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Energetics of ordering in aluminous pyroxenes

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Abstract

Electrostatic energy calculations were performed to obtain ordering energies for aluminous pyroxenes. Short-range ordering (SRO) energies were derived for Ca-Tschermak's pyroxene (CaTs), fassaite and omphacite by calculating energies for different arrangements of cations on a fixed framework for multiple cells of average structures. For CaTs, SRO energies obtained for the reaction AlAl + SiSi = 2AlSi are −73 kJ per mole (6-oxygen formula unit throughout) for pairs along the tetrahedral chains related by a *c* glide, −24 kJ per mole for the closest pairs between chains within the (100) plane related by an inversion center, and −9 kJ per mole for pairs between chains across M2 related by a 2-fold axis. For fassaite, the SRO energy obtained for the reaction between M1 and T, MgAl + AlSi = MgSi + AlAl, is −187 kJ per mole, while −38 kJ per mole was obtained for the reaction MgMg + AlAl = 2MgAl along octahedral chains. For omphacite, SRO energies are −36 kJ per mole for Al and Mg in M1, −10 kJ per mole for Na and Ca in M2, and −90 kJ per mole for the coupling of Na with Al and Ca with Mg between M1 and M2. In all cases pairs of cations with unlike valences are energetically favored relative to isovalent cation pairs. This electrostatic tendency is the energetic basis for the Al-avoidance principle.

Calculations for long-range ordering energies in Mg-Tschermak's pyroxene (MgTs) give 21 kJ per mole for exchange of Al from M1 to M2 with Mg, and a 41 kJ per mole preference for Al in TB and Si in TA versus the alternative.

Introduction

Energy calculations permit estimation of relative structural stabilities and ordering energies which are not directly accessible experimentally. They can supplement experimental methods such as X-ray diffraction, calorimetry, spectroscopy and phase equilibria studies and can help in understanding the microscopic forces behind experimental observations.

Many studies on silicates have concentrated on the long-range or coulomb part of the potential energy. For example, O'Neill and Navrotsky (1983) compared the coulomb energies of different oxide and silicate spinels. Brown and Fenn (1979) calculated energies for observed alkali feldspar structures. Other studies have included short-range repulsion terms, usually of the Born-Mayer type: $\lambda \exp(-r/\rho)$. Using potentials of this type Bish and Burnham (1984) calculated exchange or long-range ordering energies for cations in olivine. The repulsion parameters λ and ρ can be fit empirically to known structures (Catlow et al., 1982) or, as in this study, can be fit from quantum mechanical models such as the modified electron gas theory (MEG) (Muhlhausen and Gordon, 1981).

At zero pressure, the calculated energies correspond to enthalpies or internal energies if the atomic coordinates and the cell parameters are allowed to vary in order to minimize the energy. If the cell volume is fixed, the energies represent internal energies for the pressure which corresponds to the cell volume. There are strain energies as well when the cell parameters and atomic positions are not consistent with the energy minimum. The calculated energies refer to a standard state of infinitely separated ions, with shell stabilized O^{2-} ions.

It is not possible at this time to *directly* calculate ordering energies for disordered ionic solids. The coulomb potential decays slowly with distance, as 1/r, so that a direct pairwise sum of potentials which could allow for disordered states would have prohibitively slow convergence. For completely ordered structures, energies can be calculated using a rapidly convergent technique such as Ewald's method (Tosi, 1964). The virtual crystal method used by Brown and Fenn (1979) to calculate energies for disordered states, in which average cation valences are used for disordered sites, is of questionable accuracy (de Fontaine, 1979, p. 89). Methods such as the coherent potential approximation (Stocks et al., 1971; Ducastelle and Gautier, 1976; Faulkner, 1982; Gonis and Freeman, 1983) and the Cluster Bethe Lattice Method (Robbins and Falicov, 1984) have been used for qualitative and semi-quantitative calculations for disordered binary alloys. However, quantitative energy calculations on simple alloys using these techniques have not yet been published, nor have these techniques been generalized for use on disordered silicates or oxides. There is a fundamental difference between ordering in alloys and cation ordering in silicates: In alloys ordering is among

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nearest neighbor atoms but in silicates the cations are surrounded by oxygens, so that ordering is between next-nearest-neighbors.

Energies for disordered ionic solids are approximated by calculations for hypothetical supercells; energies are calculated for various long-range ordered configurations which have different next-nearest-neighbor cation probabilities. The effects of local disorder are estimated by examining the effects of next-nearest-neighbor cation occupancies on calculated energies. Using this method, Chamberlain et al. (1985) calculated ordering energies for scapolite. If the cation arrangements are parameterized in terms of long- and short-range order parameters, and the energies related to variations of these parameters, then energies for any state of order can be estimated. If the multiple cell is larger than the effective range of the short-range ordering energies, the repeat of the multiple cell has a negligible effect on the calculated energies; this can be verified by using different cell sizes.

