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The distribution of $NaAlSi_3O_8$ between coexisting microcline and plagioclase and its effect on geothermometric calculations

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Abstract

The partitioning of $NaAlSi_3O_8$ between coexisting microcline and plagioclase solid-solutions is modeled using published Margules parameters for microcline-low albite solid-solutions. Variations in the structural state of the alkali feldspar may shift the temperature calculated from coexisting feldspar pairs by as much as 100°C. The magnitude of this shift varies with the compositions of the coexisting feldspar, but will generally be less than 100°C. In nature, the effect of ordering would be less for primary orthoclase, and would not be significant if the feldspar originally equilibrated in the disordered state.

Introduction

During the last year, we have been critically evaluating the application of a revised two-feldspar geothermometer (Stormer, 1975) in a number of geologic environments (Whitney and Stormer, 1976; Stormer and Whitney, 1975; Whitney *et al.*, 1975). As a part of this evaluation, we have attempted to determine the significance of variation in the structural state of the feldspar on the $NaAlSi_3O_8$ distribution. This paper outlines the development of $NaAlSi_3O_8$ distribution models applicable to low-temperature alkali feldspars, and discusses the possible geologic significance of such models.

Development of the model

The distribution of $NaAlSi_3O_8$ between alkali feldspar and plagioclase has been recognized as a potential geothermometer since Barth (1934) first proposed the idea. There have been many discussions of the subject (Barth, 1951, 1956, 1962, 1970; Dunham, 1971; Orville, 1962; Perchuck and Ryabchikov, 1968), and a model based on very limited ternary feldspar data was developed by Saxena and Ribbe (1972). Recently Stormer (1975) presented an approximate solution model based on modern thermodynamic data from alkali feldspar solid-solutions, and applied it to extrusive volcanic assemblages. Our study of epizonal intrusives (Whitney and Stormer, 1976) also dealt primarily with high-temperature conditions. Thus, the thermodynamic parameters used (Margules parameters) were those for high sanidine given by Thompson and Waldbaum (1969) and Waldbaum and Thompson (1969). Before this tool can be used under lower-temperature conditions (500 to 800°C), the effects of structural state should be evaluated.

The original model presented by Stormer (1975) used the chemical potential of pure albite as a standard state and so was able to develop the relationship

$$(1) \qquad X_{\mathrm{ab},AF}\gamma_{\mathrm{ab},AF} = X_{\mathrm{ab},PF}\gamma_{\mathrm{ab},PF}.$$

The distribution coefficient may be written as

$$(2) \qquad K_{\mathrm{D,ab}} = X_{\mathrm{ab},AF}/X_{\mathrm{ab},PF} = \gamma_{\mathrm{ab},PF}/\gamma_{\mathrm{ab},AF}.$$

Stormer (1975) assumed the plagioclase solid-solutions to be ideal, *i.e.* $\gamma_{\mathrm{ab},PF} = 1$. We have used the activity of albite in plagioclase in all calculations to avoid assuming such ideal behavior. If ideality is assumed, then the activity will equal the mole fraction of albite in the plagioclase. This assumption still seems to be necessary for low-albite, because no better data are available to characterize the plagioclase solid-solution over a range of pressure and temperature. When a different solution model is available for plagioclase, it may be incorporated into the current model.

At low temperatures non-ideality may be important, especially in sodium-rich compositions near 500°C where the peristerite solvus is important. If the peristerite "gap" is a two-phase loop as suggested by Orville (1974), high albite would be a preferred standard state for the plagioclase while low albite would still be used for alkali feldspar at the same temperatures. There would then be a difference in the standard state chemical potentials. However this could be incorporated in the present model as a $\gamma_{PF} = \exp(\Delta\mu/RT)$ which would be independent of composition. Present thermodynamic data are not sufficiently accurate to allow evaluation of this parameter, even if the two-phase peristerite model is correct.

