

## Electrostatic energy for ion clustering in intermediate plagioclase feldspar

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**SUMMARY.** Electrostatic calculations estimated the energy of hypothetical ion clustering in intermediate plagioclase feldspars. The calculated energy appears too great to allow segregation of Ca and Na atoms into domains upon annealing without a corresponding movement of Al and Si from an original disordered structure. The calculated energy may be sufficiently small that Ca and Na atoms can disorder partially without movement of Al and Si upon heating a low-plagioclase to high temperatures.

VARIOUS models for the structure of intermediate plagioclase have been proposed, ranging from Chao and Taylor's (1940) alternating bands of albite-like and anorthite-like structures to complex models by Megaw (1960) and Korekawa and Jagodzinski (1967). The most recent model by Smith and Ribbe (1968) consists of domains of albite-like and anorthite-like regions separated by out-of-step, disordered boundaries. In the Korekawa-Jagodzinski model, emphasis is placed on Ca-rich and Na-rich regions without specification of the positions of Al and Si. In the Smith-Ribbe model, the Ca and Na atoms are closely associated with Al and Si atoms, respectively, producing regions rather like anorthite and low-albite.

Sodium and Ca atoms can diffuse more rapidly than Al and Si atoms because of their smaller bonding energies to the oxygen atoms. It might therefore be thought possible for Na-rich and Ca-rich domains to form without corresponding ordering of Al and Si atoms in an initially disordered high-plagioclase. Foit and Peacor (1967) have observed that the type (c) subsidiary reflections of low-plagioclase weaken and disappear reversibly and promptly upon rapid heating to high temperature. Smith and Ribbe (1968) have suggested that diffusion of Na and Ca atoms in an original domain structure of albite- and anorthite-like regions may explain at least partially this result. A complete literature review is given by Smith and Ribbe (1969).

In order to test the possibility of Ca and Na diffusing into domains without movement of Al and Si we have investigated the energy resulting from the clustering of Ca and Na atoms in a framework containing disordered Si and Al atoms. The first step in the calculation was estimation of how tightly Ca is bound to Al and Na to Si. The size of this binding energy provides an estimate of the tendency for local spatial coherence of Ca to  $Al_2Si_2$  and of Na to  $AlSi_3$ . The second step was construction of a simple model for estimation of the energy of clustering of Na and Ca atoms. Since the nature of the bonding in feldspars is not known precisely, we used a simple ionic model. The resulting estimates are probably significant at a semi-quantitative level and are certainly qualitatively significant.

The first step consisted of calculation of the difference in electrostatic potentials between Ca and Na sites adjacent to tetrahedral nodes in which there is either excess Si or Al over the average value. A large difference in lattice potentials would indicate that movement of Ca and Na independent of Al and Si is unlikely. A small difference in the lattice potentials would indicate only a small tendency to local coherence of Ca and Na with respect to Al and Si.

To make this calculation the crystal was assumed to be perfectly ionic. Calcium and Na ions were assumed to differ only in charge. Aluminum and silicon ions were assigned arbitrarily to tetrahedral nodes of the structure of low-albite as determined by Ribbe *et al.* (1969). Sodium and calcium ions were placed on the sites occupied by Na atoms in low-albite to yield the  $\text{Na}_{0.5}\text{Ca}_{0.5}$  composition. The arbitrary cation assignments are given in table I. The lattice potentials at the Na and Ca sites were

TABLE I. *Sites occupied in the 'plagioclase'. See Ribbe, Megaw, and Taylor (1969) for atomic co-ordinates*

Site of low albite	$xyz$	$\frac{1}{2}+x, \frac{1}{2}+y, z$	$\bar{x}\bar{y}\bar{z}$	$\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$
Na	Na	Na	Ca	Ca
T <sub>1</sub> (o)	Si	Si	Si	Si
T <sub>1</sub> (m)	Al	Al	Al	Al
T <sub>2</sub> (o)	Si	Si	Si	Si
T <sub>2</sub> (m)	Si	Si	Al	Al

calculated by the method of Ewald (Kittel, 1958). The calculation was greatly facilitated by a programme supplied and recently described (1968) by Professor S. Hafner. The potentials given by these calculations are: Na, 0.6217 unit charge/Å; Ca, 0.6359 unit charge/Å.