In this study, energy calculations have been performed for the aluminous clinopyroxenes CaTs ($Ca^{M2}Al^{M1}(AlSi)^{T}O_6$), fassaite ($Ca_2^{M2}(MgAl)^{M1}(AlSi)_2^{T}O_{12}$) and omphacite ($(NaCa)^{M2}(MgAl)^{M1}Si_4O_{12}$) in order to investigate the energetics of short-range ordering in coupled solid solutions, in which ions of different valence substitute on the same sites. These are particularly interesting applications of energy calculations because the state of short-range order is not obtainable by direct macroscopic thermodynamic or microscopic crystallographic methods for complex minerals. Yet short-range order can have a profound effect on macroscopic and microscopic properties. Short-range ordering energies provide the thermodynamic driving force for phase changes such as the ordering transition and formation of anti-phase domains in omphacite. Short-range ordering in high-temperature long-range disordered phases can lead to a drastic reduction of the configurational entropy from that predicted by the Bragg–Williams model.

The application of energy calculations to ordering problems is more likely to be successful than applications in which energies for different mineral groups are compared. When energies for similar structures are compared, some errors in the form of the potential due to polarization and covalency effects may cancel out. Also, since these ordering reactions involve ions of different valence, the coulomb terms are of greater importance than the less well characterized repulsive terms. Calculation of short-range ordering energies in simple solutions is thus expected to be more uncertain.

In order to test the energetic basis for site preferences in aluminous enstatites, long-range ordering energies were calculated for the orthopyroxene MgTs $(Mg, Al)^{M2}(Mg, Al)^{M1}(Al, Si)^{TA}(Al, Si)^{TB}O_6$ in addition to the investigation of short-range ordering energies for clinopyroxene models. Based on analysis of bond distances, Takeda (1972) suggested that Al prefers the larger TB site over the TA site in aluminous orthopyroxene. Ganguly and Ghose (1979) have suggested that no detectable Al goes into TA in orthopyroxene but that significant amounts of Al go into the M2 site, again based on bond lengths. Direct site occupancy refinement by standard X-ray methods is difficult due to the similar scattering factors of Si and Al; there has not been any direct confirmation of the proposed site preferences.

Description of short-range order

Short-range versus long-range order

Long-range order is a function of the composition of each site in a crystal and is specified by the proportions of each type of atom in each crystallographic site. The term is frequently used in the case of convergent ordering; a crystal is said to be long-range ordered if two convergently similar sites have different site occupancies: the long-range order disappears at the transition to the higher symmetry structure. In the non-convergent case, in which the sites are crystallographically different even if they have the same site occupancies, such as TA and TB in orthopyroxene, or M1 and M2 in any pyroxene, long-range order parameters still give the proportions of atoms on each site; ordering is continuous as a function of temperature.

Short-range order is specified by probabilities for particular local configurations of atoms. For example, if P_{AlSi}, the probability of finding an AlSi next-nearest-neighbor pair in the crystal, is different from the random probability, the crystal is said to be short-range ordered. In this study a pair approximation is used; short-range order is described by parameters which are functions of the probabilities of particular next-nearest-neighbor pairs of cations. Crystallographically distinct types of pairs must be distinguished. Pair probabilities such as P(i, AlSi) state the probability of having an Al–Si pair of the "i" type. Pair probabilities are straightforward extensions of site-occupancy fractions (or point probabilities) commonly used to describe mixing in solid solutions (de Fontaine, 1979).

CaTs

The structure of synthetic CaTs was refined by Okamura et al. (1974). Although they refined CaTs in the space group $C2/c$, they discussed the possibility that ordering of Al and Si in the tetrahedral sites could lead to a reduction of symmetry to space group $C2$, $C\bar{1}$, $P2/n$, or $P2_1/n$. The presence of diffractions forbidden in $C2/c$ was determined to be due to double diffraction (Grove and Burnham, 1974). We have examined CaTs by transmission electron microscopy and have observed no violations of $C2/c$ symmetry. Thus it seems that CaTs is a $C2/c$ pyroxene with Ca in the 8 coordinated M2 site, Al in the octahedral M1 site, and Al and Si mixed in the T site. Each T site is surrounded by four next-nearest-neighbor T sites (see Fig. 1). Two of these four share common oxygens with the regarded T site and belong to the same tetrahedral chain oriented along the c axis. These pairs of tetrahedra are related by a c-glide and have a T–T distance of 3.125Å [represented by T1A–T2A] (Designations using the nomenclature of Burnham et al. (1967) are given in brackets here and below.) They are designated here as A pairs. The next closest T–T

