A Practical Two-feldspar Geothermometer

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Abstract

A geothermometer based on the partitioning of the albite component between plagioclase and alkali feldspar, such as the Barth thermometer, is of great practical value, particularly since the required analyses can be made with simple optical or X-ray techniques. Modern thermodynamic data for the alkali feldspars in the form of published Margules parameters are used to derive a simple expression relating the composition of coexisting feldspars to temperature and pressure. For convenience, a set of curves has been prepared using this expression. This expression has the following advantages over previous two-feldspar geothermometers: It takes into account a significant pressure dependence; it uses a much better model of alkali feldspar solution behavior; the calibration is based on abundant experimental data for the alkali feldspar system; and it agrees well with existing experimental data for ternary feldspars as well as with naturally occurring feldspar pairs.

Introduction

A technique for determining geological temperatures based on the distribution of albite component between two coexisting feldspars is of great practical significance. The igneous and metamorphic "granitic" rocks which make up the bulk of the continental masses normally contain two such feldspars, but few methods for estimating temperature of origin are applicable to these rocks. Perhaps more importantly, the basic equipment necessary for the feldspar analysis can be found even in the most poorly equipped laboratories. A polarizing microscope and refractive index oils will suffice to determine compositions on crushed rock fragments. A two-feldspar geothermometer, perfected and presented in a useful form, would be an important aid to geological interpretation within the capabilities of field geologists throughout the world.

The concept of using the distribution of albite between alkali feldspar and plagioclase solid solutions as a geothermometer is certainly not new. Barth (1934) proposed such a thermometer 40 years ago. The original formulation has subsequently been discussed and modified in various publications (Barth, 1951, 1956, 1962; Dunham, 1971; Orville, 1962). Perchuck and Ryabchikov (1968) published a paper on nepheline and feldspar equilibria which included data for a two-feldspar geothermometer based on a relatively sophisticated treatment of limited experimental data. Barth (1970) pointed out some inconsistencies in this work, and unfortunately it seems to have been virtually ignored as a practical tool.

Barth's (1951) formulation has also been presented in a popular elementary thermodynamics text (Kern and Weissbrod, 1967) and is still widely used by field-oriented petrologists. The intent of this paper is to present a set of determinative curves, based on modern feldspar thermodynamic data, for use by a broad range of geologists. In view of the popularity and persistence of Barth's (1951) formulation and keeping in mind the very limited thermodynamic experience of many of those who will have use for this geothermometer, we feel that a rather basic presentation of the thermodynamic background is appropriate.

Thermodynamic Background

The Expression of Chemical Equilibrium

The distribution of the available albite component between plagioclase and alkali feldspar grains during crystallization from a liquid or vapor, or during reaction with or without interstitial liquid or vapor, can be expressed simply by the equation:

\[ \text{NaAlSi}_{3}\text{O}_{8}(AF) = \text{NaAlSi}_{3}\text{O}_{8}(PF) \]  

where \( (AF) \) and \( (PF) \) indicate the alkali feldspar and plagioclase mineral phases. A thermodynamic defini-
tion of chemical equilibrium states that the chemical potential ($\mu_{ab}$) of albite in each phase must be equal:

$$\mu_{ab,AF} = \mu_{ab,PF} \tag{2}$$

Other phases (liquids, vapors, other minerals), if present, will affect the albite content of the plagioclase and alkali feldspar but not the equilibrium relationship expressed in Equation (2). Variation in plagioclase and alkali feldspar compositions must thus take place in such a way that relation (2) is maintained. In this respect the arguments presented by Dunham (1971) are in error. A single expression for the distribution of albite should be applicable to all two-feldspar rocks regardless of composition. The problem lies in relating this equilibrium in theory to the actual analyzed compositions of complex natural feldspars. While expression 2 is a necessary condition of equilibrium, it alone does not suffice to establish the equilibrium. The conditions:

$$\mu_{or,AF} = \mu_{or,PF} \tag{2'}$$

and

$$\mu_{an,AF} = \mu_{an,PF} \tag{2'\prime}$$

also must be simultaneously satisfied in order to establish equilibrium between feldspars containing $\text{KAlSi}_3\text{O}_8$ (or) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (an) components. In order to rigorously derive the thermodynamic properties of feldspars containing all 3 components, expressions 2' and 2'\prime and expressions derived from them (analogous to those derived from Equation 2 below) must be considered. The principal assumption of the model proposed here, and all previous ones, is that the potassium component has no effect on the plagioclase feldspar phase and that the calcium component has no effect on the alkali feldspar phase. The rationale for this is discussed below. This assumption, although a serious limitation, greatly simplifies the problem, making it analogous to the distribution of a single component between two unrelated phases. This allows us to ignore relationships stemming from 2' and 2'\prime.

