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Structure-energy calculations on low and high albite

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ABSTRACT

Static minimum-energy ionic models of low albite calculated using MEG-derived short-range pair potentials show that Al favors the T1o site by only 0.4 to 0.7 kJ/O atom and confirm that the observed anisotropic electron density of Na atoms is due to true thermal motion. The minimum-energy low albite structure with Al in T1o has unit-cell parameters that deviate from observed values by 2.6% or less, and bond distances that compare with observed values to within 0.15 Å.

Similar calculations on high albite, carried out using fixed framework-atom positions for 56 crystallographically distinct (Al,Si) distributions that obey the Al-avoidance rule, yield minimum-energy Na positions that are slightly different for each individual (Al,Si) distribution. Comparison of the distribution of calculated Na positions with quarter-atom Na positions and temperature factors observed in X-ray structure refinements shows that the quarter atoms mimic rather well the average electron-density distribution expected from equal occupany of all calculated Na positions. The assertion that high albite possesses a large number of local (Al,Si) configurations—each of which leads to its own minimum-energy Na position—rather than some kind of domain structure involving only a small number of local (Al,Si) distributions is further supported by an additional excellent comparison between the distribution of Na positions calculated using the observed 1060°C framework and the quarter-atom Na positions reported in the 1060°C structure refinement. Observed quarter-atom Na positions from structure refinements cannot be correlated easily with four calculated Na positions that would correspond to just four distinct (Al,Si) distributions in some kind of domain arrangement.

Structure-energy calculations carried out using observed framework configurations at room temperature, 350, 600, 750, 950, and 1060°C, placing Al in the four T sites in turn and then minimizing Na positions, show that most of the static driving force favoring Al in T1o has developed when temperature lowers to about 800°C and is not increased significantly with further lowering of temperature. A significant source of the driving force is thus shown to be distortion or collapse of the framework, and its development is consistent with major ordering occurring between 775 and 700°C.

INTRODUCTION

Previous studies have demonstrated that structure-energy calculations using modified electron-gas (MEG) short-range energy terms can model quite well a variety of relatively simple mineral structures, the TiO_2 polymorphs and forsterite (Post and Burnham, 1986a), for example. These types of calculations have also provided some important insights into more complex structures, particularly with regard to short-range ordering and positional disorder. For example, Chamberlain et al. (1985) studied ordering of Cl^- and CO_3^{2-} in scapolite, Cohen and Burnham (1985) investigated short-range ordering of tetrahedral Al and Si in pyroxenes, and Post and Burnham (1986b) analyzed the positional disorder of tunnel cations in hollandite phases.

In this paper we report the results of energy-minimization modeling studies of low and high albite carried out with MEG-derived short-range pair potentials. Analysis of these models provides significant insights regarding several aspects of the albite structures that have been subject to divergent interpretations: (1) The nature of (Al,Si) disorder in high albite, (2) the origin of the driving force toward ordering in low albite, and (3) the observed anisotropy of the Na electron density in high and low albite.

Albite, $NaAlSi_3O_8$, is composed of corner-sharing AlO_4^{-5} and SiO_4^{-4} tetrahedra linked in a three-dimensional array; Na cations occupy large cavities in the tetrahedral framework (Fig. 1). On the basis of X-ray diffraction structure analyses, it is generally accepted that triclinic high albite has Al and Si randomly distributed over four crystallographically distinct tetrahedral sites, whereas low albite has the Al ordered into one of those

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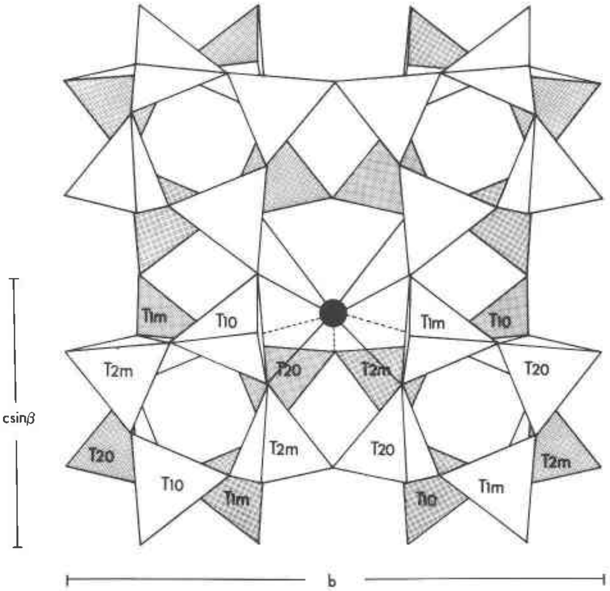

