COMMENTS ON
THE TWO-FELDSPAR GEOTHERMOMETER

By

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Barth (1961) has presented a plot showing the distribution of sodium between an alkali feldspar and a 2-molar alkali chloride solution based upon the data of Orville (1959). I have plotted more extensive data from Orville (1963) in the same manner for the sodium distribution at 500°, 600° and 700 °C in Figure 1 A, B and C. The endpoints of distribution tie lines that appear to be identical with those plotted by Barth have been circled in Figure 1 C.

If both a 2-molar alkali chloride solution and the plagioclase solid solution series are ideal solutions, then a constant sodium distribution coefficient (hence parallel tie lines on a logarithmic scale) for the alkali feldspar-alkali chloride system will result in a constant distribution coefficient in the alkali feldspar-plagioclase system as well. It is apparent from Figure 1 C that tie lines are approximately parallel for alkali feldspar compositions from Ab_4 to about Ab_{15}. It is equally apparent that tie lines are not even approximately parallel over the range Ab_{15} to Ab_{40}. It seems likely that alkali feldspar crystallized in equilibrium with albite or oligoclase at 700 °C will fall in the range Ab_{15}–Ab_{40} rather than less than Ab_{15}. The data of Orville (1956, 1963), rather than indicating a constant sodium distribution coefficient of 700° for the geologically important alkali feldspar-plagioclase assemblages, indicate that the sodium distribution coefficient will vary quite strongly within the significant compositional range. Figure 1, A and B, shows that tie lines in the alkali-feldspar-alkali chloride system at 500° and 600 °C converge strongly even for sodium-poor alkali feldspars.
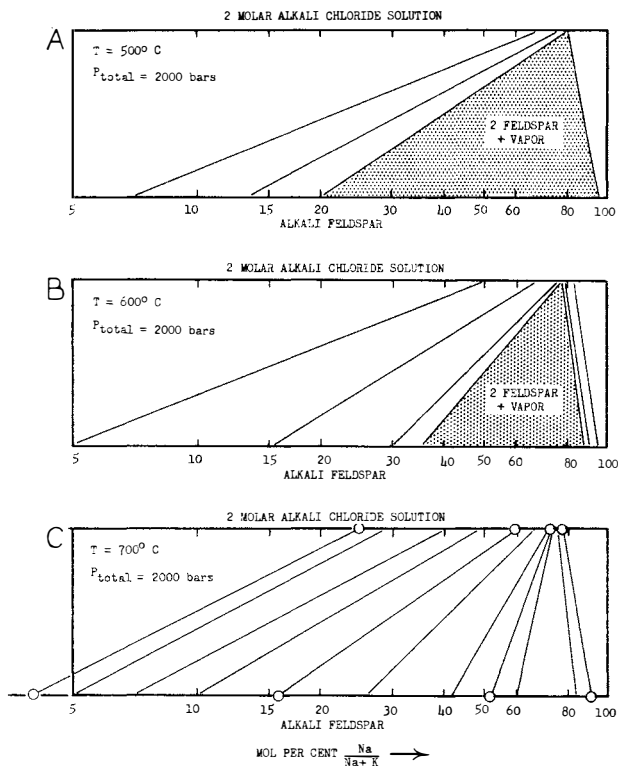
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Figure 1. Distribution of Na between a synthetic alkali feldspar phase and a 2-molar alkali chloride solution at 2000 bars total pressure and A) 500 °C, B) 600 °C, C) 700 °C. Na-content plotted as mol per cent $\dfrac{Na}{Na+K}$ on logarithmic scale. Tie lines plotted by Barth (1956, Figure 1-B) shown in C) by circles. All data from Orville (1963).

Derivation of a two feldspar geothermometer

The coexistence of a plagioclase phase and an alkali feldspar phase in stable equilibrium at a given temperature and pressure requires that,

$$^aAb \text{ alkali feld} = {}^aAb \text{ plagioclase,} \qquad 1)$$

where ^aAb is the activity of albite in a particular phase, and where unit activity of albite is represented by a pure albite phase in a given structural state at the same temperature and pressure.