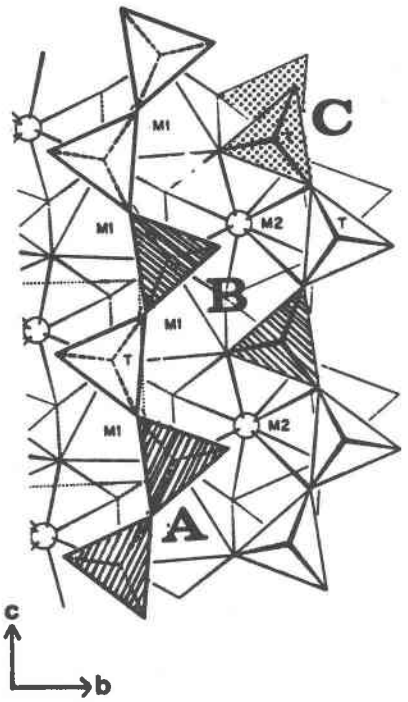

Fig. 1. Three types of next-nearest pairs of tetrahedra in *C2/c* clinopyroxene. The tetrahedra in the A pairs are related by a *c*-glide. Those in the B pairs are related by an inversion center. The C pairs are related by a 2-fold axis. After Cameron and Papike (1981).

distance is 3.421Å and is between neighboring chains within the (100) plane. These tetrahedra are related by the inversion center at 1/4, 1/4, 1/2 [represented by T1A–T2C]. This type of pair is designated as a B pair. The closest pairs between chains across M2, related by a 2-fold axis [represented by T1A–T1B], are 3.984Å apart and are designated C pairs. Thus, each T site is a member of 2 A pairs, 1 B pair and 1 C pair. (There are also pairs with distances of 4.2, 4.4, 4.7, 5.3 and 5.7Å, but the occupancies of these pairs were found to have minimal effect on the energy.)

The state of order is specified by the pair probabilities, but all the pair probabilities are not independent. There are three independent short-range order parameters, s(1), s(2) and s(3) corresponding to the A, B and C pairs, and are defined as:

$$s(i) = 2P(i, AlSi) - P(i, AlAl) - P(i, SiSi).$$

These parameters represent the extent of reaction for the equation:

$$AlAl + SiSi = 2AlSi.$$

For CaTs, the short-range order parameters can vary from -1 to 1 since there are equal numbers of tetrahedral Al and Si atoms. The value 1 represents complete short-range order (only Al–Si pairs), 0 is random and -1 represents complete segregation of Al and Si. In fassaites, solid solutions which do not have equal numbers of tetrahedral Al and Si, such parameters cannot vary from -1 to 1, and the value 0 will have no special meaning. Nevertheless, variations in these parameters still measure the extent of reaction for short-range order.

Fassaite

Fassaites are calcic clinopyroxenes containing appreciable amounts of the CaTs component. Peacor (1967) refined the structure of a natural fassaite containing ~75% Si and 25% Al in the T site, and appreciable transition metals in the M sites, in space group *C2/c*. Here the term fassaite is used in a restricted sense to represent the 50% CaTs, 50% diopside ($CaMgSi_2O_6$) composition; the M2 site contains Ca, the M1 site contains 50% Al and 50% Mg and the T site contains 25% Al and 75% Si. It is most convenient to use the same form for the tetrahedral Al–Si short-range order parameters as used for CaTs. For a random cation distribution in fassaite, each T–T short-range order parameter has the value -0.438 rather than 0 as in CaTs. Values between -0.438 and -1 represent segregation or clustering of Al and Si with greater probabilities for AlAl and SiSi pairs, and values between -0.438 and 0 represent ordering of Al and Si with a greater probability for AlSi pairs.

In fassaite, there are also pairs representing short-range order between M1 sites and T sites. Each M1 site is surrounded by 6 next-nearest-neighbor T sites and each T site is surrounded by 3 M1 sites. There are three different types of M1–T pairs at distances of 3.24, 3.26 and 3.44Å. The two shorter distances are for M1–T pairs that belong to the same I beam, while the longer distance is for the M1–T pairs between two I beams along **b**. The short-range order parameters s(4)–s(6) are defined by:

$$s(i) = P(i, MgSi) + P(i, AlAl) - P(i, MgAl) - P(i, AlSi)$$

for each type of M1–T pair.