Fig. 1. Projection of the monoclinic albite structure down **a**, showing the coordination of the Na atom.

sites, T1o (Fig. 1). Structure refinements of high and low albite show large apparent thermal parameters for the Na cations. Previous studies involving refinements at different temperatures have concluded that the anisotropy of the Na cation in low albite is in fact the result of thermal motion in the large cavity (Quareni and Taylor, 1971; Winter et al., 1977). Similar studies of high albite, however, indicate positional disorder on the Na site, the exact nature of which is uncertain (Prewitt et al., 1976; Winter et al., 1979).

Ribbe et al. (1969), Prewitt et al. (1976), and Winter et al. (1979) have attempted to analyze the Na positional disorder in high albite and have all concluded that it is a consequence of (Al,Si) disorder over the tetrahedral sites. Both Prewitt et al. (1976) and Ribbe et al. (1969) refined the Na position using a quarter-atom model that split the alkali site into four separate sites, each containing ¼ of a Na atom occupying a different position in the cavity and having its own temperature factor. The fact that this procedure led to improved refinements compared to the use of two half-atom sites for Na, or a single Na atom with exceptionally large thermal parameters, led to the notion that high albite has a domain structure, with each of four domains having a particular (Al,Si) arrangement in the tetrahedral sites with an associated distinct Na position. One explanation for the existence of four domains was that in each of these, the Al would be ordered into one of the four distinct T sites (Prewitt et al., 1976; Brown and Fenn, 1979). The major problem with a quadripartite model, however, is that there exists, at present, no X-ray or electron diffraction evidence for domains in high albite. Furthermore, Winter et al. (1979) have correctly observed that there are many more than four possible local configurations of Al and Si and that the quarter-atom model does not necessarily rule out a random distribution, with each local (Al,Si) configuration dictating a unique Na position within the cavity.

TABLE 1. Born-type short-range energy parameters used in structure-energy calculations*

Ion pair	λ (kJ/mol)	ρ (Å)
Na–O†	563 165	0.2387
Al–O	332 420	0.2461
Si–O	358 150	0.2428
O–O	291 000	0.2876

* From Post and Burnham (1986a).
† Oxygen shell radius = 1.01 Å.

Brown and Fenn (1979) carried out some electrostatic energy calculations in an attempt to understand further the Na positional disorder in high albite. In addition to Coulomb terms, they approximated short-range energy terms for Na–O interactions using bulk compressibility data for NaF; they included no other short-range interaction terms. Using atomic coordinates for the high albite framework determined by Prewitt et al. (1976), they calculated structure energies for configurations having Al ordered into each of the four tetrahedral sites, and Na located in each of the refined quarter-atom positions in turn. Their calculations showed that the most favored Na quarter-atom position does depend on the (Al,Si) arrangement and that, regardless of Na position, the lowest energy is obtained with Al in the T1o site. They explored only four ordered (Al,Si) configurations.

We have now taken advantage of improved procedures that employ MEG short-range energy parameters and make use of the energy minimization computer program, WMIN (Busing, 1981), to model the albite structure. Using the MEG procedure, we are able to calculate complete short-range and Coulomb energy terms for a variety of albite structures. We have used WMIN to determine minimum-energy low albite structures and to investigate the effects of different local (Al,Si) arrangements on the minimum-energy Na position in high albite. The results of these calculations permit us to evaluate both the domain structure model and the influence of tetrahedral (Al,Si) distribution on the Na position in high albite. In addition, minimization calculations for high albite structures determined at different temperature provide interesting insights into the ordering process that segregates Al into T1o in low albite.

