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# Statistical mechanical models for aluminum-silicon disorder in plagioclases

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## Abstract

The equilibrium aluminum–silicon disorder which occurs in plagioclase solid solutions is computed using an extension of the statistical mechanical model of Mazo. The model includes aluminum avoidance and a composition-dependent $T_1$ site preference energy. The configurational entropy and order parameter are calculated as functions of the temperature and composition, and reasonable qualitative agreement is obtained with the known composition dependence of the order parameter. A two-dimensional analogue model of albite is introduced which includes local charge balance. A limiting high-temperature configurational entropy of 1.12R per mole of Al is obtained in the two-dimensional model when local charge balance is rigorously obeyed.

## Introduction

A variety of silicate minerals exhibit order–disorder phenomena similar to those seen in binary alloys. However, the complex nature of the silicate minerals has greatly limited the understanding of the ordering phenomena in these systems. While there have been some theoretical studies of silicate solid solutions using simple thermodynamic solution models (Saxena, 1973), little work has been attempted using statistical mechanical methods. Thus little is known about the connection between the microscopic ordering process and the bulk thermodynamic properties of these systems. Recently, a statistical mechanical model has been proposed by one of us (Mazo, 1977) (hereafter referred to as I) for the low albite–high albite transformation. The work of I gave a reasonable qualitative description of the ordering phenomena in albite and demonstrated that tractable statistical mechanical models can be developed which deal with order–disorder phenomena in complex mineral systems. Another example, for a different system, is the work of Navrotsky and Loucks (1977).

The aluminum–silicon ordering which occurs in albite is also present, in varying degrees, in plagioclases of various compositions. These systems are particularly interesting since the ordering is found to be composition- as well as temperature-dependent. Statistical mechanical models have been previously proposed for plagioclase mixtures (Kerrick and Darken, 1975); however, they have not dealt with the temperature dependence of the ordering nor have they considered what effects the ordering has on the thermodynamic properties of the mixture. In addition, these models assume that plagioclases are, in some sense, ideal mixtures of albite and anorthite, while the experimental evidence strongly suggests otherwise (Seck, 1971).

This paper extends the model of I to plagioclase mixtures. The advantage of the approach of I over the models of Kerrick and Darken (1975) is that interatomic interactions thought to be important in feldspars can be incorporated into the theory. Consequently we will be particularly interested in determining the effect of short-range order due to aluminum avoidance on the long-range ordering of the aluminum atoms in the mixture.

The paper is organized as follows. In the remainder of the Introduction we briefly describe the ordering phenomena which occur in calcic and sodic feldspars. In Section II we define the model and describe some of its order-dependent thermodynamic properties. In the third and final section we discuss some of the shortcomings of the model.

Albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) both have typical feldspar structures in which the aluminum and silicon atoms are tetrahedrally bonded to oxygen atoms. The key structural unit in the crystal is that of four-member rings of $TO_4$ (T = Al,Si) tetrahedra which are bound together in a

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## Appendix A

Here we derive the free energy expression, within the quasi-chemical approximation, appropriate to our model. For a more detailed discussion of this approximation the reader is referred to Guggenheim (1952).

In Equation 9 we approximate $g(r,s,n,x)$ by the following:

$$g(r,s,n,x) = [\alpha(\frac{g^{*\frac{1}{N}}}{\beta} - 1) + 1]^N \qquad (A1)$$

where $g^*$ is equal to the number of ways that independent pairs of A and B particles can be placed on the lattice consistent with the given values of r, s, n and x. The function $g^*$ is thus

$$g^*(r,s,n,x) = \frac{N!}{r_{AA}!r_{AB}!r_{BA}!s_{AA}!s_{BB}!(\frac{s_{AB}}{2}!)^2} \qquad (A2)$$

Using Equations 3a-b and assuming $r_{AA}=s_{AA}=0$, Equation A2 can be rewritten in terms of the order parameter p and the mole fraction of albite, x, as follows

$$g^* = \left[\frac{3^{2-p}}{p^p (2-x-p)^{(2-x-p)} (1+x-2p)^{(\frac{1+x-2p}{3})} (2x-1+2p)^{(\frac{2x-1+2p}{3})}}\right]^N \qquad (A3)$$

where we have used Stirling's approximation for the various factorials.