The chemical potential, $\mu$, can be related to the chemical potential, $\mu^*$, in any convenient “standard” state, with added factors to correct for deviations from the standard state. The “correction factor” for variation in composition is the logarithm of the activity $a$, which is in turn a function of composition. (In an ideal solution, activity equals mole fraction). Thus, for alkali feldspar and plagioclase:

$$\mu_{ab,AF} = \mu^*_{ab,AF} + RT \ln a_{ab,AF} \tag{3}$$

$$\mu_{ab,PF} = \mu^*_{ab,PF} + RT \ln a_{ab,PF} \tag{4}$$

Substituting Equations (3) and (4) into Equation (2) and rearranging yields:

$$\mu^*_{ab,PF} - \mu^*_{ab,AF} = RT \ln \frac{a_{ab,AF}}{a_{ab,PF}} \tag{5}$$

Thus, the ratio of compositions as represented by activity is controlled by the difference in chemical potential between the standard states.

The Barth Model

Barth’s (1951) model is based on the Nernst distribution law for dilute solutions. Such a model assumes that the activity of a component (in this case albite) becomes a linear function of composition as the solution becomes increasingly dilute (Henry’s Law, Fig. 1). The standard state then is conveniently chosen to be a hypothetical pure albite with a chemical potential related to a linear extrapolation of activity from the very dilute region. A dilute solution in the region where the activity does in fact become nearly linear—and where, therefore, activity equals mole fraction—can be referred to as “ideally dilute.” The extent to which any solution follows this “law” may be quite limited. In Figure 1 the activities of albite in alkali feldspars depart significantly from Henry’s Law except in very albite-poor feldspars or at very high temperatures. Equation (5) could then be written:

$$\mu^*_{ab,PF} - \mu^*_{ab,AF} = RT \ln \frac{X_{ab,AF}}{X_{ab,PF}} \tag{6}$$

The ratio of mole fractions on the right side of this
equation is often expressed as the distribution coefficient $K_D$. Rearrangement produces:

$$\ln K_{D,ab} = \frac{\mu_{ab,PF}^* - \mu_{ab,AF}^*}{RT} \tag{7}$$

The Nernst distribution law includes the further assumption that the chemical potential term, on the right side of Equation (7), is a linear function of absolute temperature. Equation (7) may then be replaced by the linear equation:

$$\ln K_{D,ab} = \frac{a}{T} + b \tag{8}$$

Barth empirically determined the coefficients $a$ and $b$ in Equation (8) by reference to natural specimens, whose temperatures were inferred from other geological evidence. His presentation of the results (1951) is reproduced in Figure 2. Although a simple, imaginative, and worthwhile approach at the time of its proposal, it has several disadvantages which can be overcome with present knowledge: (1) the alkali feldspars deviate considerably from Henry’s Law in the composition range of interest; (2) the temperature calibration is based on empirical rather than experimental data; and (3) the effect of pressure is not considered.

**Proposed Distribution Model**

A better model, which we propose here, begins by taking Equation (5), which describes the equilibrium without assumptions. Modern data on the solution behavior of feldspars then enables us to use the actual chemical potential of pure albite as the standard-state value for both alkali feldspar and plagioclase solid solutions. Since the standard-state chemical potentials are identical, the difference becomes zero and Equation (5) becomes:

$$O = RT \ln \frac{a_{ab,AF}}{a_{ab,PF}} \tag{9}$$

therefore:

$$a_{ab,AF} = a_{ab,PF} \tag{10}$$

If both solutions were truly ideal (i.e., $a = X$) the albite content in coexisting plagioclase and alkali feldspar would always be equal. Obviously they are not both ideal solutions. The extent of non-ideality can be expressed in the activity coefficient, $\gamma$, a factor relating activity to actual mole fraction:

$$X_{ab,AF} \cdot \gamma_{ab,AF} = X_{ab,PF} \cdot \gamma_{ab,PF} \tag{11}$$

The distribution coefficient is then simply related to the ratio of activity coefficients.