In alkali feldspars, $\gamma_{\mathrm{ab},AF}$ may be derived from one of several formulations. The Margules parameters have proven to be one useful method of representing solution models. The original presentation of Stormer (1975) used the parameters

$$(3)\quad W_G^{\mathrm{Ab}} = 6326.7 + 0.0925P - 4.6321T\ (\text{for NaAlS}_3\text{O}_8)$$

$$(4)\quad W_G^{\mathrm{Or}} = 7671.8 + 0.1121P - 3.8565T\ (\text{for KAlSi}_3\text{O}_8)$$

(Thompson and Waldbaum, 1969; Waldbaum and Thompson, 1969).

The various terms in these expressions are further discussed in the Appendix. In order to model the effect of low-temperature structural-state alkali feldspar (*i.e.* microcline) on the distribution of $NaAlSi_3O_8$, we must use appropriate Margules parameters for these solutions, and low-albite as a standard state in both solutions. Currently, the only published Margules parameters available are those given by Bachinski and Muller (1971) for microcline–low albite solid-solutions, which are based on the sodium content of 22 pairs of coexisting feldspars from fused-salt alkali-exchange experiments. Using their expressions for W_G^{Ab} and W_G^{Or}, and assuming the pressure coefficients (W_V^{Ab} and W_V^{Or}) in both expressions equal approximately 0.11 cal/bar as suggested by Orville (1967), the Margules parameters for these solid solutions are given by the expressions

$$(5)\qquad W_G^{\mathrm{Ab}} = 7973.1 + 0.11P - 6.48T$$

$$(6)\qquad W_G^{\mathrm{Or}} = 7490.9 + 0.11P - 2.17T.$$

Following Stormer's (1975) equation 17 we can derive the relationship

$$(7)\quad \ln K_{\mathrm{D,Ab}} = \ln(X_{\mathrm{ab},AF}/X_{\mathrm{ab},PF}) = \ln\gamma_{\mathrm{ab},PF} - \ln\gamma_{\mathrm{ab},AF} = \ln\gamma_{\mathrm{ab},PF} = -1/RT(1 - X_{\mathrm{ab},AF})^2[W_G^{\mathrm{Ab}} + 2X_{\mathrm{ab},AF}(W_G^{\mathrm{Or}} - W_G^{\mathrm{Ab}})],$$

which yields the following rather complex temperature function:

$$(8)\quad T(\mathrm{K}) = [7973.1 - 16910.6X_{\mathrm{ab},AF} + 9901.9X_{\mathrm{ab},AF}^2 + (0.11 - 0.22X_{\mathrm{ab},AF} + 0.11X_{\mathrm{ab},AF}^2)P]/[-1.9872\ln(X_{\mathrm{ab},AF}/a_{\mathrm{ab},PF}) + 6.48 - 21.58X_{\mathrm{ab},AF} + 23.72X_{\mathrm{ab},AF}^2 - 8.62X_{\mathrm{ab},AF}^3]$$

assuming the alkali feldspars have equilibrated as microcline. Representative "curves" for this distribution model are shown in Figure 1 for comparison with Barth's original formulation and the high-temperature model of Stormer (1975).

Another convenient method of representing equilibrium is in the form of determinative curves. Two isobaric diagrams are shown in Figure 2. Since alkali feldspars at temperatures above about 900°C are almost certainly completely disordered, we have not carried the calculation to higher temperatures. The determinative curves previously calculated from high sanidine data are also shown for comparison. If the plagioclase is assumed to be an ideal solution, the activity of albite in plagioclase will be equal to its mole fraction.

Since many feldspars of interest crystallized as orthoclase at intermediate temperatures, it is unfortunate that there are no parameters currently available in the literature for intermediate structural states. However, it seems reasonable to assume that the thermodynamic properties will be between those of the disordered and ordered varieties, although we cannot necessarily assume a regular variation. Temperature values for feldspars crystallizing as orthoclase would probably lie between those defined for sanidine and microcline, although they might not be exactly half-way between.

