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The Two-Feldspar Geothermometer*

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(With 4 text-figures)

BARTH'S METHOD

T. F. W. BARTH made the suggestion that the compositions of coexisting plagioclase and alkali feldspar could be used as a geothermometer (BARTH, 1951, 1956, 1962 and 1968). The method has been criticized by several authors (e.g. ORVILLE, 1962; PIWINSKI, 1968) on the grounds that the original calibration is crude, as BARTH himself has said, and that the rather meagre evidence from experiments is not consistent with the thermometer.

Barth suggested that the ratio of the mole fraction of the albite molecule in potassium feldspar to the mole fraction of the albite molecule in coexisting plagioclase should be a constant for a given temperature and pressure.

Let x_{Ab}^{Kf} be the mole fraction of albite in alkali feldspar.

Let x_{Ab}^{Pl} be the mole fraction of albite in plagioclase.

Then, according to Barth,

$$K_{B(P,T)} = \frac{x_{Ab}^{Kf}}{x_{Ab}^{Pl}}$$

However $K_{B(P,T)} = e^{-\frac{(\Delta G)}{RT}}$

Therefore $\ln K_B = -\frac{(\Delta G)}{RT}$

where ΔG is the Gibbs free energy change on the passage of one mole of albite from plagioclase to alkali feldspar. Thus a plot of $\ln K_B$ versus $1/T^\circ C$ should be a straight line of slope $-\frac{(\Delta G)}{R}$.

Using values of K from rocks whose temperature of formation could be estimated, Barth derived an equation for the line:

$$\ln K_B = -\frac{1400}{T} + 0.8$$

As KERN AND WEISBROD (1967) point out this suggests by analogy with the relation

$$\ln K_B = -\frac{(\Delta H)}{RT} + \frac{(\Delta S)}{R}$$

that (ΔH) is roughly $+2800$ cal/mole and (ΔS) is roughly 1.6 cal/mole.

BARTH'S 1951 calibration graph is reproduced in Figure 1, with the data assembled by PIWINSKI (1968), which is not consistent with the thermometer. This data is the result of experiments on charges of known composition held at known temperatures and pressures. The compositions of the resulting feldspars were then measured.

A REVISED EQUILIBRIUM CONSTANT

BARTH'S equilibrium constant depends on the assumption that the chemical potential (μ) of albite must be the same in the two coexisting feldspar phases.

* Received December 29, 1970; presented by OTHON H. LEONARDOS.

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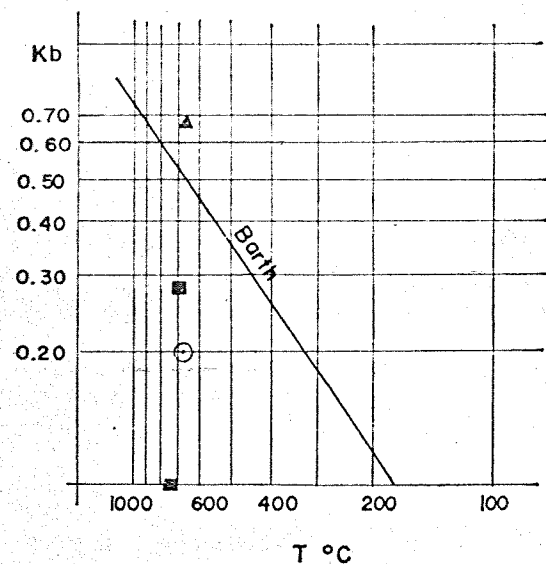


Fig. 1 — Plot of K_B against $T^\circ\text{C}$ on a log scale, after Barth, (1951). The line represents Barth's thermometer. ○ — from Piwinski (1968), ▲ — from STEPHIL (1962), ■ — from YODER ET AL. (1957).