$$K_{D,ab} = \frac{X_{ab,AF}}{X_{ab,PF}} = \frac{\gamma_{ab,PF}}{\gamma_{ab,AF}} \tag{12}$$

**Activity Coefficient Data**

The plagioclase series has generally been considered to be nearly ideal at higher temperatures (Bowen, 1928, p. 176), although the peristerite solvus indicates it to be non-ideal at low temperatures. Orville (1972) indicated that at 700°C and 2 kbar plagioclase could be considered as an ideal solution of albite, from Ab100 to about Ab46, so that $\gamma_{ab,PF} = 1.0$. Since virtually all plagioclase feldspars which coexist in nature with alkali feldspar fall in this range we may assume that, at the pressures and temperatures which are of most interest, $\gamma_{ab,PF}$ has a value near one and may therefore be dropped from Equation (12), leaving:

$$K_{D,ab} = \frac{1}{\gamma_{ab,AF}} \tag{13}$$

For albite in alkali feldspars, any of several recent formulations for the activity coefficient may be used. We have selected those developed by Thompson and Waldbaum (1969a, 1969b) in the form of Margules
parameters; these expressions represent the contribution of each component, in this case NaAlSi$_2$O$_6$ and KAlSi$_2$O$_6$, to the non-ideality of the resultant solutions. The actual values of these parameters are obtained by mathematical fitting of curves involving these parameters to a series of experimental data. The parameters given by Thompson and Waldbaum include terms for both pressure and temperature.

\[
W_G^{ab} = 6326.7 + 0.0925P - 4.6321 T \quad \text{(for NaAlSi$_2$O$_6$)} \\
W_G^{ab'} = 7671.8 + 0.1121P - 3.8565T \quad \text{(for KAlSi$_2$O$_6$)}
\]

There are several alternate formulations of the Margules parameters which could be used to model the alkali feldspar solution behavior. Luth and Fenn (1973) conclude that there are measurable differences between the solvi for peralkaline and peraluminous systems and between sets of Margules parameters describing them. Depending upon the details of the analytical and mathematical procedures, several formulations could even be derived from the same data set. The various parameters given by Luth and Fenn do result in temperatures differing by as much as 100°C in some parts of our diagram. However, to some extent these temperatures tend to converge in the region of most interest.

The parameters here selected represent an adjusted set of values for experimental runs with peralkaline starting materials. Thompson and Waldbaum have presented (1969a, p. 828) a reasonable argument that the peralkaline experimental systems should yield feldspars resembling most closely those found in natural rocks. These parameters are reasonably consistent with several sets of alkali feldspar solvus data and with the liquidus data of Schairer (1950, cf Thompson and Waldbaum 1969b, Fig. 5). There is some evidence (Luth, 1974) that the pressure terms in these parameters are inaccurate for higher pressures. However, no alternate set of parameters appears to fit available ternary feldspar data significantly better.

The data discussed above were determined from experimental work on the binary alkali feldspar and plagioclase systems. Some assumption must be made concerning their applicability to natural feldspars, where the alkali feldspar will have a small amount of anorthite in solution and plagioclase will contain some of the potassium component. One model which has been used with considerable success in treating ternary solutions makes use of the approximation that each component approaches Henry's Law as it becomes very dilute (i.e., as the ternary solution approaches a binary solution of the remaining two components; see Lewis and Randall, 1961, Chap. 34). Consideration of Equation 34-20 of Lewis and Randall shows that the activity coefficients of the two major components will approach and equal the values of the coefficients in the binary system as the minor component approaches and follows Henry's Law. This equation cannot be rigorously evaluated for the feldspar system at this time. However, we can make the assumption that the small amounts of anorthite in alkali feldspar and potassium in plagioclase are within a range where Henry's Law is at least approximately obeyed so that:

\[
\gamma_{(ab, \text{ternary feldspar})} = \gamma_{(ab, \text{binary feldspar})}
\]

Using a similar assumption, Saxena and Ribbe (1972) made an evaluation of the thermodynamic properties of coexisting feldspar based on Seck's (1971) and Orville's (1972) data. Solution properties calculated for the alkali feldspars were noted to be very similar to those found by Thompson and Waldbaum (1969a). Results, based on Orville's data for plagioclases, indicated $\gamma_{(ab, \text{plagioclase})}$ \approx 1.0 over the range Ab$_{100}$-Ab$_{6}$ although their interpretation of this behavior differed from that of Orville.

