with semi-core states included for the Ca atoms, and calculations were performed with the generalised gradients approximation (GGA).

To determine the chemical potentials, we considered the separate contributions to the energy:

$$E = E_0 + E_{\rm TT} + E_{\rm OO} + E_{\rm TO} + E_{\mu} \tag{6}$$

from which it is assumed that the difference between the exchange energy $(E_{\rm TT} + E_{\rm OO} + E_{\rm TO})$ and the total energy E of a configuration is due to differences in the value of E_0 , the constant term, and E_{μ} , the energy due to the chemical potential. For each configuration, the exchange energies, computed from the J and $N_{\rm Al-Al}$ values, were subtracted from the energies of the relaxed structures calculated using SIESTA. The value of μ_3 was set to zero as an arbitrary origin, and the values of E_0 , μ_1 and μ_2 were adjusted to give the least discrepancy between the SIESTA energy and the sum of E_0 , the exchange energy and the chemical potential energy. This procedure led to a level of agreement represented in Figure 9, the correlation coefficient R^2 is 0.81.

The μ values obtained are given in Table 7. As it happens, these values are not too different from those calculated with GULP (hence the similar R^2 values, 0.83 and 0.81). Contributions to the chemical potentials from elastic (strain) effects and those from bonding effects can have different degrees of significance in different systems, the former being modelled well by GULP and the latter being modelled well by SIESTA. Where the agreement between the two methods is high, one can infer that the tschermakite chemical potentials are mostly due to strain (size-related effects).

Finally, as was the case for glaucophane, it should be noted that the energy contribution from the J values is of the same order of magnitude as that from the chemical potentials, so the behaviour of the system cannot simply be predicted from the J values or chemical potentials alone; both contributions must be included.

Monte Carlo simulations

The procedure employed in the Monte Carlo (MC) simulations is explained in detail in an earlier review paper (Warren et al., 2001). The program used to perform the simulations is OSSIA, see http://www.esc.cam.ac.uk/ossia for details. We will not consider the details of the MC simulation process here, but we note that for the purposes of the MC simulations, it is more convenient to express the energy of the system in the following form:

$$E = \sum_{\langle i,j \rangle} J_{ij} S_i S_j + \sum_j \mu_j S_j \tag{7}$$

In Equation 7, the quantity S denotes a site variable which is defined to be 1 if the site is occupied by Al and zero otherwise. J_{ij} is the interaction parameter between site i and site j, with the angle brackets $\langle \dots \rangle$ denoting that no interaction is counted twice, and μ_j is the chemical potential associated with a particular site j. Equation 7 is thus equivalent to Equation 1, with the omission of the constant term E_0 , which does not affect the ordering process and therefore does not need to be included in the MC simulations. Implicit in this formalism is the representation of the system of interest as a set of spins interacting with a specified connectivity and specified energies of interaction (the J parameters); these spins are then mapped onto a crystal structure at the end of the simulation.

OSSIA can output the thermodynamic averages of the energy $\langle E \rangle$ and order parameter $\langle Q \rangle$ of the system at a particular temperature, together with the mean squared values

 $\langle E^2 \rangle$ and $\langle Q^2 \rangle$. These quantities are useful since they allow direct calculation of the heat capacity C and susceptibility χ of the system:

$$\chi = \frac{\langle Q^2 \rangle - \langle Q \rangle^2}{k_{\rm B}T} \tag{8}$$

$$C = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_{\rm B} T^2} \tag{9}$$

At a phase transition, there will be anomalies in both the heat capacity and susceptibility, thereby enabling one to determine whether or not a system exhibits a phase transition by examining the simulation data.

In this work, we have performed several MC simulations for tschermakite. The first simulation is of one isolated tetrahedral double chain, excluding interactions with other chains. This system is interesting because it can be considered as a quasi-1D system, and it is a well-known result that 1D systems do not exhibit phase transitions.

The second simulation is of interacting tetrahedral double chains. This increases the dimensionality of the system. Our interest here is in investigating whether interacting chains will still order in the same pattern as the non-interacting chain, and whether the inter-chain interactions constrain the order in one chain with respect to that in the next. Previous work on muscovite (Palin et al., 2001) suggested that ordering within one sheet of tetrahedrally-coordinated cations occurred independently of neighbouring sheets — interactions between sheets were much weaker than those within sheets. One might expect the quasi-1D tetrahedral chain to show different behaviour from the muscovite sheet, which is effectively two-dimensional.