In most applications of the quasi-chemical approximation the function $\alpha$ in Equation A1 is chosen to be identically one. The function $\beta$ is then a correction factor which normalizes $g(r,s,n,x)$. In the present model this normalization condition is

$$\sum_{r_{AA},s_{AA}} g(r_{AA},s_{AA},n,x) = \frac{(\frac{N}{4})!(\frac{3N}{4})!}{n!(\frac{N}{4}-n)!(\frac{N}{4}(2-x)-n)!^2} \qquad (A4)$$

While such a choice for $\alpha$ and $\beta$ produces an excellent approximation for g

near its maximum value, it can result in a quite poor approximation for the more ordered states of the system (Prigogine, Mathot-Sarolea and Van Hove, 1952). In the present model, such choices for $\alpha$ and $\beta$ result in a value of $-N \ln 2$ for the entropy of ordered anorthite. Therefore we choose $\beta$ such that $g^*$ is one in ordered albite and anorthite and then satisfy equation A4 by an appropriate choice of $\alpha$. This worsens the quality of the approximation to g near its maximum, but improves overall agreement. The functional form for $\beta$ is therefore

$$\beta = \left[ \frac{N!^2}{(\frac{N}{2}(1+x))!(\frac{N}{2}(1-x))!^3 (Nx)!} \right]^{\frac{1}{N}} \tag{A5}$$

which can be reexpressed as

$$\beta = \left[ (1+x)^{(\frac{1+x}{2})} (1-x)^{\frac{3}{2}} (1-x)^x 2^{(x-2)} \right]^{-1} \tag{A6}$$

Using the maximum term in the summation of equation A4, $\alpha$ is found to be

$$\alpha = \left[ \left( \frac{(\frac{N}{4})!(\frac{3N}{4})!}{n!(\frac{N}{4}-n)!(\frac{N}{4}(2-x-\frac{4n}{N}))!(\frac{N}{4}(1+x+\frac{4n}{N}))!} \right)^{\frac{1}{N}} - 1 \right] \cdot (\frac{g^{*\dagger}}{\beta} - 1)^{-1} \tag{A7}$$

where $g^{*\dagger}$ is the value of $g^*$ in a completely random distribution <u>without</u> aluminum avoidance. In terms of the order parameter and the composition Equation A7 can be reexpressed as

$$\alpha = \frac{\left[ \frac{3^3}{p^p (1-p)^{(1-p)} (2-x-p)^{(2-x-p)} (1+x+p)^{(1+x+p)}} \right]^{\frac{1}{4}} - 1}{\frac{3^3 (1-x)^{\frac{3}{2}(1-x)} (1+x)^{\frac{1+x}{2}} x^x 2^{x-2}}{(2-x-p)^{(2-x-p)} (1+x+p)^{(1+x+p)} p^p (1-p)^{1-p}} - 1} \tag{A8}$$

The molar free energy for the system is given by combining Equations 8, 11 and 13 of Section II and is found to be

$$-\frac{A}{kT} = \ell n\ g^{\frac{1}{N}} - \frac{(u+vx)p}{4kT} \tag{A9}$$

where g is given by Equations A1, A3, A6 and A8. The equilibrium value of p is then obtained by minimizing the free energy with respect to p,

$$\frac{1}{g^{\frac{1}{N}}}\left(\frac{\partial g^{\frac{1}{N}}}{\partial p}\right)_{T,x} - \left(\frac{u+vx}{kT}\right) = 0 \tag{A10}$$

The derivative $\left(\frac{\partial g^{\frac{1}{N}}}{\partial p}\right)_{T,x}$ is given by

$$\left(\frac{\partial g^{\frac{1}{N}}}{\partial p}\right)_{T,x} = \left(\frac{\partial \alpha}{\partial p}\right)_{T,x}\left(\frac{g^{*\frac{1}{N}}}{\beta} - 1\right) + \alpha \frac{\partial}{\partial p}\left(\frac{g^{*\frac{1}{N}}}{\beta}\right)_{T,x} \tag{A11}$$

where $g^{*\frac{1}{N}}$, $\alpha$ and $\beta$ are given by equations A3, A8 and A6 respectively and the derivatives in Equation A11 are found to be

$$\left[\frac{\partial\left(\frac{g^{*\frac{1}{N}}}{\beta}\right)}{\partial p}\right]_{T,x} = \frac{g^{*\frac{1}{N}}}{\beta}\ \ell n\left[\frac{2-x-p}{3p}\left(\frac{1+x-2p}{2x-1+2p}\right)^{2/3}\right] \tag{A12}$$

$$\left(\frac{\partial \alpha}{\partial p}\right)_{T,x} = \frac{\left(-\frac{3}{4}D_1D_2 + D_2 - \frac{D_1}{4}\right)}{(D_2-1)^2}\ \ell n\left[\frac{(2-x-p)(1-p)}{(1+x+p)p}\right] \tag{A13}$$

where

$$D_1 = \left[\frac{3^3}{p^p(1-p)^{(1-p)}(2-x-p)^{(2-x-p)}(1+x+p)^{(1+x+p)}}\right]^{\frac{1}{4}} \tag{A14}$$

$$D_2 = \frac{3^{3(1+x)}\ 2^{\frac{1+x}{2}}\ (1-x)^{\frac{3}{2}(1-x)}\ x^{x}\ 2^{(x-2)}}{p^p(2-x-p)^{(2-x-p)}(1+x+p)^{(1+x+p)}(1-p)^{(1-p)}}$$