Finally, the short-range order parameter s(7), for Mg and Al order along the octahedral M1 chain for pairs related by the *c*-glide is given by:

$$s(7) = 2P(7, MgAl) - P(7, MgMg) - P(7, AlAl).$$

The M1–M1 distance is 3.08Å.

Omphacite

At high temperatures, omphacite has the same *C2/c* structure as CaTs and fassaite. The M2 site contains 50% Na and 50% Ca, the M1 site contains 50% Al and 50% Mg, and the T site contains Si. There are 4 types of next-nearest-neighbor pairs in omphacite: s(1) is the short-range order parameter for M1–M1 pairs related by a *c*-glide at a distance of 3.08Å, s(2) is for M2–M2 pairs at a distance of 4.38Å related by a *c*-glide, s(3) is for M1–M2 pairs at 3.19Å [such as M1(1)–M2] and s(4) is for M1–M2 pairs [such as M1–M2] at 3.42Å. We define for omphacite:

$$s(1) = 2P(1, MgAl) - P(1, MgMg) - P(1, AlAl)$$

$$s(2) = 2P(2, NaCa) - P(2, NaNa) - P(2, CaCa)$$

$$s(3, 4) = P(3, 4, AlNa) + P(3, 4, MgCa) - P(3, 4, AlCa) - P(3, 4, MgNa).$$

Notice that s(1) for omphacite corresponds to s(7) for fassaite.

Methods

For each composition of clinopyroxene, energies were calculated for different cation arrangements on a fixed framework. For CaTs, the observed structure determined by Okamura et al. (1974) was used. For the other compositions, average *C2/c* structures were determined by distance least squares (DLS) (Bish and Burnham, 1984) using the program DLS76 (Baerlocher et al., 1978). The prescribed distances were obtained from known pyroxene structures and structural systematics given in Cameron and Papike (1981) and Clark et al. (1969). In each case, it was necessary to fix the cell parameters, because they were not well determined by the DLS procedure. For fassaite and omphacite, experimental cell parameters for synthetic pyroxenes of the proper compositions were used (Newton et al., 1977; Wood et al., 1980). For MgTs, the parameters were extrapolated from those of enstatite (Ganguly and Ghose, 1979) and pyrope composition pyroxene (Ohtani et al., 1981).

It was necessary to use a fixed structure rather than a minimum energy structure because of the ionic nature of the model. Burnham and Post (1983) have found that a purely ionic energy minimization on diopside results in an unrealistic structure in detail. This is probably because of neglect of polarization and covalency effects, particularly since pyroxenes contain over- and under-saturated oxygens in terms of Pauling's rules. Catlow et al. (1982) performed energy minimizations on diopside using empirical short-range potentials. However, they were satisfied with discrepancies of up to 0.25Å from the known diopside structure. Errors in ordering energies determined from energy minimized structures would be extremely difficult to ascertain, whereas the qualitative effects of using average structures are relatively straightforward (see below).

The repulsive parameters were obtained by fitting calculated MEG repulsive energies to a Born exponential (Burnham and Post, 1983). A shell stabilized O^{2-} wave function was used with a shell radius of 1.0Å. The parameters used are given in Table 1. The program WMIN (Busing, 1981), which calculates the coulomb energy using Ewald's method, was used for the energy calculations.

Energies were calculated for various arrangements of cations in hypothetical supercells. For CaTs, calculations were performed on cells with a doubled *c* cell dimension and on cells with a quadrupled *c* dimension, with a total sampling of 35 cation arrangements. Many more arrangements are possible. A smaller number of calculations were first performed for the doubled cell and the short-range ordering energies determined. After doubling the cell again and doing more calculations, the derived ordering energies did not change within error. Four of the cation arrangements correspond to complete ordering in the normal unit cell of tetrahedral Al and Si in space groups *C2*, C1, *P2/n* and $P2_1/n$. For fassaite and omphacite, a cell with a doubled *c* dimension was used: 49 calculations were performed on fassaite and 32 on omphacite. All cation arrangements for which energies were calculated were subsequently characterized by short-range order parameters. Multiple regressions of energies versus the short-range order parameters were then performed in order to see how well the variations in cohesive energies are predicted by the short-range order parameters.

Table 1. Repulsive energy parameters

	λ kJ/mole	ρ Å
Al - O	332420	0.2461
O - O	291020	0.2876
Si - O	358180	0.2428
Ca - O	671401	0.2516
Mg - O	359200	0.2457
Na - O	563227	0.2387

A different procedure was followed for MgTs. DLS structures were determined for three cases: Al in M1 and TB, Al in M2 and TB, and Al in M1 and TA. Prescribed bond distances for Si–O, Mg–O and O–O were taken from enstatite (Ganguly and Ghose, 1979), while those for Al–O were determined by multiplying the Mg–O or Si–O distances by the ratio of the cation–oxygen distances predicted from the ionic radii (Shannon and Prewitt, 1969).