Since

$$^aAb = {}^fAb \cdot {}^mAb , \qquad 2)$$

where ^{f}Ab and ^{m}Ab are the activity coefficient and molar fraction, respectively, of albite in a particular phase, then

$$^f\text{Ab alkali feld.} \cdot {}^m\text{Ab alkali feld.} = {}^f\text{Ab plagioclase} \cdot {}^m\text{Ab plagioclase} \quad 3)$$

or

$$\frac{^m\text{Ab alkali feld.}}{^m\text{Ab plagioclase}} = \frac{^f\text{Ab plagioclase}}{^f\text{Ab alkali feld.}} \quad 4)$$

The two feldspar geothermometer proposed by Barth (1956) requires that the left hand side of eq. 4) be approximately constant at a given temperature and pressure, although the role of pressure is regarded as distinctly subordinate to that of temperature. Barth points out that the albite distribution ratio, ^{m}Ab alkali feld./^{m}Ab plagioclase, is not actually constant for a given temperature since it depends also on the composition of the feldspar phases (see especially Barth, 1956, p. 13–14). The two feldspar geothermometer is meant to represent an "average" value of the albite distribution ratio at a particular temperature for rocks exhibiting a normal, but restricted, range of bulk compositions.

The important practical question is whether the "average" values for the albite distribution ratio at two different temperatures will be sufficiently different from one another that they can be distinguished even if composition changes. If variation in the albite distribution ratio due to changing composition results in overlap of the distribution ratios, then the two temperatures cannot be distinguished from one another with certainty and false temperature differences of at least this amount can be read into rocks that differ only in composition.
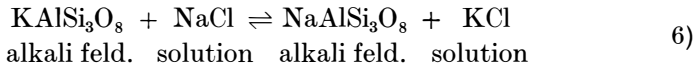
Barth (1961, p. 3) specifically limits the application of the proposed geothermometer to feldspar assemblages in which the plagioclase is Ab-rich (An-content 5–35) and he emphasized that the particular calibration of the geothermometer proposed in the 1956 paper is tentative and is based only upon observed natural feldspar assemblages from geologic environments in which temperature can be estimated roughly to plus or minus 50 °C.

Since the application of the geothermometer is restricted to albite-rich plagioclase feldspars, it can be assumed that the activity coefficient of albite in the plagioclase phase, ^{f}Ab plagioclase, is approximately unity and therefore eq. 4) reduces to,

$$\frac{^m\text{Ab alkali feld.}}{^m\text{Ab plagioclase}} \simeq \frac{1}{^f\text{Ab alkali feld.}} \qquad 5)$$

It is possible to check both the particular calibration and certain of the basic assumptions of the two feldspar geothermometer by means of data obtained in the synthetic alkali feldspar system by cation exchange experiments (Orville (1963)).

The alkali feldspar-alkali chloride exchange reaction is,

$$\text{KAlSi}_3\text{O}_8 + \text{NaCl} \rightleftharpoons \text{NaAlSi}_3\text{O}_8 + \text{KCl} \qquad 6)$$
$$\text{alkali feld.} \quad \text{solution} \quad \text{alkali feld.} \quad \text{solution}$$

and the equilibrium expression at constant temperature and pressure is,

$$k = \frac{^a\text{Ab alkali feld. } ^a\text{KCl sol.}}{^a\text{Or alkali feld. } ^a\text{NaCl sol.}}$$
$$= \frac{(^f\text{Ab } ^m\text{Ab}) \text{alkali feld.} \quad \cdot (^f\text{KCl } ^m\text{KCl}) \text{sol.}}{(^f\text{Or } ^m\text{Or}) \text{alkali feld.} \quad \cdot (^f\text{NaCl } ^m\text{NaCl}) \text{sol.}} \qquad 7)$$

It was found that the equilibria ara not significantly affected by changes in the total alkali chloride concentration which indicates that

$$\frac{^f\text{KCl sol.}}{^f\text{NaCl sol.}} = \text{constant} \qquad 8)$$

and therefore eq. 7) may be modified to

$$\frac{(^f\text{Ab } ^m\text{Ab}) \text{ alkali feld. } ^m\text{KCl sol.}}{(^f\text{Or } ^m\text{Or}) \text{ alkali feld. } ^m\text{NaCl sol.}} = \frac{k}{\text{constant}} = k' \qquad 9)$$

When ^mOr is near unity, $^f\text{Or} \simeq 1$ and, from eq. 9),

$$\frac{^f\text{Ab alkali feld.}}{k'} \simeq \frac{^m\text{Or alkali feld. } ^m\text{NaCl sol.}}{^m\text{Ab alkali feld. } ^m\text{KCl sol.}} \qquad 10)$$

If ^fAb alkali feld. is constant or nearly constant at a given temperature and pressure, then the right hand side of eq. 10) must also be constant or nearly constant. This function has been evaluated for a range of alkali feldspar compositions at 700°, 600° and 500 °C from the data of Orville (1963, Figures 4, 5 and 8) and the results are given in rows 2, 3 and 6 of Table 1.

If K' is known at a particular temperature and pressure, ^fAb alkali

Table 1.