Finally, the whole set of calculated parameters is combined, and whole-cell simulations performed. This is a realistic model of the behaviour of the whole system, and it should give several insights — whether the T–O interactions affect the ordering seen in the tetrahedral sheet; if so, what the nature of the new ordering behaviour is; whether the system undergoes any phase transitions; and whether any comparisons can be drawn with experimentallyobserved behaviour. A final whole-cell simulation is performed for magnesiohornblende, in order to investigate any differences between its overall behaviour and that of tschermakite.

Results

Monte Carlo simulations of tschermakite

Simulation of an isolated tetrahedral double chain

Since the tetrahedral double chain is a quasi-1D system, we performed some MC simulations of simpler chains, in order to draw comparisons with the real system. These simulations were of chains based on a square lattice, with varying widths W (see Figure 10). A 1:1 ratio of atoms was used, and interactions were defined only between nearest-neighbour atoms. The results for the 1D case (i.e. W = 1) and for W = 2, 3, 4, 8 are shown in Figure 11; it can be seen from these results that there is no phase transition in the 1D system, nor in any of the quasi-1D systems — although the rapid drop to zero of the order parameter suggests that phase transitions occur, the heat capacity graphs are characteristic broad, asymmetric peaks ("Schottky anomalies"), not the divergent peaks one would associate with a phase transition. Results for a 2D simulation (that is, $W = \infty$) are also shown in Figure 11; the sharper heat capacity anomaly is clearly visible. The results for the 1D and 2D systems are in exact agreement with the well-known theoretical results for 1D and 2D Ising models.

The tetrahedral double chain is topologically similar to the W = 2 case, but with every other cross-link missing. The two systems are not identical because only one J value (that for nearest neighbours) was used in the W = 2 case, whilst the simulation of the real system used the first five J values (i.e. all the intra-chain interactions), and $\mu(\text{T1})$ from Table 4(b). Furthermore, the composition of the double chain was that of tschermakite, i.e. Al:Si = 1:3, and not 1:1 as in the test cases. The double chain simulation results for the heat capacity show two Schottky peaks superimposed on one another, but no anomaly corresponding to a phase transition. Representative examples of the chain configurations at different temperatures are shown in Figure 12, and for further clarification, Figure 13 shows the evolution of the numbers of each type of interaction as a function of temperature, together with the heat capacity profile. These figures show that at the lowest temperatures, all Al occurs on the T1 sites, interacting via J_3 interactions. This gives rise to a "para" arrangement of Al atoms. At slightly higher temperatures, Figure 12 shows that some J_2 interactions begin to occur, giving rise to some "meta" configurations; there are considerable numbers of "meta" configurations as T increases. The "meta" configurations result in an increase in the energy, however, which is a less favourable situation than the 100% "para" configuration. The presence of both configurations is consistent with NMR measurements of pargasite (Welch et al., 1998), which has the same Al:Si ratio as that simulated.

Visual examination of the configurations in Figure 12 suggests that the first Schottky peak in Figure 13 corresponds to the formation of J_2 linkages (and hence the generation of some "meta" configurations); it is somewhat less straightforward to determine the origin of the second, broader Schottky peak.

Simulations of a system of interacting tetrahedral double chains

The next stage of the investigation was to include the interactions between tetrahedral double chains. Hence, this simulation included all the Js and $\mu(T1)$ in Table 4(b). In this system, a phase transition occurs, with Al atoms ordering onto T1 sites, interacting via J_3 interactions (the "para" configuration mentioned above). Figure 14 shows the sudden changes in the numbers of certain interactions — at low T all the intra-chain Al interactions

are J_3 , but a sudden decrease in nJ_3 (and corresponding sudden increase in nJ_2 (T1–T1,T1–T2)) can be seen with increasing T.