Results

We find that the calculated cohesive energies can be represented very well by equations of the simple form: $E = E_o + \Sigma\ W(i)s(i)$. It is thus convenient to define W(i), the derivatives of the energy with respect to the short-range order parameters, $W(i) = \partial E/\partial s(i)$, as the short-range ordering energies. From these ordering energies, the ΔE for any short-range ordering reaction can be calculated for constant composition. The ordering energies are thus the coefficients of the short-range order parameters in multiple linear regressions. It was found that these derivatives are essentially constant as a function of the state of short-range order. Significance was tested with the T-test. Estimated standard deviations for the coefficients were calculated from the external estimate of the variance (Deming, 1943, p. 27) and the coefficients of determination, R^2, were calculated from the regression statistics.

The coordinates determined for the DLS structures used for the energy calculations are given in Table 2. Table 3 gives the ordering energies, estimated standard deviations and T-ratios for short-range ordering in CaTs, fassaite and omphacite. All energies are given as kJ per 6 oxygen formula unit.

For CaTs, the regression gives an R^2 of 87%. Four of the CaTs structures correspond to the completely ordered states discussed by Okamura et al. (1974). The calculated

Table 2. Results of distance least squares (DLS) refinements

Assumed Cell Parameters

	a	b	c	Beta
Fassaite	9.666	8.775	5.281	106.26
Omphacite	9.570	8.749	5.246	106.79
MgTs	18.099	8.475	5.196	90.00

Final Coordinates

	Fassaite			Omphacite		
	X	Y	Z	X	Y	Z
M1	0	0.9093	0.2500	0	0.9080	0.2500
M2	0	0.2923	0.2500	0	0.2993	0.2500
T	0.2919	0.0903	0.2349	0.2909	0.0928	0.2294
01	0.1166	0.0759	0.1361	0.1144	0.0804	0.1396
02	0.3520	0.2621	0.3194	0.3622	0.2568	0.3036
03	0.3629	0.0200	0.0014	0.3548	0.0124	0.0022

	MgTs: Al in M1 and TB			Al in M2 and TB			Al in M1 and TA		
	X	Y	Z	X	Y	Z	X	Y	Z
M1	0.3701	0.6605	0.8592	0.3743	0.6490	0.8537	0.3808	0.6631	0.8721
M2	0.3722	0.4992	0.3569	0.3700	0.5044	0.3446	0.3821	0.4971	0.3682
TA	0.2751	0.3439	0.0378	0.2751	0.3335	0.0715	0.2686	0.3574	0.0595
TB	0.4777	0.3536	0.7992	0.4710	0.3369	0.8082	0.4708	0.3413	0.8022
01A	0.1866	0.3266	0.0465	0.1870	0.3380	0.0277	0.1759	0.3280	0.0602
01B	0.5705	0.3263	0.8266	0.5654	0.3444	0.8086	0.5598	0.3291	0.8138
02A	0.3096	0.5166	0.0328	0.3085	0.5071	0.0536	0.3187	0.5236	0.0465
02B	0.4276	0.5037	0.6874	0.4223	0.4723	0.6454	0.4355	0.5014	0.7037
03A	0.3089	0.2309	0.8094	0.3101	0.2106	0.8589	0.3053	0.2155	0.8526
03B	0.4460	0.1900	0.6155	0.4473	0.1619	0.6394	0.4412	0.2016	0.5994

stabilities are given in Table 4; the order of relative stability was found to be $P2_1/n > C2 > C\bar{1} > P2/n$. For fassaite, the three ordering energies which correspond to ordering reactions in CaTs were taken as equal to those in CaTs. It was found that the three ordering energies between M1 and T corresponding to s(4) − s(6) were statistically indistinguishable. Thus in the final regression these were accounted for as a single M1–T ordering energy. The regression gave an R^2 of 96%. The regression for omphacite gave an R^2 of 92% using the four short-range order parameters. It can be seen that the ordering energy per pair is essentially identical for the two types of M1–M2 pairs in omphacite. In summary, a simple linear model gives highly significant regressions between calculated cohesive energies for different cation distributions in a fixed structure and the short-range order parameters derived from each distribution.