## Appendix B

Here we outline a model for "two dimensional albite"which includes charge balance in addition to aluminum avoidance. We start with a primary square planar lattice of 4N sites where the length of the side of a unit cell is $\ell$. A secondary square planar lattice of N sites is then constructed among the primary lattice sites such that the length of a unit cell in the secondary lattice is $2\ell$. An example of such a lattice is given in Fig. 5 where the sites of the secondary lattice are indicated by crosses. Each secondary site has four primary sites as nearest neighbors. The Al and Si atoms occupy the primary sites with the sodium atoms of albite occupying the remaining secondary sites. Local charge balance in the model then corresponds to each secondary site (Na) having one Al atoms and three Si atoms located on its four nearest neighbor primary sites. It should be pointed out that this definition of local charge balance eliminates many configurations of the atoms on the primary sites which would violate the aluminum avoidance principle.

Since the aluminum atoms can be at any of the four sites surrounding a secondary site, the high temperature limit for the entropy, without explicitly imposing aluminum avoidance, is $R \ln 4 = 1.39\ R$. This compares to a value of 2.25 R for a completely random distribution of the atoms on the primary sites.

It is straightforward to include aluminum avoidance into the model using a quasi-chemical approximation quite similar to that used in Sec. II. Here we limit the calculation of the configurational entropy, subject to aluminum avoidance, to only its high temperature limit.

Let us associate with each secondary site an arrow which can point in any of four different directions. We then associate with each different state of occupation of the four nearest neighbors of the secondary site a given direction of the arrow. The configurational state of the model is then given by the configurational state of the arrows. The entropy of the system is then

$$\underline{\underline{S}} = k \ln g \qquad \text{(B1)}$$

where g is equal to the number of ways the arrows can be placed on the lattice subject to aluminum avoidance. Here we assume that g is proportional to the number of ways independent pairs of arrows can be placed on the lattice. There are 32 possible configurations for a nearest neighbor pair of arrows, 4 of which violate the aluminum avoidance principle. In the high temperature limit all 28 configurations which satisfy aluminum avoidance are equally probable. Thus g in Equation B1 is proportional to $(28)^{2N}$ where the exponent 2N is a result of there being 2N independent pairs of arrows. The proportionality constant is then fixed by the condition that g in a completely random configuration, without aluminum avoidance, would have the value $4^N$. Thus g is

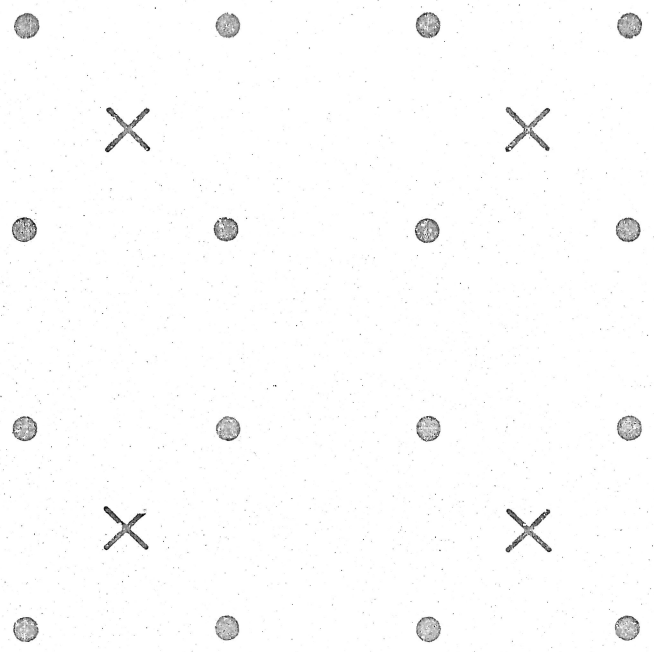
$$g = 4^N \left(\frac{28}{32}\right)^{2N} \qquad \text{(B2)}$$

and the limiting value for the entropy is

$$\underline{\underline{S}} = R \ln 4 \left(\frac{28}{32}\right)^2 \qquad \text{(B3)}$$

$$= 1.12R$$

Subsequent to the writing of this Appendix, the properties of this two-dimensional model have been worked out for arbitrary temperatu . The details will be published elsewhere (Andersen and Mazo, 1979).



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| FIGURE 5 | |

Fig. 5. Simple quadratic lattice for "two-dimensional albite." The solid circles and crosses indicate lattice positions occupied by the aluminum-silicon and sodium atoms respectively.