Application

Obviously, the temperature relationship calculated from the microcline parameters will not have the direct application found for the sanidine construction. Microcline itself is not stable at temperatures much in excess of 500°C, and in many cases has transformed from feldspar originally crystallized in a more disordered structural state. Thus, these curves would only be correct at low temperatures, in the range where the method is not very accurate because of uncertainty in the plagioclase thermodynamic data. However, these values act as boundary conditions and place limits on the direction and magnitude of the shift in estimated temperatures that may be caused by structural-state variations in the alkali feldspars.

In volcanic rocks, the alkali feldspars crystallizing from the melt are usually sanidine or anorthoclase. Indeed, in almost all experimental work (*e.g.* Tuttle and Bowen, 1958; Luth and Tuttle, 1966; Whitney, 1975), feldspars crystallized from synthetic material at any temperature seem to form in the high-temperature or disordered state. Most natural feldspar grown from hydrothermal solutions is thought to have originally formed in a disordered state (Poty *et al.*, 1974). If the feldspar pairs established inter-crystalline chemical equilibrium in the disordered state, then the disordered parameters would be the correct ones to use, even if the feldspars have subsequently reequilibrated internally to an ordered structural state.

In granitic plutonic rocks, which crystallized slowly from a melt, it may be possible to get a certain degree of ordering while the feldspars are still in equilibrium with the liquid, and through the liquid, with each other. In the temperature range 600 to 800°C, however, the most ordered feldspar which could be stable would be orthoclase. Therefore, the shift in estimated temperature would be considerably less than that shown by the microcline curves, but the temperatures calculated from the sanidine model could be too low by as much as 50°C. At temperatures of crystallization above about 800°C or so, the feldspar should be essentially disordered, and minimal discrepancy between calculated and true temperature will be introduced by assuming the high-temperature model.

In high-grade metamorphic rocks the ordering problem may create the greatest discrepancies. Here, equilibration would be in the solid state, at upper amphibolite- and granulite-grade temperatures where the stable feldspar would probably be orthoclase. In addition, since order–disorder reactions are very sluggish, some order may be inherited from a lower temperature state, as in the alkali exchange experiments. In these instances, it may be important to evaluate what the structural state of the feldspars was during the equilibration process and take the effect of structural state on $NaAlSi_3O_8$ distribution into consideration, at least in a qualitative fashion, if temperature estimates are to be reliable. If orthoclase were the stable phase, the temperatures estimated from the high-temperature feldspar determinative curves would be too low by up to 50°C, while those determined using microcline parameters would be too high by a similar amount.

Summary

If the two-feldspar geothermometer is to be applied to high-grade metamorphic rocks, or slowly crystallized plutonic rocks, the effects of structural state on the calculated temperature must be considered. The model derived for microcline solid-solutions supplies one limit on the effects of structural state and allows some estimation of the temperature of equilibration between alkali feldspar and plagioclase, even when the alkali feldspar has equilibrated in an intermediate structural state.