The DLS coordinates determined for ordered MgTs are given in Table 2 and the cohesive energies are given in Table 4. These give −21 kJ per mole for the exchange reaction:

$$Al^{M2} + Mg^{M1} = Mg^{M2} + Al^{M1}$$

and −41 kJ per mole for the reaction:

$$Al^{TA} + Si^{TB} = Si^{TA} + Al^{TB}.$$

Table 3. Short-range ordering energies

		Pairs per 6 O	Reaction	S.R.O. Energy kJ/6 O (esd)	T Ratio
CaTs	W1	2	AlAl + SiSi = 2AlSi	-73(5)	-14.0
	W2	1	AlAl + SiSi = 2AlSi	-24(4)	-5.5
	W3	1	AlAl + SiSi = 2AlSi	-9(4)	-2.3
Fassaite	W4	6	AlSi + MgAl = AlAl + MgSi	-187(7)	-26.7
	W5	1	MgMg + AlAl = 2MgAl	-38(2)	-22.1
Omphacite	W1	1	MgMg + AlAl = 2MgAl	-36(3)	-12.0
	W2	1	NaNa + CaCa = 2NaCa	-10(3)	-3.4
	W3	2	NaMg + CaAl = NaAl + CaMg	-60(5)	-11.7
	W4	1	NaMg + CaAl = NaAl + CaMg	-30(4)	-7.2

Discussion

Short-range ordering energies in clinopyroxenes

The high R^2 values of the regressions show that, to a very good approximation, the configurational energy can

Table 4. Stability of ordered CaTs and MgTs structures

	Long-range Ordering			
	CaTs		MgTs	
Space Group	Cohesive Energy kJ/6 O mole		Cation Arrangement	Cohesive Energy kJ/6 O mole
$P2_1/n$	-32909		Al in M1 and TB	-33055
$C2$	-32903		Al in M2 and TB	-33034
$C\bar{1}$	-32884		Al in M1 and TA	-33014
$P2/n$	-32856			

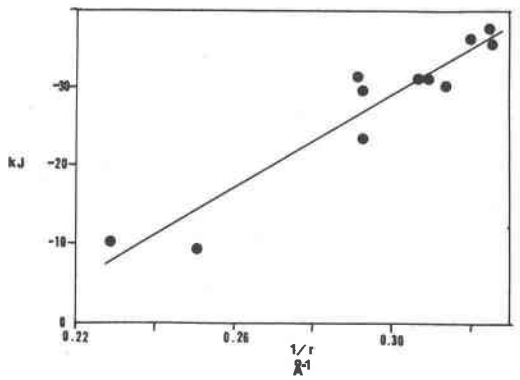

Fig. 2. Short-range ordering energies in kJ per pair per 6 oxygen mole versus 1/r. 'r' is the distance in ångströms between the two sites of a pair.

be taken as a function of the next-nearest-neighbor pair probabilities. It does not appear necessary to include higher coordination shells or many-body interactions in spite of the long-range nature of the coulomb potential. The ordering energies are plotted against 1/r in Figure 2. A linear relationship holds (within error) giving a regression equation ($R^2 = 91\%$) of:

$$E(\text{kJ/pair 6 O mole}) = 60.8 - 300(1/r(\text{Å})).$$

This equation can be used to estimate the interionic coulomb contribution to the short-range ordering energies in pyroxenes involving heterovalent substitutions of other cations and vacancies, over the distance range examined here.

For each short-range ordering reaction, it is found that next-nearest-neighbor cations of different valence are energetically favored over cation pairs of the same valence. This preference arises from electrostatics since the short-range ordering reactions involve the effective transfer of one electron of charge between pairs. The potential for each pair interaction is: $q_1q_2/\varepsilon_{eff}r_{12}$, where the q's are the ionic charges, r_{12} is the distance between the ions and ε_{eff} is an effective dielectric constant (Kröger, 1964). This gives an energy preference of $e/\varepsilon_{eff}r_{12}$, where e is the charge on an electron, for cation pairs of unlike valence over like cation pairs.

The electrostatic preference for next-nearest-neighbor cation pairs with unlike valence provides an energetic basis for the aluminum avoidance principle proposed by Lowenstein (1954). Laves and Goldsmith (1955) suggested an electrostatic basis for the preference of Al–Si pairs by referring to Pauling's rules. However, Smith (1974, p. 78–79) pointed out that even in ordered anorthite, Pauling's second rule cannot be rigorously obeyed and he questioned the uncritical acceptance of the "so-called" aluminum avoidance rule. Indeed, there is probably nothing particularly unfavorable about Al–Al pairs so that the term Al-avoidance is misleading. In fact, there are crystals with structures which contain exclusive Al–Al pairs, such as some dialuminates. The principle should be restated to the effect that in a crystal of fixed composition, Al–Si pairs will be energetically more favorable than Al–Al and Si–Si pairs. The same can be stated for Ca–Na versus Ca–Ca and Na–Na pairs, etc. Aluminum avoidance should not be viewed as a "law" but only as an energetic preference; in a structure where order is variable, the number of like-cation pairs will increase as temperature is increased since disorder increases the entropy. Thermodynamic models which assume complete aluminum avoidance (Kerrick and Darken, 1975; Ganguly and Ghose, 1979), imply a zero temperature, ordered state for tetrahedral Al and Si, coexisting with a high temperature, random state for non-tetrahedral cations. Such models are not satisfactory for treating short-range order.