	.05	.10	.15	.20	.25	.30	.35	.40
1. ^{m}Ab alkali feld.	.05	.10	.15	.20	.25	.30	.35	.40
700° C								
2. ^{f}Ab alkali feld./k'	8.6	8.2	7.5	6.8	5.8	5.1	4.3	3.8
600° C ($k' = .42$)								
3. ^{f}Ab alkali feld./k'	15.5	14.7	11.3	9.6	8.1	7.4	6.0	
4. 1/^{f}Ab alkali feld.	.154	.161	.208	.250	.294	.322	.400	
5. ^{m}Ab plagioclase	.32	.62	.72	.80	.85	.93	.89	
500° C ($k' = .27$)								
6. ^{f}Ab alkali feld./k'	28.5	25.6	22.0	17.6				
7. 1/^{f}Ab alkali feld.	.129	.143	.166	.208				
8. ^{m}Ab plagioclase	.39	.70	.90	.96				

feld. can be determined directly from eq. 10). At 600° and 500 °C two alkali feldspars, one Ab-rich and one Or-rich, can coexist in equilibrium with a solution having a unique $^mKCl/^mNaCl$ ratio. It can be assumed that the activity coefficient of Ab in the Ab-rich phase and the activity coefficient of Or in the Or-rich phase are very nearly equal to one and therefore, for these coexisting feldspar phases,

$$k' = \frac{^m\text{Ab Ab-rich feld.} \cdot {}^m\text{KCl sol.}}{^m\text{Or Or-rich feld.} \cdot {}^m\text{NaCl sol.}} \qquad 11)$$

At 600 °C and 2000 bars total pressure ^{m}Ab Ab-rich feldspar $= 0.89$, ^{m}Or Or-rich feldspar $= 0.65$, $^mKCl/^mNaCl = 0.307$, therefore $K' = 0.42$. At 500 °C and 2000 bars total pressure ^{m}Ab Ab-rich feldspar $= 0.96$, ^{m}Or Or-rich feldspar $= 0.80$, $^mKCl/^mNaCl = 0.259$, and therefore $K' = 0.27$. Values of 1/^{f}Ab alkali feld. for Or-rich feldspars at 600° and 500° C have been calculated on the basis of these K' values and are presented in rows 4 and 7 of Table 1.

If it is assumed that the activity of albite in the plagioclase phase is equal to the molar proportion of albite, that the presence of a very small amount of anorthite in the Or-rich alkali feldspar has no significant effect on the activities of either orthoclase or albite in the alkali feldspar phase, and that both feldspar phases are in a high temperature structural state corresponding to that of the synthetic alkali feldspars, then the albite content of the plagioclase phase coexisting with a particular composition of alkali feldspar at 600° or 500 °C can be

calculated from eq. 5) using the values of $1/{}^f\text{Ab}$ alkali feldspar given in Table 1. These plagioclase compositions are given in rows 5 and 8 of Table 1 as molar proportions of albite, ${}^m\text{Ab}$. The amount of ortho-clase in the plagioclase phase will be small compared with that of anorthite except in the Ab-rich pure alkali feldspar phase that coexists with $\text{Or}_{65}\text{Ab}_{35}$ at 600 °C and with $\text{Or}_{80}\text{Ab}_{20}$ at 500 °C.

Discussion of data in Table 1

First of all it is apparent that ${}^f\text{Ab}$ alkali feld./k' at a particular temperature is not constant and therefore the calibration of the geothermometer depends rather strongly upon the composition of the feldspar phases. Even though ${}^f\text{Ab}$ alkali feld. cannot be constant, the two feldspar geothermometer will work approximately if ${}^f\text{Ab}$ alkali feld. changes rapidly with temperature compared to its change with composition. The calculated values of $1/{}^f\text{Ab}$ alkali feld. at 600° and 500 °C show that, although they are higher at 600° for most alkali feldspar compositions, there is some overlap with values at 500 °C. The calculated plagioclase compositions given in rows 5 and 8 show that nearly the same ${}^m\text{Ab}$ alkali feld./${}^m\text{Ab}$ plagioclase ratio would be given at 600 °C by the feldspar pair $\text{Ab}_{65}\text{An}_{35}$–$\text{Or}_{90}\text{Ab}_{10}$ and at 500 °C by the pair $\text{Ab}_{90}\text{An}_{10}$–$\text{Or}_{85}\text{Ab}_{15}$. The effect of structural inversions to a lower temperature form in either, or both, of the feldspar phases would be to increase the apparent difference in ${}^f\text{Ab}$ alkali feld. values over the temperature range in which the inversion takes place. This would decrease or even eliminate overlap in ${}^f\text{Ab}$ alkali feld. values over that temperature interval.