The low-temperature ordering within one chain in a simulation with interacting tetrahedral double chains is therefore the same as that in a simulation of just one tetrahedral double chain, although the isolated chain simulation has no phase transition and the interacting chains do. The similarly-ordered structures do not imply that the inter-chain interactions are insignificant; in fact, the converse is true: most of the inter-chain parameters are large and positive, so they are energetically not favoured. This is reflected in the nJ plot in Figure 14 which shows the occurrences of most of the inter-chain interactions decreasing to zero with decreasing T. Conversely, the smallest of the inter-chain parameters is J_7 , and this is manifested by an increase in the number of J_7 interactions with decreasing T. Inspection with $Cerius^2$ of the ordered state reveals that the ordering in each I-beam does line up with respect to that in the next, with Al atoms interacting by means of J_7 interactions. J_7 is a T1–T1 interaction between I-beams; a straight line drawn between the two interacting T1 sites is approximately equidistant from three "A" sites (which are vacant in these structures), yet all the other inter-I-beam interactions are unfavourable. It is clear from the values of J_{13} and J_{14} that interactions between tetrahedral sites in different chains but the same I-beam are unfavourable, an interesting fact given that these sites are separated by the octahedral ribbon. These facts all illustrate that there are many complicated controls on the behaviour.

Whole-cell simulations

The final simulations on tschermakite included the T-T interactions from Table 4(b), the T-O interactions from Table 5 and the O-O interactions from glaucophane (Table 2). The chemical potentials used were those from Table 7.

The simulation results indicate that there is no ordering phase transition in tschermakite

— the heat capacity profile shows a Schottky anomaly. Figure 15(a)) shows the evolution of the number of certain Js of various types as a function of temperature; all of these Js show a continuous change with temperature. Also shown is a plot of the Al site occupancies as a function of temperature (Figure 15(b)). These occupancies are derived from order parameter variations in the simulation; the plot shows that there is little variation. These site occupancies suggest an Al preference for the T1 site over the T2 site (T1:T2 \approx 60:40) and for the M2 site over the M1 and M3 sites (M1:M2:M3 \approx 30:60:10).

Monte Carlo simulations of magnesiohornblende

In the whole-cell MC simulation of magnesiohornblende, the J and μ values used were the same as those for the tschermakite whole-cell simulations, with the only difference between the two simulations being the compositions.

In contrast with the tschermakite simulations, the changes in the nJ plot (Figure 16(a)) for magnesiohornblende are somewhat more obvious. In particular, the numbers of $J_2(T1-T1, T1-T2)$ and J_3 linkages are high at high temperature, but drop to zero as T decreases. The numbers of O–O interactions can also be seen to diverge at $T \sim 1700$ K, where e.g. the $J_{1-4}(O-O)$ interactions are increasing in number and the $J_5(O-O)$ interactions are decreasing in number. In spite of these changes in the nJ plot, this probably does not indicate a phase transition — the changes are not discontinuous, and visual examination of randomly-selected ribbons of tetrahedra and octahedra shows a small amount of shortrange order and occasional medium-range order, but no long-range order. Moreover, the heat capacity anomaly for magnesiohornblende is not dissimilar from that in tschermakite, where there was definitely no phase transition.

The Al site occupancy plot (Figure 16(b)) shows that over experimentally-viable temperatures (i.e. < 2000 K), the simulated Al site occupancy of the M2 site is $\sim 60\%$, and that of the T1 site is $\sim 70-80\%$. There is also a significant amount of Al at M1 ($\sim 30\%$).

Discussion

The aluminous tremolite model formulated here is the most complex model that we have studied, with a total of 38 J values and three chemical potentials. Both whole-cell simulations suggest an Al preference for T1 over T2, and for M2 over M1 and M3. It is not possible to compare the tschermakite results with experiments, since tschermakite is a fictive end-member, not realised as a macroscopic phase in nature or experiment. However, experiments on magnesiohornblendes are in agreement with this simulated T1 preference. The consistency with experimental data is not as clear for octahedral sites. Experimental studies of ^[6]Al occupancy have always concluded that Al should occur at M2, but the issue of M1/M3 occupancy has been somewhat more difficult to resolve, with more recent studies concluding that Al can occur at M3 but not M1. Our simulations show Al at M2 in accordance with experiment, but the fact that the M1 component (~30%) is larger than that at M3 (~15%) is at odds with experimental findings. It is not clear from this work why this is the case, as the quality of the fit for the whole-cell model (Figure 9) was high, with $R^2 = 0.81$. The results presented here suggest that further study of these minerals may be necessary in order to rationalise their behaviour.