Omphacite has an ordering phase transition from $C2/c$ to $P2/n$ which involves ordering of cations in the M1 and M2 octahedral chains. The derived short-range ordering energies W1 and W2 for omphacite (Table 3) predict correctly that the M1 cations will order to a greater extent than the M2 cations (Clark et al., 1969). The ordering energy along M1 chains for omphacite is the same, within error, as that for fassaite. The high ordering energies for fassaite suggest that a phase change might occur at lower temperatures if not kinetically inhibited. Since natural fassaites are usually far from the $Di_{50}CaTs_{50}$ composition and contain abundant Fe^{3+}, Fe^{2+} and Ti^{4+}, which would lower the transition temperature, it is not surprising that natural fassaites with symmetry less than $C2/c$ have not yet been reported. Synthetic fassaites may be metastably disordered, or may be disordered because of the high temperatures of synthesis (over 1200°C). Ordered fassaites would be expected in space group $C2$, or possibly $P2$.

It is important to emphasize that the short-range ordering energies defined here describe the configurational energy as a function of short-range order (not the total mixing enthalpy as a function of composition.) Even in the absence of short-range order between pairs or at high temperature, there may be a significant excess enthalpy from ionic size differences and long-range electronic interactions. We can write: $H^m = H^c + H^x$ where H^m is the total mixing enthalpy, H^c is the configurational enthalpy, which is estimated here and H^x is the component of the enthalpy which results from the non-pairwise interactions. The latter is primarily composition dependent and is generally positive. The configurational enthalpy, H^c, can be positive or negative depending on the state of order. The term H^x was not investigated here since energies in that case must be calculated for completely relaxed crystal structures and repulsive parameters must be well known in order to estimate the energy contributions from ionic size differences.

Of particular importance are the assumptions and possible errors which will systematically affect the calculated cohesive energies, since effects which are not systematic will be smoothed out by the regressions. Since less favorable configurations might be expected to have a slightly larger cell volume because of the lower cohesive energy, holding the cell parameters constant might systematically increase the ordering energies. Relaxation of microscopic strains would probably reduce ordering energies as well. By far the

largest source of error, however, is probably due to the ionic nature of the model. In a real solid solution containing cations of different valence, the electron clouds should deform so as to reduce local charge imbalances. Polarization and covalency effects change both the short-range part of the potential as well as the long range part. Screening (Harrison, 1980, p. 280-314), caused by deformation of the electron clouds, will lead to short-range ordering energies which are lower than those calculated.

It seems reasonable to conclude that the calculated short-range ordering energies are too high, but that they are probably in approximately proper proportions to *each other*. Comparison of statistical mechanical calculations with experimental data suggests that the short-range ordering energies should be multiplied by a constant with a value of 0.25 ± 0.05 Cohen (1985). The inverse of this factor may be considered an effective dielectric constant which accounts in a rudimentary way for the effects of polarization, screening, and covalency on short-range ordering energies. This factor is determined by estimating the configurational entropy of CaTs from calorimetry, phase equilibria data and NMR spectroscopy and will be discussed in another paper.

Ground states for CaTs

Four of the cation configurations for CaTs correspond to completely ordered configurations of Al and Si. The ground state stabilities, neglecting differences in vibrational energies, etc., are estimated from the calculated cohesive energies. The most favorable structure has $P2_1/n$ ordering. In this space group, long-range ordering is achieved with respect to A, B and C pairs (Fig. 3). That is, each type of pair involves a crystallographically distinct T1 and T2 site, thus permitting favorable Al–Si alternation for all three types of next-nearest-neighbor pairs. The next most favorable structure is *C*2 in which A and B pairs still contain a T1 and a T2, but C pairs split into C1 pairs consisting of two T1's, and C2 pairs consisting of two T2's. Thus, long-range ordering will form unfavorable like-cation C pairs of tetrahedra. In $C\bar{1}$, the A and C pairs can order favorably, while B will order unfavorably. Since the B interaction (W2 for CaTs, Table 3) is stronger than the C interaction (W3), $C\bar{1}$ is less favorable than *C*2. The least favorable ordered structure is *P*2/*n*, in which only the A pairs can order favorably.