CALCULATIONS

Structure-energy calculations were performed using the computer program WMIN (Busing, 1981), modified to employ a Born exponential expression (Kittel, 1971) for calculating short-range energy terms for cation-anion and anion-anion pair interactions (cation-cation repulsion terms are considered to be negligible). The parameters λ_{ij} and ρ_{ij} in the Born expression were derived for each distinct ion pair (Table 1) from the MEG theory (Muhlhau-

TABLE 2. Low albite minimum-energy model structures calculated for Al ordered into each of the four T sites

	Observed* Al in T1o	Calculated Al in T1o	Calc − Obs (%)	Calculated, with Al in		
				T1m	T2o	T2m
a (Å)	8.14	8.35	2.6	8.41	8.19	8.20
b	12.79	13.01	1.7	13.02	13.30	13.24
c	7.16	7.23	1.0	7.25	7.13	7.11
α (°)	94.19	94.63	0.5	86.18	90.69	93.18
β	116.61	116.51	−0.1	116.98	115.73	115.66
γ	87.68	87.27	−0.5	92.87	90.50	89.63
V (Å^3)	663.81	664.67	0.1			
T1o-OBO	1.75	1.72	−1.7	1.58	1.54	1.60
T1o-OA1	1.75	1.73	−1.1	1.56	1.59	1.60
T1o-OCO	1.74	1.72	−1.1	1.60	1.60	1.56
T1o-ODO	1.75	1.74	−0.6	1.60	1.61	1.57
T1m-OCM	1.62	1.60	−1.2	1.72	1.56	1.60
T1m-ODM	1.62	1.60	−1.2	1.73	1.57	1.60
T1m-OBM	1.60	1.58	−1.2	1.71	1.59	1.54
T1m-OA1	1.60	1.56	−2.5	1.73	1.61	1.60
T2o-OCM	1.61	1.58	−1.9	1.54	1.70	1.58
T2o-OBO	1.59	1.56	−1.9	1.61	1.73	1.60
T2o-OA2	1.63	1.59	−2.5	1.61	1.74	1.55
T2o-ODM	1.62	1.60	−1.2	1.57	1.75	1.61
T2m-OA2	1.64	1.61	−1.8	1.59	1.55	1.74
T2m-OCO	1.59	1.54	−3.1	1.58	1.58	1.70
T2m-OBM	1.62	1.61	−0.6	1.56	1.59	1.72
T2m-ODO	1.60	1.57	−1.9	1.60	1.61	1.75
OCO-ODO	2.62	2.60	−0.8	2.47	2.47	2.51
OBM-ODO	2.66	2.52	−5.3	2.51	2.50	2.50
OA1-OBO	2.73	2.81	2.9	2.60	2.60	2.61
OA2-OCM	2.57	2.70	5.1	2.68	2.98	2.67
Na-*x*	0.268	0.251		0.247	0.292	0.293
y	0.989	0.992		0.008	0.992	0.987
z	0.146	0.141		0.140	0.213	0.209
W_{calc} (kJ per oxygen atom)		−5054.2		−5053.8	−5053.5	−5053.8

* Harlow and Brown (1980).

sen and Gordon, 1981), using the procedure described by Post and Burnham (1986a).

A shell-stabilized Hartree-Fock wave function with a shell charge of +2 and radius of 1.01 Å was used for O^{2-} in the MEG calculation. The charged spherical shell approximates the potential surrounding O^{2-} within the crystal and serves to stabilize this normally unstable anion. The shell radius is an appropriate average value that yields self consistency with the site potentials calculated for oxygen atoms in albite. The Coulomb portion of the structure energy is summed by WMIN using the Ewald (1921) and Bertaut (1952) methods to limits of 5.1 Å and 0.52 Å^{-1} in direct and reciprocal space, respectively. All structure energies include, for each oxygen atom, self-energy values of 1113 kJ/atom arising from O^{2-} (shell stabilized) → $O^{1-} + e^-$. The energy-minimization calculations were performed using Newton's method (Busing, 1981), and full formal charges were used on all ions.

LOW ALBITE

Calculations of minimum-energy low albite structures were carried out in space group $C\bar{1}$; unit-cell parameters and atom positions were allowed to vary simultaneously, resulting in a total of 45 adjustable parameters per minimization. Initial atom positions and cell parameters were those determined for high albite at room temperature by Prewitt et al. (1976). During the intitial calculation for low albite, Al was ordered into the T1o site; calculations were subsequently performed with Al ordered into each of the other T sites.