At first sight, the significant (20–30%) ^[4]Al at T2 in magnesiohornblende is unexpectedly high. However, minor Al at T2 occurs in some high-temperature, Al-rich calcic and sodic-calcic amphiboles. A ²⁹Si MAS NMR study (Welch et al., 1998) of tetrahedral ordering in calcic and sodic-calcic amphiboles considered fluoredenite, a sodic-calcic amphibole with the same tetrahedral Al:Si ratio as magnesiohornblende, and concluded that all Al occurred at T1. However, pargasite, with the same tetrahedral Al:Si ratio as tschermakite, was also studied; in contrast to fluoredenite, it was concluded that pargasite had as much as 0.55 Al per formula unit (i.e. just over 25% of the total ^[4]Al) at T2. The latter result was surprising, being unlikely on bond-valence grounds (Hawthorne, 1997), but confirmed later by neutron powder diffraction experiments (Welch and Knight, 1999). A suggested rationalisation of this situation was that in pargasite, at high temperatures, distortions can occur around the O4 atom (which is more underbonded if T2 = Al than if T2 = Si). Such distortions would allow a higher valence sum to be incident at O4. Fluoredenite, on the other hand, has only Mg on the M sites, and these divalent cations will result in a lower bond valence sum at O4 than in pargasite, so that, even at high temperatures, it is not possible to accommodate such a low sum.

A final noteworthy result of these simulations is that the T–O interactions in aluminous tremolites are shown to be important. They are of the same order of magnitude to the nearest-neighbour T–T and O–O interactions, and this supports the suggestion that coupling between Al in the octahedra and tetrahedra is at least as important in controlling ordering as are the T–T and O–O couplings. All the nearest-neighbour T–O interactions are negative, implying favourable Al–Al coupling between tetrahedra and octahedra. The correlated errors on the values unfortunately do not permit the singling out of any specific T–O coupling as being more important than others.

Conclusions

This paper has discussed the application of a computer simulation approach to studying the behaviour of complex amphiboles. The complex model we have formulated incorporates a large number of variables. Simulations of an isolated tetrahedral double chain yielded interesting results with respect to the dimensionality of the system. The extension of the model to a system of interacting tetrahedral double chains produced different thermodynamic behaviour, but the same intra-chain cation distribution at low temperatures, which demonstrates the complexity of the controls on the ordering behaviour of the system. Finally a whole-cell model was simulated, with interactions between tetrahedra, interactions between octahedra and interactions between the two. Neither the tschermakite nor the magnesiohornblende compositions exhibited a phase transition. Additionally, the simulation of interacting chains exhibits a phase transition, while the whole-cell model does not — this shows that the incorporation of T–O interactions results in different behaviour from that observed in T-only and O-only simulations. We also observed this phenomenon in our study of Al/Mg and Al/Si ordering in phengite (Palin et al., 2003a).

By considering whole-cell simulations of aluminous tremolites, we have shown some simulation results for magnesiohornblende which compare reasonably well with experimental results from real samples. A particular advantage of this work is that it has been possible to model the site occupancies for each crystallographic site, which is difficult to achieve by experiment, and there was reasonable agreement at experimentally-viable temperatures between most of the magnesiohornblende site occupancies and corresponding values from experiment.

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Figure 1: (a) The amphibole structure viewed down z. The M4 (six- to eight-fold), tetrahedral and octahedral sites are labelled (M1 is obscured by the M2 and M3 sites in this projection), and the A site is shown as vacant (dotted circle) here. The box indicates the unit cell, and also shown at the bottom right (in cartoon form) is one "I-beam" unit. (b) The octahedral ribbon showing M1–3 sites. (c) The tetrahedral double chain showing T1 and T2 sites.



Figure 2: Examples of distances corresponding to J parameters for tschermakite intra-chain T–T interactions.



Figure 3: End-on view of tetrahedral double chains in the tschermakite structure (top), with cartoon view (bottom) showing groupings of inter-chain T–T interactions according to w, the difference in the fractional x-coordinates of interacting sites. Boxes indicate unit cells.



Figure 4: Projection on (100) of selected tetrahedral sites in tschermakite, showing examples of distances corresponding to J parameters for inter-chain w = 0.41 and w = 0.59 T–T interactions. Solid lines correspond to interactions for which w = 0.41, dotted lines to interactions for which w = 0.59. Box indicates unit cell.