Long-range ordering energies in MgTs

The sources of errors in the long-range ordering or exchange energies are somewhat different than those discussed above. Since a DLS structure was obtained for each cation arrangement, the microscopic strains should be small. Since completely ordered structures were modeled, and the occupancies of crystallographically distinct sites were changed, long-range screening and polarization should have a much smaller relative effect than in the short-range ordering case. Thus the calculated exchange energies may be reasonable estimates of the actual exchange energies without use of a phenomenological effective dielectric constant. In orthopyroxene solid solutions, two things could affect the exchange energies in opposite senses. First, the DLS minimizations were performed for completely ordered structures; in real orthopyroxenes the polyhedra will be configured differently depending on the local environment. Mg in an M2 site would cause an adjacent M2 site to be larger than Al would prefer, so that the exchange energies would be somewhat higher than those calculated. On the other hand, because of unlike valence preference, short-range ordering energies would drive some Al into M2 or TA, exchanging with Mg or Si respectively. These effects may partially cancel out. Based on a single structure refinement of a synthetic orthopyroxene, Ganguly and Ghose (1979) determined a free energy of 11 kJ per mole for Al for Mg exchange from M1 to M2, which compares favorably with the exchange energy of 21 kJ per mole calculated here. Also, the energy calculations suggest that Al should partition heavily into TB over TA, though the exclusion of Al from TA suggested by Ganguly and Ghose (1979) is not borne out by the calculations. A direct determination of the Al site occupancies in orthopyroxene by a method such as neutron diffraction could resolve this problem, which is very important to thermodynamic solution modeling used for geobarometry and geothermometry.

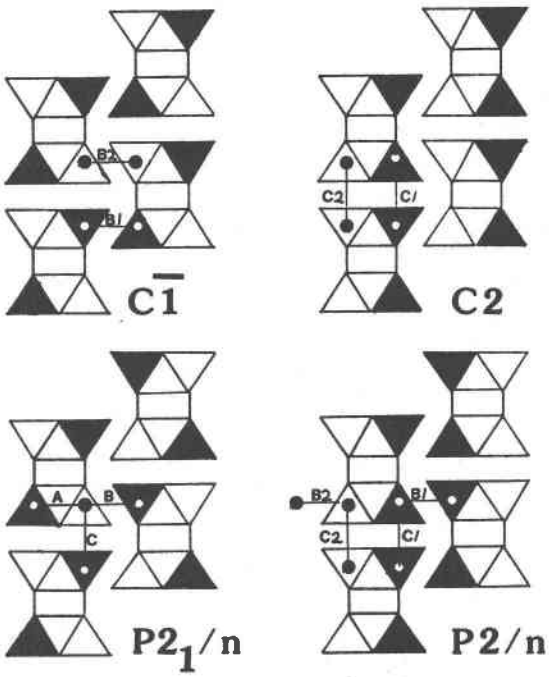

Fig. 3. View down *c* of the pyroxene I-beams showing ordered distribution of crystallographically distinct tetrahedra in several possible space groups for CaTs. Long-range ordering allows A, B and C pairs to order favorably in $P2_1/n$, but in the other space groups long-range order induces unfavorable ordering in some pairs.

Conclusions

1. Energy calculations can be used to calculate relative short-range ordering energies in silicates which involve

mixing of cations of different valence. Energies for short range ordered silicates can be represented fairly well by pair probabilities alone. Higher order cluster probabilities do not seem necessary at this point, given errors in the forms of the potentials.

2. Consideration of the form of the coulomb potential and the cohesive energies explains what has been known as the Al-avoidance principle, which should probably be called 'unlike valence preference."

3. Calculated short-range ordering energies correctly predict the ordering of omphacite, and suggest that some fassaites may be long-range ordered in subgroups of $C2/c$, probably $C2$ or $P2$.

4. Ordered CaTs structures are stable in the sequence: $P2_1/n > C2 > C\bar{1} > P2/n$.

5. Large degrees of short-range order are expected in crystals in which cations of different valence mix, such as coupled solid-solutions.

6. Some Al is expected in both the M2 sites and the TA sites, as well as M1 and TB, in aluminous orthopyroxenes.

7. Development of a method for calculating ordering energies in silicates directly, such as those being developed for alloys would be very useful, but probably does not lie in the near future. Until such a method is developed, it will be necessary to obtain ordering energies as small differences between large cohesive energies.

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