Unit-cell parameters and some selected bond distances of the minimum-energy low albite structure having Al ordered into T1o are compared with the experimentally observed low albite values in Table 2. Considering the purely ionic nature of our modeling procedure, it is perhaps surprising how well this minimum-energy low albite model compares with the observed structure. Linear unit-cell parameters are within 2.6% of the empirical values, and cell angles differ from observed by 0.5% or less; model and observed cell volumes are essentially the same. The calculated Si–O and Al–O distances are, in general, slightly shorter than those in the observed structure, which is consistent with behavior observed during previous MEG calculations on other silicate minerals (Post and Burnham, 1986a). In the minimum-energy low albite structure, Si–O bond lengths range from 1.54 to 1.61 Å (mean = 1.58 Å), compared with the observed range of 1.59 to 1.64 Å (mean = 1.61 Å). Al–O distances fall between 1.72 and 1.74 Å (mean = 1.73 Å) in the model, and between 1.74 and 1.75 Å (mean = 1.75 Å) in the observed structure. In general, the senses of the T–O bonds correspond rather well between the calculated and actual

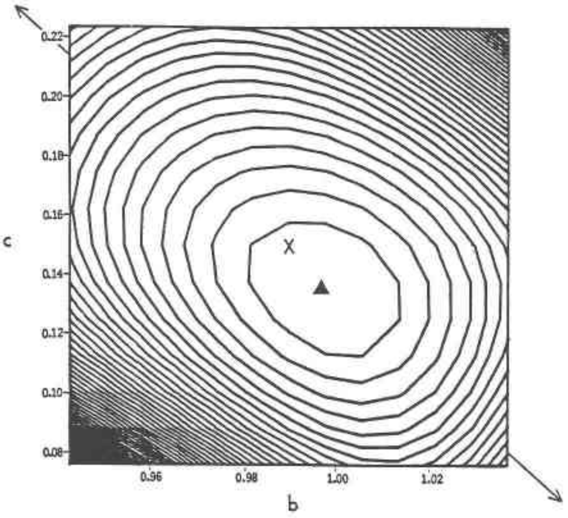

Fig. 2. A **b**-**c** section through the low albite structure at $x = 0.268$ showing the structure energy as a function of Na position. Contour interval is 0.5 kJ per oxygen atom. "X" represents the Na in the Harlow and Brown (1980) refinement of the low albite structure; the triangle indicates our minimum-energy Na position. The actual calculated minimum-energy position is 0.06 Å below this section. Diagram covers 1.2 × 1.2 Å and has been plotted with $\alpha = 90°$.

low albite structures. The largest discrepancies revealed in Table 2 involve O–O bond lengths, with differences between observation and model of up to about 5% (0.14 Å).

The Na position in the minimum-energy low albite model is approximately 0.2 Å from the Na site determined by single-crystal structure refinements (Harlow and Brown, 1980). The distances in our model from Na to the nearest eight oxygen atoms range from 2.57 to 3.60 Å (mean = 2.9 Å), compared with 2.37 to 3.27 Å (mean = 2.71 Å) in the observed structure.

Low albite minimum-energy model structures were also calculated for Al ordered into T1m, T2o, and T2m, with results summarized in Table 2. Note that although the energy of the case with Al ordered into T1o is lowest, it is so by only 0.4 to 0.7 kJ/anion, corresponding to 3.2 to 4.0 kJ/mol. Furthermore, the energy differences between the other three distributions are 0.3 kJ/anion (2.4 kJ/mol) or less. These energy differences are small; indeed, they are less than octahedral crystal-field site-preference energies for Fe^{2+} in orthopyroxene (5.8 kJ/mol) or Ni^{2+} in olivine (15.5 kJ/mol) (Burns, 1985), and less than static site-preference energies calculated for several easily disordered binary olivine systems (Bish and Burnham, 1984). This suggests that either the static driving force toward ordering of Al into T1o is larger at temperatures of 700 to 775°C, where the equilibrium state of order is observed to increase rapidly on cooling (Goldsmith and Jenkins, 1985; Salje et al., 1985), or that dynamical effects further contribute to the energetic favorability of the observed ordered distribution.