The values of "K" taken from the 1956 feldspar geothermometer curve (Barth, 1956, Fig. 9) are 0.34 at 600 °C and 0.23 at 500 °C. The range of values of $1/{}^f\text{Ab}$ alkali feld. given in Table 1 for the bracketed feldspar assemblages is 0.40–0.15 at 600 °C and is 0.21–0.13 at 500 °C. The precise values of $1/{}^f\text{Ab}$ alkali feld. given in Table 1 cannot be taken too seriously because of the approximations and assumptions involved in their derivation but the variation in values with com-position is real and cannot be neglected in any rigorous application of the two feldspar geothermometer.

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Comments on
"Comments on the two Feldspar Geothermometer"
by P. M. Orville

By

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The K-values of Barth's geothermometer are calculated by

$$K = \frac{{}^m\text{Ab alk. f.}}{{}^m\text{Ab plag.}} = \frac{{}^f\text{Ab plag.}}{{}^f\text{Ab alk. f.}}$$

As a first approximation we assume no solid solution on the albite
side. Consequently the activity of albite in alkali feldspar will increase
sharply and reach the maximum value at the solvus on the ortho-
clase side (Figure 1. $m^* = m_{\text{Ab}}$ on that side of the solvus). Then the
activity coefficient of albite will be $f_{\text{Ab}} \simeq \dfrac{1}{m^*}$. From Orville's measured
values a better approximation results. Following Orville we assume
$f_{\text{Ab}} \simeq 1$ on the Ab side of the solvus (Figure 2, x, 0 and + values after
Orville; assuming $K' = 0.45$ for $700°$ C).

   In the plagioclase solid solution the first approximation is again
$f_{\text{Ab}} \simeq 1$ for the whole range. So the K-values must be $K \approx m^*$ (Table 1).

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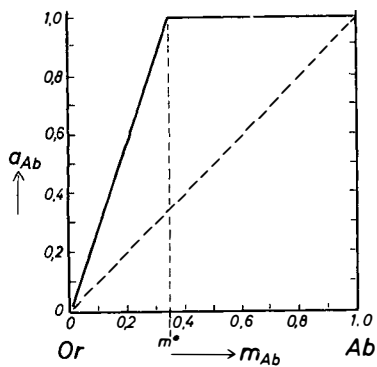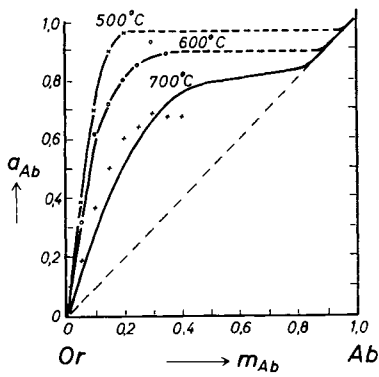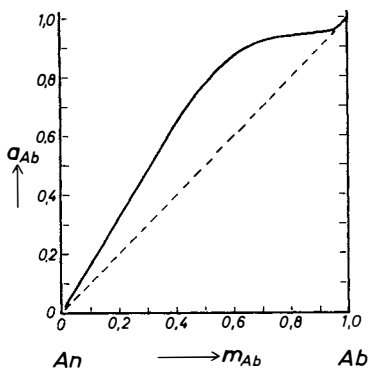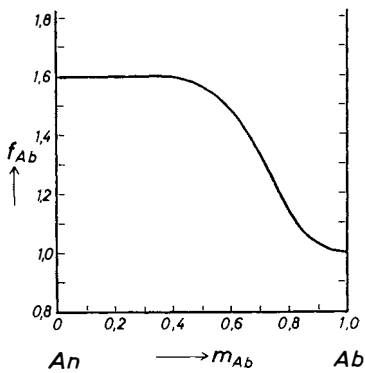[2] Mineralogisk-Geologisk Museum, Oslo.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Table 1. m^*- and K-values for coexisting plagioclase and K-feldspar at different temperatures.

Temp	m^*	K
500° C	.20	.22
600° C	.35	.33
650° C	.47	.40

Thus there is a fair agreement between the values obtained in this way from Orville's solvus data and the original values of Barth.

However, the presence of peristerites indicates that the f-values

close to the albite end member differ appreciably from 1 (Figure 3). The figures in lines 5 and 8 of Table 1 of Orville's paper are therefore the activities and not the molar fractions. The curve thus suggested in Figure 3 would demand a change of f-values from 1 to approximately 1.6 as shown in Figure 4. Because of the changing f-values for constant temperature the corresponding K-values show only a small variation with composition.