Figure 5: Projection on (100) of selected tetrahedral sites in tschermakite, showing examples of distances corresponding to J parameters for inter-chain w = 0.09 T–T interactions. Box indicates unit cell.



Figure 6: Agreement between observed and calculated lattice energies for tschermakite (T–T Js). Left: initial model ($R^2 = 0.956$), right: simplified model with combined J parameters ($R^2 = 0.953$). Straight lines indicate perfect agreement.



Figure 7: Examples of distances corresponding to T-O J parameters between sites in the same I-beam. The tetrahedral double chain is shown in dark grey and an adjacent octahedral ribbon in light grey; the box indicates the unit cell.



Figure 8: Examples of distances corresponding to T–O J parameters between sites in different I-beams. Unit cell is indicated by the box.



Figure 9: Agreement between observed (GULP) and calculated lattice energies (model Hamiltonian, using chemical potentials from SIESTA) for the whole-cell tschermakite model. The straight line indicates perfect agreement. The correlation coefficient R^2 for this model is 0.81.



Figure 10: Example of a quasi-1D system — a chain with width W (W = 4 in this example), based on a square lattice, with periodic boundary conditions governing its length, but not its width. Interacting sites are joined by solid lines.



Figure 11: MC simulation results for simple square-lattice-based chains such as that in Figure 10. Order parameter (Q), heat capacity (C) and energy (E) results are shown.



Figure 12: Simulated structure of one tetrahedral double chain at various temperatures. Grey = Si, black = Al.



Figure 13: Plot of number of interactions of various types as a function of temperature, for a simulation of an isolated tetrahedral double chain. The heat capacity profile is also shown.



Figure 14: Plot of number of interactions as a function of temperature, for a simulation of interacting tetrahedral double chains.



Figure 15: (a) Evolution of numbers of Js as a function of temperature for selected interactions in the tschermakite whole-cell simulation. (b) Evolution of tschermakite Al site occupancies with temperature.



Figure 16: (a) Evolution of numbers of particular interactions with temperature for selected interactions in the magnesiohornblende whole-cell simulation. (b) Evolution of Al site occupancies with temperature in magnesiohornblende.

| Type and species ^{a} | | Para | meter values | | $\operatorname{Reference}^{b}$ |
|--|-----------------------------------|---------------------------------------|------------------------------------|---------------------------------------|--------------------------------|
| Buckingham: | A (eV) | ρ (Å) | $C \text{ (eV Å}^{-6})$ | | |
| Si c $-$ O1 c | 999.9 | 0.3012 | 0 | - | 1 |
| Si c $-$ O2 s | 1283.907 | 0.3205 | 10.66 | | 1 |
| Al c $-$ O1 c | 1142.677 | 0.2991 | 0 | | 2 |
| Al c $-$ O2 s | 1460.3 | 0.2991 | 0 | | 1 |
| O2 s - O2 s | 22764 | 0.149 | 27.88 | | 1 |
| O1 c – O2 s | 22764 | 0.149 | 27.88 | | 1^c |
| O1 c – O1 c | 22764 | 0.149 | 27.88 | | 1^c |
| H c $-$ O2 s | 311.97 | 0.25 | 0 | | 1 |
| Mg c – O1 c | 1142.677 | 0.2945 | 0 | | 3 |
| Mg c - O2 s | 1428.5 | 0.2945 | 0 | | 1 |
| Ca c - O2 s | 2272.74 | 0.2986 | 0 | | 4 |
| Ca c – O1 c | 2272.74 | 0.2986 | 0 | | 4^c |
| Spring (core-shell): O2 c – O2 s | $\frac{K \ (eV \ Å^{-2})}{74.92}$ | | | | 3 |
| <i>Morse:</i> O1 c – H c | $\frac{D(\text{eV})}{7.0525}$ | α (Å ⁻¹) 2.1986 | r_0 (Å) 0.9485 | $\frac{r_{\rm max}~({\rm \AA})}{1.4}$ | 1 |
| Three-body: | $k \; (eV \; rad^{-2})$ | $	heta_0~(^\circ)$ | $r_{\rm max}(1-2) \ ({\rm \AA})^d$ | $r_{\rm max}(1-3)$ (Å) | |
| $O - Si c - O^e$ | 2.0974 | 109.47 | 1.8 | 3.2 | 1 |
| O - Al1 c - O | 2.0974 | 109.47 | 1.95 | 3.4 | 1^f |
| O - Al2 c - O | 2.0974 | 90 | 2.2 | 3.2 | 1 |
| O – Mg c – O | 2.0974 | 90 | 2.2 | 3.2 | 3 |
| | | | | | |

^{*a*} c = core, s = shell.