**Proposed Analytical Formula**

Taking the logarithmic form of Equation (13) and Thompson's (1967) Equation (8 a) for the activity coefficient in terms of Margules parameters, we can derive an expression relating temperature, pressure, and composition over a wide range of conditions:

\[
\ln K_{D, ab} = \ln \left( \frac{X_{ab, AF}}{X_{ab, PF}} \right) = \gamma_{ab, AF} \left[ \frac{W_G^A - 2X_{ab, AF}(W_G^{orb} - W_G^{ab})}{(1 - X_{ab, AF})^2} \right]
\]

Substitution of the $P$ and $T$ functions for $W_G$ and solution of the equation for $T$ leads to a rather complex function of albite mole fraction:

\[
T(\text{C} K) = \frac{(16326.7 - 9963.2X_{AF} + 943.3X_{AF}^2 + 2690.2X_{AF}^3 + (0.0925 - 0.1458X_{AF} + 0.0141X_{AF}^2 + 0.0392X_{AF}^3)P)}{-1.9872 \ln \frac{X_{AF}}{X_{PL}} + 4.6321 - 10.815X_{AF} + 7.7345X_{AF}^2 - 1.5512X_{AF}^3}
\]
A few representative “curves” for this proposed distribution model are also shown in Figure 2 for comparison with the Barth model. It is obvious that both pressure and alkali feldspar composition have strong influences on the distribution coefficient $K_D$, confirming the fact that these were serious deficiencies in Barth’s (1951) model. Our “curves” are also linear on this plot since the Margules parameters at any given composition and pressure are linearly related to $T$.

**Determinative Curves**

A series of isotherms relating feldspar compositions to temperature for several different pressures have been plotted in Figure 3. These provide a more convenient method of temperature determination than does Equation (18) and, in view of the probable uncertainty in the model, provide more than adequate precision. The curves may also serve as a visual reminder of the limitations of the method as discussed below.

The validity of these curves was tested against the experimental work of Seck (1971). His data—in effect the only published experimental data for ternary feldspars which consider a wide range in feldspar composition as well as a significant range of pressure—is addressed primarily to the problem of albite distribution. In general, the agreement between our model and Seck’s data is very good. There is a serious discrepancy only at very low albite contents. There are many possible problems which might contribute to this discrepancy. Perhaps the most likely is the probability, indicated by Orville’s (1972) and Saxena and Ribbe’s (1972) work, that the activity of albite in plagioclase cannot be considered to be ideal at higher anorthite contents. In this case, the problem should be more acute at higher pressures (which seems to be the case) and at lower temperatures. However, experimental difficulties may also contribute to the problem. Unfortunately, as pointed out by Seck, there is no direct way to analyze for the Ab, An, Or components of the coexisting feldspars in the fine grained products of such experiments. The determination is critically dependent upon analysis by the 201-method (Wright, 1968). Seck’s analysis is also dependent on a geometrical projection through the bulk composition. This may magnify errors in the potassium analysis of the feldspar products. The feldspar bulk composition may also be subject to error if the aqueous fluid phase dissolves significant amounts of feldspar components incongruously. This is also likely to be a more serious problem at higher pressures. For instance, Luth and Tuttle (1969) found 5 to 8 percent alkali feldspar and quartz dissolved incongruently in a vapor phase at 2 to 10 kilobars. Most other ternary feldspar data suffer from similar problems, probably to an even greater extent. We feel that the present evidence is insufficient to resolve accurately the experimental problems and mixing properties. However, if our primary concern is a practical geothermometer, we can find comfort in the fact that plagioclase with less than 55 percent albite is virtually never found coexisting in equilibrium with alkali feldspar in natural rocks.

A problem also exists for albite-rich compositions. In this region at low pressure and high temperatures there is complete ternary solid solution extending from plagioclase to potassium feldspars through anorthoclase compositions. The activity coefficients here almost certainly differ from those in the binary systems, and the proposed geothermometer will contain some error when the plagioclase is rich in potassium as well as sodium.