Thus $\mu_{\text{Ab}}^{\text{Kf}} + RT \ln a_{\text{Ab}}^{\text{Kf}} = \mu_{\text{Ab}}^{\text{Pl}} + RT \ln a_{\text{Ab}}^{\text{Pl}}$ where $a_{\text{Ab}}^{\text{Kf}}$ means the activity of albite in alkali feldspar. The activity of albite in either phase is related to the mole fraction by the relations:

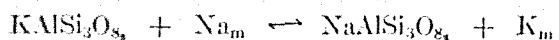
$$a_{\text{Ab}}^{\text{Kf}} = x_{\text{Ab}}^{\text{Kf}} \times \gamma_1 \quad \text{and} \quad a_{\text{Ab}}^{\text{Pl}} = x_{\text{Ab}}^{\text{Pl}} \times \gamma_2$$

where γ_1 and γ_2 are activity coefficients. Barth assumed that both feldspar series were perfect solutions, so that $\gamma_1 = \gamma_2 = 1$.

These relations do not take into account the fact that other phases, liquids, solids, or vapours may be present, which also may contain some of the elements contained in feldspars.

Let us imagine the process of crystallization of two feldspars from a melt. Each of the feldspar phases is reacting continuously with the melt. So the following two reactions can be written:

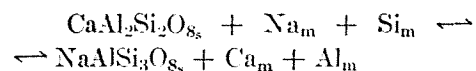
Reaction 1,



$$\text{Thus } K_1 = \frac{[Ab^{\text{Kf}}][K_m]}{[Kf^{\text{Kf}}][Na_m]} \text{ where } [] \text{ stands}$$

for activity;

Reaction 2,



$$\text{Thus } K_2 = \frac{[Ab^{\text{Pl}}][Ca_m][Al_m]}{[An^{\text{Pl}}][Na_m][Si_m]}$$

where s and m stand for solid and melt.

However both reactions are taking place simultaneously.

$$\text{Therefore, } K_3 = \frac{K_1}{K_2} = \frac{[Ab^{\text{Kf}}][K_m]}{[Kf^{\text{Kf}}][Na_m]} \times \frac{[An^{\text{Pl}}][Na_m][Si_m]}{[Ab^{\text{Pl}}][Ca_m][Al_m]}$$

Re-arranging terms,

$$K_3 = \left\{ \frac{[Ab^{\text{Kf}}][An^{\text{Pl}}]}{[Ab^{\text{Pl}}][Kf^{\text{Kf}}]} \right\}_{\text{Solid}} \times \left\{ \frac{[K_m][Si_m]}{[Ca_m][Al_m]} \right\}_{\text{Melt}}$$

Note that the first ratio on the right hand side of the equation represents Barth's equilibrium constant K_B , if $\gamma_1 = \gamma_2 = 1$. Thus the relative amounts of K, Ca, Si, and Al in the melt will influence K_3 at any particular temperature and pressure.

PREDICTIONS FROM THE EQUILIBRIUM CONSTANT

At the present time there is no data concerning the activity coefficients of the various elements in the melt, or in the solid phases, so we must unfortunately make the same assumption as Barth did that the activity coefficients are all close to one. With this assumption, and also ignoring the small amounts of potassium feldspar in plagioclase, and anorthite in alkali feldspar, it is possible to make some qualitative estimates of the effect of other components. This can be done by consideration of the ratios $[K_m]/[Ca_m]$ and $[Si_m]/[Al_m]$.

Consider a mixture of feldspars of bulk composition as shown by the dot in Figure 2. A set of tie-lines are drawn through this point. Barth's equilibrium constant and the inferred