In an attempt to explain the large anisotropic temperature factors that have previously been determined for Na in low albite, we mapped the structure energy as a function of Na position, using the low albite framework determined by Harlow and Brown (1980). The map shown in Figure 2 was prepared by holding the framework fixed, moving the Na to points on a grid covering the alkali site, and calculating the structure energy at each grid point. The map reveals a broad, elongated energy valley with its direction of elongation almost exactly parallel to the principal axis of the refined Na thermal-vibration ellipsoid having the maximum rms amplitude. This result supports the conclusions of previous studies that the anisotropy of the observed Na electron density arises from true thermal motion. Figure 2 also shows that our calculated Na position (using the fixed low albite framework) is very close to that determined by Harlow and Brown (1980); the corresponding energy difference between the two positions is less than 0.5 kJ per oxygen atom.

HIGH ALBITE

Because of the uncertainty of the (Al,Si) distribution, it is not a straightforward problem to use energy calculations to model the high albite structure. Some previous studies have used average charges ($0.25 \times Al^{3+} + 0.75 \times Si^{4+}$) on the tetrahedral sites. It is rather clear, however, that this is not a physically reasonable approach; in fact, Giese (1975) has shown that assignment of average charges to disordered sites yields erroneous results. Alternatively, one could perform a minimization assuming a particular (Al,Si) configuration, but that would simply yield the minimum energy structure for that ordered case. In addition, no ordered case will be representative of the actual high albite structure—at least not as determined by single-crystal refinements—which is an average of unit cells having a variety of (Al,Si) arrangements. Ideally, one might try to model a large high albite supercell in which each subcell, equal in size to a high albite unit cell, would have a different (Al,Si) configuration. Unfortunately, such a calculation would take a tremendous amount of computer time and is probably beyond the present capabilities of our method. Consequently, we have not attempted to carry out a complete minimization for high albite. Instead, we have used a fixed high albite framework and determined structure energies and minimum-energy Na positions for a variety of (Al,Si) arrangements.

Undoubtedly, the assumption of a fixed framework introduces some degree of error into calculated Na positions and structure energies; indeed, analysis of temperature factors refined for the high albite framework atoms over a range of temperatures by Prewitt et al. (1976) indicates some spatial disorder for these atoms. Presumably, the disorder is the result of slight shifts in positions of the tetrahedral cations and oxygen atoms caused by different local (Al,Si) distributions in different domains or unit cells. We are assuming, however, that these slight shifts will not significantly affect our results. This is sup-

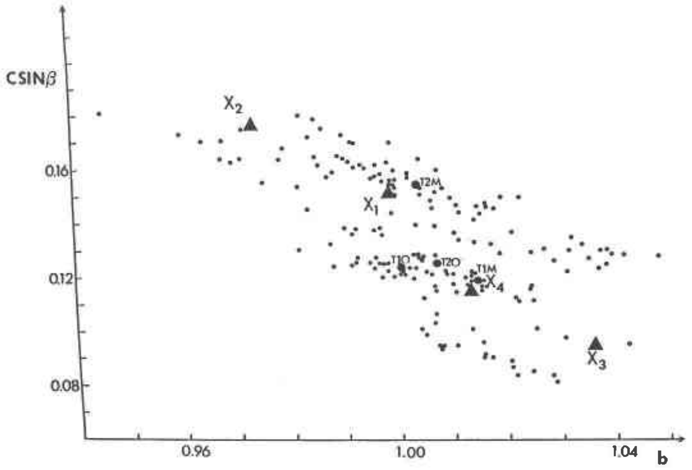

Fig. 3. Projection down **a** of the 175 different minimum-energy Na positions determined for the 56 unique arrangements of 4Al and 12Si over 16 tetrahedral sites per unit cell, assuming Al avoidance is operative. "X's" and triangles represent Na quarter-atom positions determined in high albite structure refinements by Prewitt et al. (1976) and Ribbe et al. (1969), respectively. Larger filled circles show the minimum-energy Na positions corresponding to Al ordered into each of the four distinct tetrahedral sites.

ported by the fact that our calculated Na position for Al ordered into the T1o site in the high albite framework is within about 0.2 Å of the observed Na position in low albite.