^b References: 1 — Winkler et al. (1991), 2 — Schröder et al. (1992), 3 — Sainz-Diaz et al. (2001), 4 — Bush et al. (1994).

 \hat{c} Assumed by analogy with similar potentials in specified reference.

^d $r_{\text{max}}(1-2) = r_{\text{max}}(2-3)$. ^e "O" denotes any oxygen atom (O1 or O2).

 $f_{\rm max}$ values modified from potential in specified reference.

Table 1: Parameters used in interatomic potentials (Equations 2–5).

| Parameter | Distance (Å) | Type | Value (eV) |
|-----------|--------------|--------------|------------|
| J_1 | 3.077 | Intra-ribbon | 0.60(3) |
| J_2 | 3.098 | Intra-ribbon | " |
| J_3 | 3.107 | Intra-ribbon | " |
| J_4 | 3.148 | Intra-ribbon | " |
| J_5 | 5.313 | Intra-ribbon | 0.20(3) |
| J_6 | 5.369 | Inter-ribbon | -0.02(5) |
| J_7 | 5.400 | Intra-ribbon | 0.23(4) |
| J_8 | 6.155 | Intra-ribbon | 0.21(4) |
| J_9 | 6.176 | Intra-ribbon | 0.21(3) |
| J_{10} | 6.296 | Intra-ribbon | 0.20(11) |
| J_{11} | 6.325 | Inter-ribbon | 0.02(5) |
| J_{12} | 6.652 | Inter-ribbon | 0.01(5) |
| J_{13} | 7.267 | Inter-ribbon | -0.01(5) |
| J_{14} | 7.381 | Inter-ribbon | 0.01(2) |

Table 2: Assigned J parameters for glaucophane. Figures in brackets indicate the standard error on the final digit. Taken from Palin et al. (2003b).

| | | T | | |
|-------------|------------------------|-------------------|-------------|------|
| Parameter | Distance (A) | Interacting sites | Type | w |
| J_1 T1–T1 | 3.0653 | T1-T1 | Intra-chain | - |
| J_1 T1–T2 | 3.0565 & 3.1165 | T1-T2 | Intra-chain | — |
| J_5 | 3.5809 | T2-T2 | Inter-chain | 0.09 |
| J_6 | 3.9074 | T2-T2 | Inter-chain | 0.41 |
| J_7 | 4.058 | T1-T1 | Inter-chain | 0.41 |
| J_8 | 4.2459 | T2-T2 | Inter-chain | 0.09 |
| J_9 | 4.3855 | T1-T2 | Inter-chain | 0.09 |
| J_{10} | 4.5425 | T1-T2 | Inter-chain | 0.41 |
| J_{11} | 5.0856 | T1-T1 | Inter-chain | 0.41 |
| J_2 T1–T1 | 5.3171 | T1-T1 | Intra-chain | — |
| J_2 T2–T2 | 5.3171 | T2-T2 | Intra-chain | _ |
| J_2 T1–T2 | $5.3236 \ \& \ 5.3583$ | T1-T2 | Intra-chain | _ |
| J_{12} | 5.4892 | T1-T2 | Inter-chain | 0.41 |
| J_{13} | 5.5727 | T1-T1 | Inter-chain | 0.59 |
| J_{14} | 5.7263 | T2-T2 | Inter-chain | 0.59 |
| J_3 T1–T1 | 6.1374 | T1-T1 | Intra-chain | _ |
| J_3 T2–T2 | 6.198 | T2-T2 | Intra-chain | _ |
| J_4 T1–T2 | 8.094 & 8.162 | T1-T2 | Intra-chain | _ |
| J_4 T2–T2 | 8.166 | T2-T2 | Intra-chain | _ |

Table 3: Distances corresponding to T–T J parameters for tschermakite.