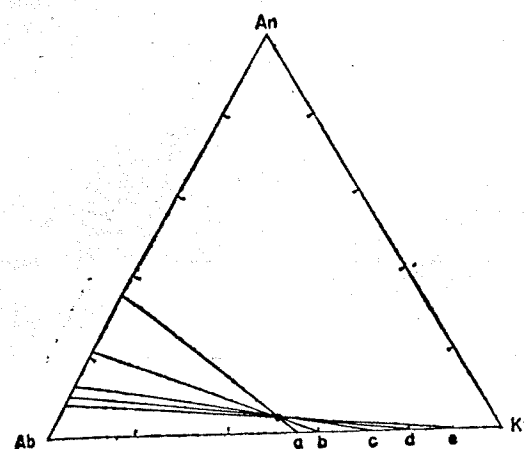


Fig. 2 — Plot of Anorthite-Albite-Potassium Feldspar showing hypothetical tie-lines ● — Bulk composition of the feldspars. a, b, c, d, and e are tie-lines shown in TABLE I.

temperature are given for each tie-line in TABLE I. This demonstrates the wide range of compositions that could be produced from this bulk composition under metamorphic and igneous conditions. To illustrate the effect of a change in the $[Si_m]/[Al_m]$ ratio let us now add SiO_2 to the original bulk composition of Figure 2, and investigate the

TABLE I

Tie-line	K_B	$T^\circ\text{C}$
a	0.68	900
b	0.51	680
c	0.35	500
d	0.23	350
e	0.11	<200

amount of rotation of the tie-line caused by such an addition. Using tie-line b, which has 40 mole per cent albite in the alkali feldspar, and assuming the melt is very close to the bulk composition in composition, it is then possible to calculate K_3 , which is found to have the value 5.05. Now let us add silica so that the ratio of $[Si_m]/[Al_m]$ is now 4.3 instead of 3. This makes the bulk composition that of Nöckolds' (1954) average alkali granite. If T is held constant then K_3 does not change, so it is now possible to calculate

the compositions of the feldspars, again making the assumption that the melt lies close to the bulk composition in composition. The calculated values of the various parameters are shown in TABLE II.

TABLE II

Parameter*	No added SiO_2	Nöckolds' Av. Granite
$[Ab^{\text{Kf}}]$	40	36
$[Kf^{\text{Kf}}]$	60	64
$[Ab^{\text{Pl}}]$	78	81
$[An^{\text{Pl}}]$	22	19
$[Si_m]/[Al_m]$	3	4.3
$[K_m]/[Ca_m]$	9	9
K_3	5.05	5.05
K_B	0.51	0.44
$T^\circ\text{C}_{\text{Barth}}$	680	600

* It is assumed that all activity coefficients have the value of 1.

It can be seen that an increase in the $[Si_m]/[Al_m]$ ratio causes a rotation of the tie-line, so that the plagioclase becomes more sodic and the alkali feldspar more potassic. These two tie-lines illustrate the difference between syenitic rocks and granitic rocks. K_B for the two tie-lines and the temperatures read from Barth's graph are also shown in TABLE II. These indicate a temperature difference of 80°C between the two samples, whereas one of the conditions of the calculation was that T remained constant, so that K_3 would remain constant. This change of orientation of the tie-line is shown in Figure 3. Such changes in tie-line orientation have been shown to exist, by RAHMAN AND MACKENZIE (1969, Figure 6), in a comparison of the coexisting feldspars in trachytes and rhyolites.

Even within the feldspar composition triangle the $[Si_m]/[Al_m]$ ratio changes (Figure 4). Thus for a given temperature and pressure the tie-lines will not have the orientation predicted from Barth's equilibrium constant. In addition the $[K_m]/[Ca_m]$ ratio is also changing in the same sense as the $[Si_m]/[Al_m]$.

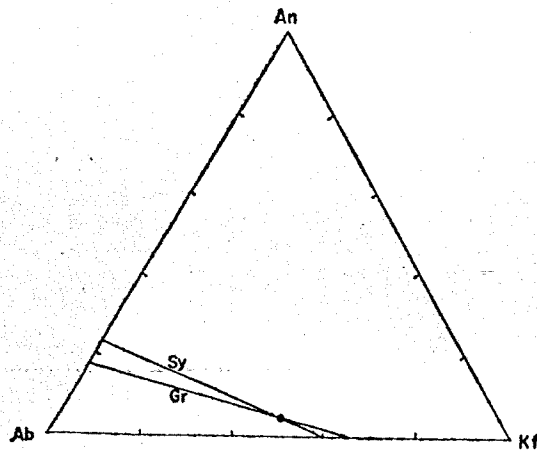


Fig. 3 — Plot of Anorthite-Albite-Potassium Feldspar showing the rotation of the tie-line caused by adding silica to the bulk composition shown in Figure 2. Gr — Granitic Tie-Line, Sy — Syenitic Tie-Line