For our initial set of minimization calculations on high albite, the unit-cell parameters and framework-atom positions were held fixed to the room-temperature values determined by Prewitt et al. (1976), and only the Na positions were allowed to vary. The calculations were carried out in space group *P*1, and minimum-energy positions for all four Na atoms per unit cell were determined simultaneously. Minimization calculations were performed for all of the unique (Al,Si) configurations that satisfy the Al-avoidance rule. There are a total of 1820 ways of arranging 12 Si and 4 Al atoms on 16 tetrahedral sites per unit cell; of these, 210 obey the Al-avoidance rule and only 56 are symmetrically unique.

The minimum-energy Na positions (four per calculation) for the 56 unique (Al,Si) configurations are plotted in Figure 3, along with the Na quarter-atom positions for high albite determined by Ribbe et al. (1969) and Prewitt et al. (1976). It is obvious from this figure that the minimum-energy Na position is a function of the local (Al,Si) distribution in tetrahedra surrounding the cavity. The calculated Na positions for the cases with Al ordered into each of the crystallographically distinct T sites are indicated in Figure 3; quite obviously they do not match the observed quarter-atom positions. Likewise, the Na positions for the minimum-energy low albite structures, with Al ordered into each of the four T sites (see Table 2), do not coincide with the quarter-atoms. Apparently then, a domain structure in which each of four domains has Al ordered into a different T site is not consistent with the observed Na electron density. Of course, it is possible that some other four (Al,Si) ordering schemes might give rise to a domain structure having Na positions that match the refined quarter-atom sites. The results of our calculations, however, indicate that it is not necessary to invoke a domain-structure model to explain the observed Na electron density in high albite.

The calculated structure energies, after minimizing Na positions, for the 56 (Al,Si) configurations considered in Figure 3 are shown in a histogram in Figure 4. The energies ranges from −4985 to −4999 kJ per oxygen atom, and the energetically most favorable case has Al ordered into T1o. The relatively narrow and continuous range of structure energies shown in Figure 4 suggests that many or all of these (Al,Si) distributions probably occur in a high albite crystal. There would appear to be little impetus for short-range ordering of Al and Si, and therefore the formation of a domain structure, in high albite.

Let us examine the simpler model for high albite that has Al and Si nearly completely disordered over the tetrahedral sites (Winter et al., 1979), within the bounds of

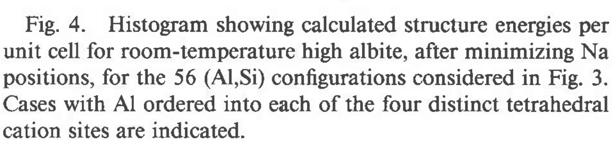

Fig. 4. Histogram showing calculated structure energies per unit cell for room-temperature high albite, after minimizing Na positions, for the 56 (Al,Si) configurations considered in Fig. 3. Cases with Al ordered into each of the four distinct tetrahedral cation sites are indicated.

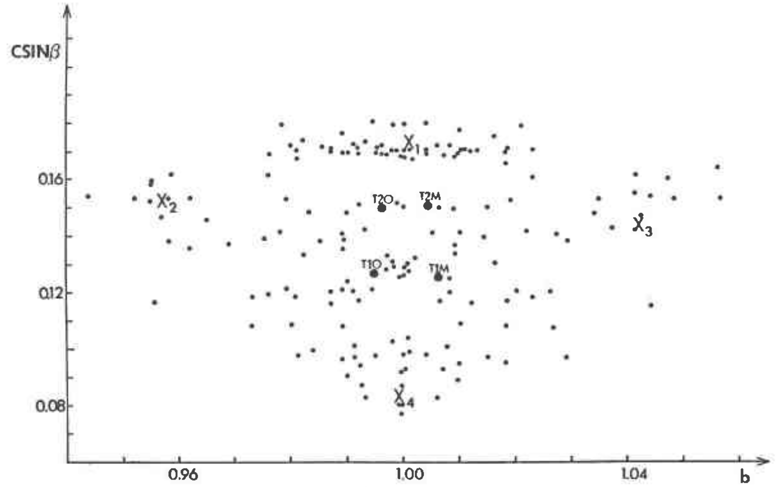

Fig. 5. Minimum-energy Na positions, projected down **a**, calculated for the same (Al,Si) configurations represented in Fig. 3, but using the 1090°C high albite framework reported by Prewitt et al. (1976). "X's" indicate Na quarter-atom positions reported by Prewitt et al. (1976).