| (a) |
|-----|
|-----|

| (| b) |
|---|--------|
| | \sim |

| Parameter | Value (eV) | | Parameter | Value (eV) |
|-------------|------------|---------|-------------------|------------|
| J_1 T1–T1 | 1.05(9) | | J_1 | 0.98(4) |
| J_1 T1–T2 | 0.96(4) | J_{2} | $_{2}T1-T1,T1-T2$ | 0.13(4) |
| J_5 | 0.24(8) | | J_2 T2-T2 | 0.29(7) |
| J_6 | 0.28(7) | | J_3 | 0.08(5) |
| J_7 | 0.03(8) | | J_4 | 0.01(3) |
| J_8 | 0.16(7) | | J_5 | 0.26(8) |
| J_9 | 0.19(5) | | J_6 | 0.28(7) |
| J_{10} | 0.32(5) | | J_7 | 0.03(8) |
| J_{11} | 0.21(8) | | J_8 | 0.16(7) |
| J_2 T1–T1 | 0.09(6) | | J_9 | 0.21(5) |
| J_2 T2–T2 | 0.30(8) | | J_{10} | 0.33(5) |
| J_2 T1–T2 | 0.16(4) | | J_{11} | 0.17(8) |
| J_{12} | 0.25(6) | | J_{12} | 0.25(6) |
| J_{13} | 0.45(8) | | J_{13} | 0.42(7) |
| J_{14} | 0.38(8) | | J_{14} | 0.36(7) |
| J_3 T1–T1 | 0.15(7) | | $\mu({ m T1})$ | -0.50(7) |
| J_3 T2–T2 | 0.03(9) | | | |
| J_4 T1–T2 | 0.00(4) | | | |
| J_4 T2–T2 | 0.02(6) | | | |
| $\mu(T1)$ | -0.54(11) | | | |

Table 4: (a) J and μ values for initial model with separate consideration of T1 and T2 sites. (b) J and μ values for simpler model with some combination of Js with similar values. Figures in brackets represent the standard error on the final digit.

| Parameter | Distance (Å) | Type |
|-------------------|--------------|--------------------------|
| $J_{1\mathrm{a}}$ | 3.18 | T1–M3, same I-beam |
| $J_{ m 1b}$ | 3.185 | T1–M1, same I-beam |
| $J_{ m 1c}$ | 3.216 | T1–M2, same I-beam |
| $J_{ m 1d}$ | 3.217 | T2–M1, same I-beam |
| $J_{1\mathrm{e}}$ | 3.222 | T2–M2, same I-beam |
| $J_{ m b}$ | 3.327 | T2–M2, different I-beams |
| $J_{ m c}$ | 4.42 | T1–M1, same I-beam |
| $J_{ m 1f}$ | 4.47 | T2–M3, same I-beam |
| $J_{ m d}$ | 5.123 | T2–M1, different I-beams |
| $J_{ m e}$ | 5.182 | T1–M2, different I-beams |
| $J_{ m f}$ | 5.384 | T1–M3, same I-beam |
| $J_{ m g}$ | 5.455 | T2–M3, same I-beam |

Table 5: Distances corresponding to T–O Js.

| Parameter | Value (eV) |
|-------------------|------------|
| $J_{1\mathrm{a}}$ | -0.6(2) |
| $J_{ m 1b}$ | -0.4(2) |
| $J_{ m 1c}$ | -0.4(2) |
| $J_{ m 1d}$ | -0.7(1) |
| $J_{1\mathrm{e}}$ | -0.4(2) |
| $J_{ m b}$ | -0.5(2) |
| $J_{ m c}$ | -0.1(2) |
| $J_{ m 1f}$ | -0.3(2) |
| $J_{ m d}$ | -0.1(2) |
| $J_{ m e}$ | 0.1(2) |
| $J_{ m f}$ | 0.0(2) |
| $J_{ m g}$ | 0.0(2) |
| $\mu(ext{M1})$ | 0.0(4) |
| $\mu(M2)$ | -0.3(5) |
| $\mu(T1)$ | -0.8(3) |

Table 6: T–O J and μ values as calculated from GULP. Figures in brackets represent the standard error on the final digit.

| Parameter | Value (eV) |
|-----------|--------------|
| $\mu(M1)$ | -0.2(2) |
| $\mu(M2)$ | -0.3(2) |
| $\mu(T1)$ | -0.7(1) |
| | |

Table 7: Chemical potentials for tschermakite, calculated using SIESTA.