Application of this geothermometer to many natural feldspar pairs gives very reasonable temperature estimates. A few interesting examples are given in Table 1. Although these are primarily from volcanic rocks with which I am familiar, the usefulness of this technique extends to plutonic and higher grade metamorphic rocks. This method, used with careful petrographic interpretation of textural features, is giving a consistent and reasonable picture of the crystallization history of several postmetamorphic granites from the Piedmont province of Georgia (Whitney and Stormer, in preparation). The feldspars in the trachyte from France and the pitchstone from Eigg give equilibrium temperatures which are virtually identical, at 1 kbar, to temperatures derived from the iron-titanium oxide geothermometer. The feldspar phenocrysts in rhyolite from Mono Craters, California, also give temperatures corresponding to iron-titanium oxide values if we assume they originated at depths of 15 to 30 km. This difference, as seen in the change of feldspar tieline orientation between rhyolites and trachytes, has often been noted (cf Carmichael, Turner, and Verhoogen, 1974, p. 225) and attributed to differences in magma composition. The relationship here suggests that the differences could largely result because the rhyolite phenocrysts may have formed at a lower temperature and generally higher pressure.

The data for shoshonite and nepheline trachyte lavas have been taken from unpublished microprobe analyses plotted in Figure 5–2 of Carmichael et al
Fig. 3. Determinative curves for temperature based on the proposed model of albite distribution between coexisting plagioclase and alkali feldspars. Crosses represent experimental determinations of this distribution at 650°C by Seck (1971) as discussed in the text. Reasonable accuracy cannot be expected in the region of dashed curves. Results for very potassium-rich plagioclase or calcium-rich alkali feldspars may be poor.
were mentioned above. The proposed curves represent geothermometers in that the very important influence temperature determinations. The possibility also exists that, if the temperature of equilibration of coexisting feldspars can be determined by some other means, a crude determination of pressure may be possible.

Although some other formulation might be selected on various experimental or theoretical grounds, we believe the complexity of natural feldspars, not only the ternary solid solution of Na, K, Ca, but also Si, Al, and Fe substitution will continue to represent a greater uncertainty than the selection of thermodynamic parameters from any particular set of experimental measurements. Textural and strain effects are also capable of greatly altering equilibrium relationships (Robin, 1974). Probably the greatest source of error in temperature determinations will not lie in the solution model but in subjectively petrographic decisions as to what minerals or zones of minerals were in equilibrium.

Conclusions

The determinative curves derived from Equation (18) and presented here in Figure 3 should be widely useful as a practical geothermometer. The method is, of course, only an approximation of actual ternary feldspar behavior, but the agreement with existing ternary feldspar experimental data is good within the range of compositions found in common rocks. The precision of determinations within the area of solid isotherms in Figure 3 is probably within ± 30°C, although the absolute accuracy of any determination may be adversely affected by various factors which were mentioned above. The proposed curves represent a significant improvement over previous feldspar geothermometers in that the very important influence of pressure is considered. Therefore, a rough estimate of the pressure of origin will be necessary for accurate temperature determinations. The possibility also exists that, if the temperature of equilibration of coexisting feldspars can be determined by some other means, a crude determination of pressure may be possible.

Although some other formulation might be

### Table 1. Feldspar Equilibration Temperatures—Natural Examples

<table>
<thead>
<tr>
<th>Specimen Description</th>
<th>Ab in alk.fsp.</th>
<th>Ab in plagioclase</th>
<th>T(°C) Feldspar</th>
<th>T(°C) Fe-Ti Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porphyritic trachyte, Murat, Cantal, France*</td>
<td>.46 .56</td>
<td>1010 (1 kbar)</td>
<td>1010</td>
<td></td>
</tr>
<tr>
<td>Porphyritic pitchstone, Isle of Eigg, Scotland**</td>
<td>.51 .80</td>
<td>740 (1 kbar)</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>Rhyolite, Mono Craters, California, U.S.A.***</td>
<td>.36 .34</td>
<td>625-705 (1 kbar)</td>
<td>790-820</td>
<td></td>
</tr>
<tr>
<td>Shoshonite, Oregon. U.S.A.****</td>
<td>.54</td>
<td>1350 (1 bar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plagioclase core, Ab48</td>
<td>.43</td>
<td>2492 (1 bar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plagioclase + alk.fsp., Ab48</td>
<td>.45</td>
<td>1340 (1 bar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nepheline trachyite**</td>
<td>.61</td>
<td>1132 (1 bar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plagioclase + alk.fsp., Ab48</td>
<td>.33</td>
<td>782 (1 bar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plagioclase + alk.fsp., Ab48</td>
<td>.63</td>
<td>1130 (10 kbar)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


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