Al avoidance, in the light of our calculations. Looking at Figure 3, we see that the distribution of calculated Na positions matches rather closely the refined quarter-atom positions, in the context that those quarter-atoms are attempting to account for a very smeared overall Na electron density. Prewitt et al. (1976) reported isotropic temperature factors, *B*, of 1.54, 2.19, 1.79, and 1.37 for quarter-atoms Na1, Na2, Na3, and Na4, respectively, suggestive that quarter-atom sites Na1 and Na4 might be more fully occupied—meaning that they represent a higher electron density—than Na2 and Na3. Note in Figure 3 that the density of calculated Na positions is greater near Na1 and Na4 than near Na2 and Na3, meaning that if all these (Al,Si) distributions have an equal likelihood of occurring, there will be more Na atoms near Na1 and Na4 than near Na2 and Na3, and our calculations then fully explain the structure-refinement results. We believe our calculations indicate, therefore, that almost complete long-range disorder of Al and Si in high albite is accompanied by little or no tendency toward formation of partially ordered domains. Na occupies not just four positions, as refinements using quarter-atom models imply, but rather is distributed over many positions that reflect the many different local (Al,Si) arrangements.

Maps of structure energy vs. Na position, like the one for low albite in Figure 2, were also calculated for several (Al,Si) arrangements using the high albite framework. In general, the maps resemble Figure 2, although the orientation of the minimum valley varies, suggesting large thermal motion of Na in high albite. Such large real thermal motion will also contribute to the smearing out of the observed electron density on the Na site.

To further test our conclusions, we calculated minimum-energy Na positions for the (Al,Si) arrangements represented in Figures 3 and 4 using the high albite framework refined by Prewitt et al. (1976) at 1090°C. The results of these calculations are shown in Figure 5 along with the observed Na quarter-atom positions in the 1090°C structure. The distribution of calculated Na positions is considerably different from that for the room-temperature case, but it again matches the refined quarter-atom positions quite well. Also the refined isotropic temperature factors, *B*, of 4.86, 7.75, 7.84, and 5.79 for Na1, Na2, Na3, and Na4, respectively, are consistent with Figure 5, which shows that the density of calculated Na positions near Na1 and Na4 is greater than that near Na2 and Na3.

Haselton et al. (1983) have pointed out that neither experimental thermochemical data nor phase-equilibrium studies of albite ⇌ jadeite + quartz require any contribution to zero-point configurational entropy from occupation of multiple cavity sites by Na. If, as we assert, the Na position in any given cavity is controlled by the electrostatics of the local (Al,Si) distribution, then the resulting multiplicity of Na positions involve no Na disorder and thus will not add to configurational entropy, whose value will be determined by the extent of (Al,Si) disorder alone. Haselton et al. (1983) have further noted that their calorimetric investigation of alkali feldspars showed no heat-capacity effects that could be attributed to Na disorder over the multitude of cavity sites, again consistent with the notion that only one energetically favorable Na position exists in each cavity.

It is, of course, true that the zero-point configurational entropy of high albite depends on the extent to which Al avoidance is operative (Mazo, 1977). Hemingway et al. (1981) have carried out a careful analysis of phase-equilibrium data bearing on this issue and have argued that the data do not, unfortunately, lead to an unequivocal answer. By carrying out calculations only for local (Al,Si) arrangements satisfying Al avoidance, we have not meant to imply that other arrangements are not present; the

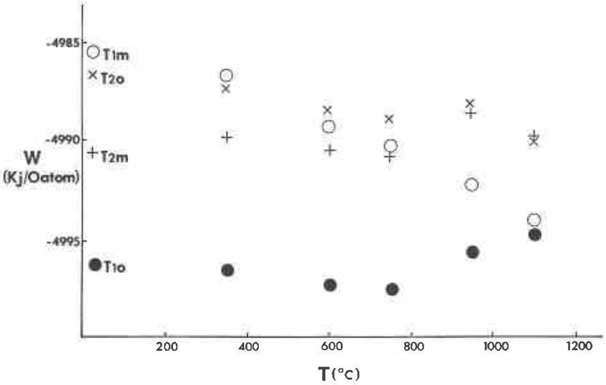

Fig. 6. Calculated structure energy vs. temperature for high albite structures with Al ordered into each of the four crystallographically distinct tetrahedral sites. Calculations at each temperature were made by using a fixed high albite tetrahedral framework defined by atom coordinates and unit-cell dimensions reported for that temperature by Prewitt et al. (1976), distributing the Al into each of the T sites in turn, and varying the Na position during each energy minimization.

choice was made simply to keep the computational task to realistic proportions. It is conceivable that an exhaustive effort to calculate structure energies and determine minimum-energy Na positions for framework-cation distributions violating Al avoidance might permit an assessment as to whether such distributions exist in the high albites whose structures have been refined.