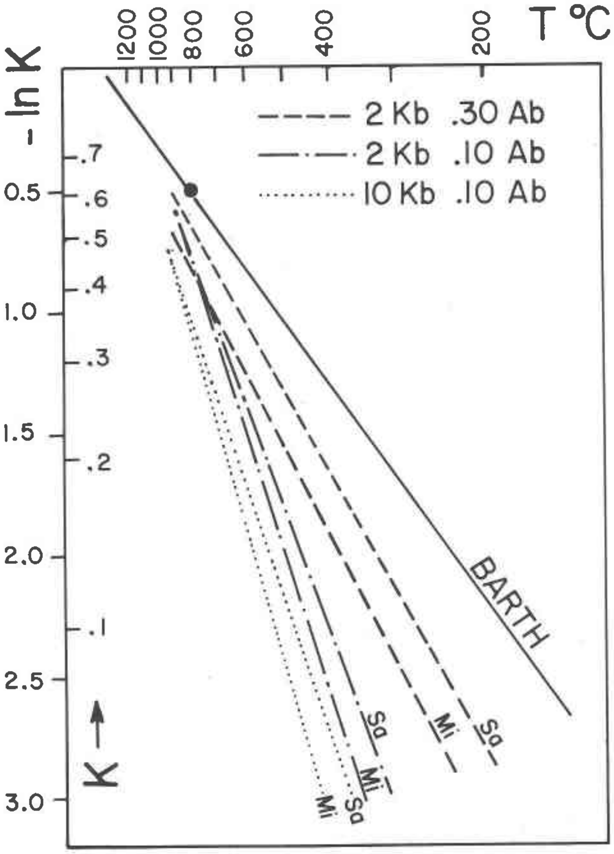

Fig. 1. Albite distribution coefficient *vs.* temperature from Barth (1951) and Stormer (1975). Typical curves calculated from thermodynamic data have been added to illustrate the effects of structural state compared to those caused by pressure and composition of the alkali feldspar; Sa = sanidine, Mi = microcline.

Appendix

As more and more data on alkali feldspar solid-solutions become available, it will be advisable to update the temperature equations and determinative curves derived from current parameters. Such a procedure is facilitated by relating the numerous coefficients in the temperature equation [18 of Stormer (1975) and 8 in this paper] directly to the Margules parameters.

The significance of the Margules formulation has been discussed thoroughly by Thompson (1967)

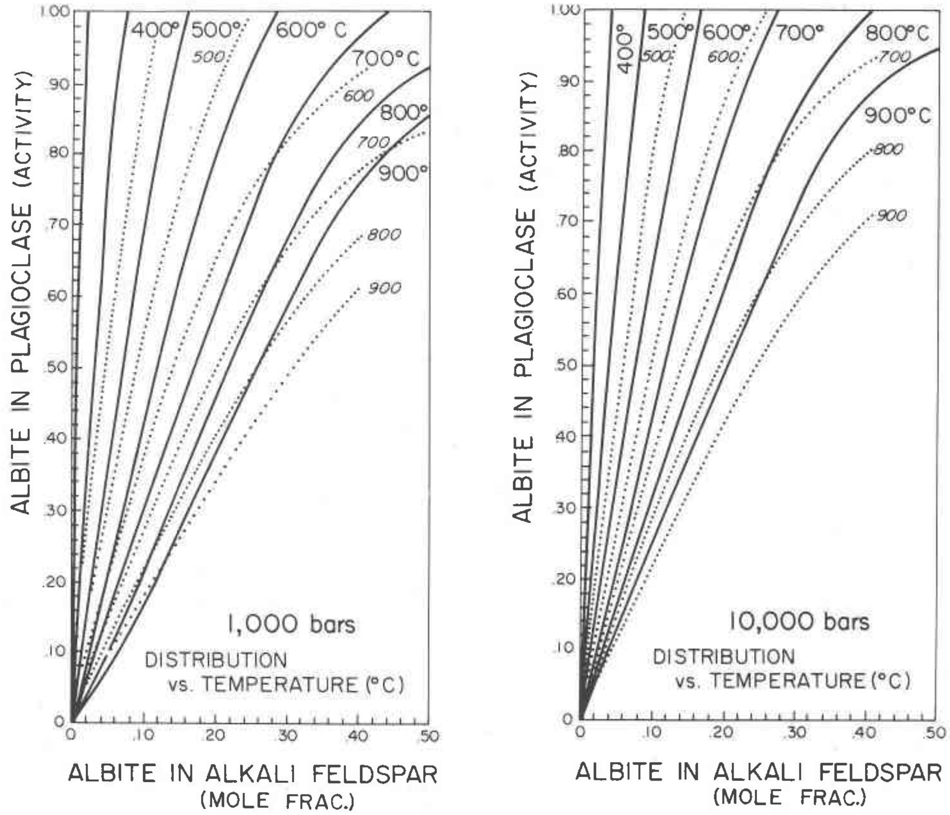

Fig. 2. Determinative curves for temperature based on the proposed model of albite distribution between coexisting plagioclase and alkali feldspars. Dotted lines are from Stormer (1975) and were calculated using sanidine solid-solution parameters. Solid curves have been calculated as described in the text from low-temperature data on microcline solid-solutions. If plagioclase solid-solutions are assumed to be ideal, the albite activity will be equal to mole fraction for the plagioclase coordinate.