Complete disorder of Ca and Na would result in an average of two 'misplaced' charges per unit cell. (By 'misplaced' is meant that an Na or Ca cation is in a site least favourable for local charge balance with respect to the Al and Si ions on the neighbouring tetrahedral nodes.) The calculated potential times the charge difference converts to 0.20 eV per misplaced charge or a little over one Kcal per mole of  $\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$  (270.2 g). This energy indicates a significant tendency to local ordering of Ca and Na at lower temperatures but is hardly large enough to prevent local disordering of Ca and Na at higher temperatures.

The second step of the investigation was estimation of the electrostatic energy of clustering Ca and Na atoms into regions composed of several unit cells without a corresponding movement of Al and Si atoms. In order to explain the observed subsidiary reflections, domains of 30–100 Å in shortest dimension are needed (e.g. Smith and Ribbe, 1969). These distances correspond to 3 to 10 unit cells. Exact calculation of clustering energies by Ewald's method is not practical since a domain consisting of  $5 \times 5 \times 5$  unit cells would require twenty calculations of Ewald potentials in a unit cell of 52 000 atoms, and the method's accuracy would not be meaningful. A reasonable semi-quantitative estimate of the energy was obtained by calculating direct lattice sums for a simple cubic model.

This model assumed that the charged unit cells contain pairs of single charges separated by 10 Å in a cubic array. For simplicity, cubic domains were considered ranging in size from two to five unit cells on a side. A computer calculation of direct lattice sums over a volume of 11 × 11 × 11 domains converged to ± 10 %. To allow for covalence of bonding and secondary adjustment of charge distribution, a uniform dielectric constant of 6.0 was assumed (Clark, 1964).

TABLE II. *Direct lattice sums for simple model of domains*

Domain dimensions (unit cells)	uvw*	Sum†	Multiplicity	Av. sum†	kcal/mole
2 × 2 × 2	111	0.005	8	0.005	0.14
3 × 3 × 3	111	0.15	8	0.25	7
	112	0.23	12		
	122	0.37	6		
	222	0.61	1		
4 × 4 × 4	111	0.33	8	0.59	16
	112	0.44	24		
	122	0.66	24		
	222	1.12	8		
5 × 5 × 5	111	0.54	8	1.03	28
	112	0.67	24		
	113	0.69	12		
	122	0.94	24		
	123	1.01	24		
	133	1.08	6		
	222	1.55	8		
	223	1.71	12		
	233	1.89	6		
	333	2.11	1		

\* Indices of unit cell within domain (111 taken at corner).

† Units are unit charge per Å.

The calculated lattice sums, presented in table II, and the resulting energies are so large that consideration of other domain configurations seems unnecessary. The apparent energy required to put Ca and Na into separate domains of sufficient size to explain supersatellite reflections without a corresponding movement of Al and Si is of the same order of magnitude as the heat of fusion. Hence, it seems inconceivable for such a segregation and charge accumulation to occur spontaneously on cooling of a disordered high-plagioclase.

The first and second steps in the calculations have indicated that energies for local disordering of Ca and Na with respect to Al and Si are not extremely large so long as charge does not build up over more than a few unit cells. Upon rapid heating of a fully ordered low-plagioclase, some disordering of Ca and Na atoms, especially across domain boundaries, should occur without movement of Al and Si. It might be possible for this disorder to become great enough to weaken the subsidiary reflections as observed by Foit and Peacor (1967) for a heated andesine. This phenomenon is discussed further by Smith and Ribbe (1969).

In conclusion, it appears that the high activation energy for Al and Si atoms together with the spatial charge linkage to Na and Ca atoms enforces very strict requirements on the ordering of high-plagioclase.

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