AL ORDERING IN LOW ALBITE

In addition to their structure refinements at room temperature and 1090°C, Prewitt et al. (1976) also refined the high albite structure at 350, 600, 750, and 950°C. Each of these analyses provides details of the framework at that temperature, which we have used to calculate structure energies for hypothetical ordered structures with Al assigned to each distinct T site, in an effort to understand further the driving force toward Al ordering that exists in high albite with decreasing temperatures. Each calculation was carried out as described previously: framework atoms were fixed at high albite atom coordinates reported by Prewitt et al. (1976), Al was distributed into each of the crystallographically distinct T sites in turn, and the Na atom was permitted to vary during each energy minimization. The results are plotted in Figure 6.

As temperature decreases from that of the monalbite → high albite transition, it becomes increasingly more favorable energetically for Al to order into T1o relative to the other T sites. Most of the cohesive-energy differences favoring Al in T1o in the model high albite framework structures are achieved through changes in framework geometry that take place during cooling to around 700 to 800°C. From these temperatures to room temperature, further framework-configuration changes yield relatively minor additional increases in cohesive-energy differences. Since for a given Al distribution, our calculated changes in static cohesive energy with temperature can arise only from changes in observed framework geometry (with a possible minor contribution from the concomitant small change of Na position), the calculated increases in energy differences between Al in T1o and Al in the other sites are necessarily a consequence of framework-geometry changes. Thus a substantial impetus for ordering of Al into T1o is provided by contraction, or collapse, of the high albite framework with decreasing temperature, with most of the impetus developed before the temperature reaches 700°C. This result is consistent with other ordering studies on albite—both experimental and theoretical—that have suggested that the major ordering takes place between 775 and 700°C (e.g., Senderov, 1980; Goldsmith and Jenkins, 1985; Salje et al., 1985).

SUMMARY

Structure-energy minimizations using MEG short-range repulsion terms model the albite structure surprisingly well. Unit-cell parameters of our minimum-energy low albite structure deviate from the observed values by <2.6%, and bond distances compare to within 0.15 Å. The structure energies for the minimized low albite structures with Al ordered in turn into each of the four crystallographically distinct T sites are essentially identical, suggesting that if there were no impetus for Al to order into T1o at high temperatures, it would be accommodated equally well in any of the T sites at room temperatures. A map of energy vs. Na position for low albite shows an anisotropic well whose major axis of elongation has the same orientation as the major axis of the experimentally determined thermal-vibration ellipsoid. This result supports the conclusions of previous studies that the anisotropic electron density exhibited by Na in low albite is a consequence of true thermal motion.

Our calculations for high albite show that the Na position is dependent on the local (Al,Si) configuration; we did not, however, find evidence for short-range ordering of Al and Si atoms that might give rise to a domain structure. Structure energies for high albite structures with various (Al,Si) configurations all fall within a relatively narrow range; thus it is likely that many or all of these configurations occur in real high albite crystals. Furthermore, the distribution of minimum-energy Na positions calculated for all of the (Al,Si) distributions that do not violate the Al-avoidance principle readily explains the previously refined Na quarter-atom positions. We conclude, therefore, that Na occupies not four positions as refinements using quarter-atom models imply, but rather is distributed over many positions that reflect the numerous different local (Al,Si) arrangements.

The calculated variation of structure energy with temperature for high albite structures with Al ordered in turn into each of the four distinct T sites indicates that as temperature is lowered, it becomes increasingly more favorable for Al to order into T1o relative to the other tetrahedral sites. Collapse of the framework provides the major impetus for ordering, and most of the cohesive-energy driving force has been achieved before cooling temperatures reach about 700°C.

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