among others, and will not be repeated here. The Margules parameters, W_G^{Ab} and W_G^{Or}, are analogous to Gibbs free energy, and are generally composed of a constant, a pressure term, and a temperature term. These are often presented in a general format at

$$(9) \qquad W_G^{Ab} = W_E^{Ab} + W_v^{Ab}P - W_s^{Ab}T$$

$$(10) \qquad W_G^{Or} = W_E^{Or} + W_v^{Or}P - W_s^{Or}T.$$

Note that the minus sign before the temperature term is a function of the equation and not the sign of the W_s parameter.

The temperature calculation equation may be written in the form

$$(11) \quad T(°K) = (A + BP)/[-1.9872 \ln(X_{\text{ab},AF})/a_{\text{ab},PF} + C]$$

where A, B, and C are polynomials in $X_{\text{ab},AF}$;

$$(12) \quad A = a_0 + a_1X_{\text{ab},AF} + a_2X^2_{\text{ab},AF} + a_3X^3_{\text{ab},AF}$$

$$(13) \quad B = b_0 + b_1X_{\text{ab},AF} + b_2X^2_{\text{ab},AF} + b_3X^3_{\text{ab},AF}$$

$$(14) \quad C = c_0 + c_1X_{\text{ab},AF} + c_2X^2_{\text{ab},AF} + c_3X^3_{\text{ab},AF}$$

All the coefficients, a_i, b_i, and c_i, are equal to the following functions of the Margules parameters which were defined in equations 9 and 10;

$$(15) \quad a_0 = W_E^{Ab}$$

$$a_1 = -(4W_E^{Ab} - 2W_E^{Or})$$

$$a_2 = 5W_E^{Ab} - 4W_E^{Or}$$

$$a_3 = (2W_E^{Ab} - 2W_E^{Or})$$

$$b_0 = W_v^{Ab}$$

$$b_1 = -(4W_v^{Ab} - 2W_v^{Or})$$

$$b_2 = 5W_v^{Ab} - 4W_v^{Or}$$

$$b_3 = -(2W_v^{Ab} - 2W_v^{Or})$$

$$c_0 = W_s^{Ab}$$

$$c_1 = -(4W_s^{\mathrm{Ab}} - 2W_s^{\mathrm{Or}})$$

$$c_2 = 5W_s^{\mathrm{Ab}} - 4W_s^{\mathrm{Or}}$$

$$c_3 = -(2W_s^{\mathrm{Ab}} - 2W_s^{\mathrm{Or}})$$

By substituting these values back into the polynomials A, B, and C, the temperature can be calculated for any set of Margules parameters.

Similarly, the equation used to calculate determinative curves may be related to the generalized set of parameters. In this case, the general form is given by the relationship

$$(16)\quad a_{\mathrm{ab},PF} = X_{\mathrm{ab},AF}\cdot\exp\left[(A + BP - CT)/1.9872T\right]$$

where A, B, and C are the same polynomials given in equations 12, 13, and 14, with polynominal coefficients as defined in 15. By substituting the Margules parameters into the polynominal coefficients (15) and substituting the derived polynomials into equations 16, the variation in $X_{\mathrm{ab},PF}$ with respect to $a_{\mathrm{ab},AF}$ may be calculated at any pressure and temperature.

When arranged in this fashion, the calculations involved are easily carried out on any modern computer facility or portable calculator.

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