ratio (Figure 4), and by more than an order of magnitude in the geologically interesting region. Thus the richer in anorthite the bulk composition, the richer the potassium feldspar and the poorer the plagioclase will be in albite, in comparison with Barth's pairs of feldspar for a given temperature.

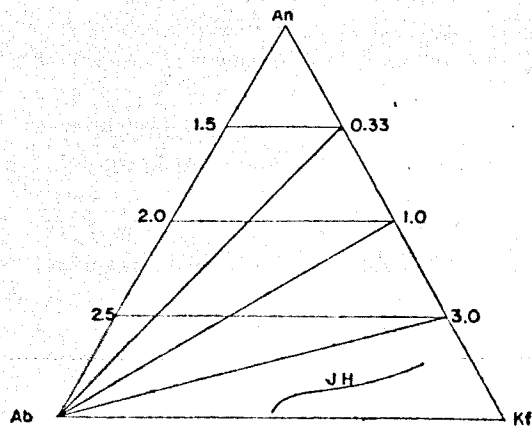


Fig. 4 — Plot of Anorthite-Albite-Potassium Feldspar showing lines of equal $[Si_m]/[Al_m]$ (Horizontal), and equal $[K_m]/[Ca_m]$ (Radiating from the albite corner). Also plotted is the projected trace of the two-feldspar surface with the quartz-feldspar surface in the system Ab-An-Al-Qz at 1 kilobar water vapour pressure (JH), from JAMES AND HAMILTON (1969).

The projection of the intersection of the two feldspar surface with the quartz-feldspar surface in the system $NaAlSi_3O_8-KAlSi_3O_8-CaAl_2Si_2O_8-SiO_2$ at one kilobar water vapour pressure is also shown in Figure 4 (JAMES

AND HAMILTON, 1969). Notice that for much of its length it is nearly parallel to the lines of equal $[K_m]/[Ca_m]$, and not very divergent from the lines of equal $[Si_m]/[Al_m]$. Hence in granites whose crystallization is being controlled by these equilibria Barth's equilibrium constant is a reasonable approximation. This also applies to a series of syenites crystallizing within the feldspar system. The comparison between the two series is not good, however; in fact in both series only relative temperatures can be estimated using Barth's constant.

Accurate temperatures must await calibration from the results of experimental petrology. A carefully designed set of experiments should enable the activity coefficients to be evaluated, and also if sufficient precision can be achieved, such experiments might indicate what species are present in the melt. The present equilibrium constant is based on the simplest possible species. The presence of sodium and potassium ions in the melt is probably a reasonable guess, but the silicon and aluminium is probably present in a polymerized form with oxygen (e.g. LACY, 1960).

A further complication lies in the assumption made in the previous discussion that the small amounts of potassium feldspar in plagioclase, and anorthite in alkali feldspar can be ignored. This is probably a safe assumption in the light of the present rather crude data, but if these small amounts can be measured more accurately, for example with the electron microprobe, then there is the possibility of three separate thermometers to use with the feldspars.

CONCLUSIONS

1. Barth's equilibrium constant has been revised to take into account other components, giving the following expression:

$$K_{3(p.t.)} = \left\{ \frac{[Ab^{Kf}][An^{Pl}]}{[Ab^{Pl}][Kf^{Kf}]} \right\}_{solid} \times \left\{ \frac{[K_m][Si_m]}{[Ca_m][Al_m]} \right\}_{melt}$$

2. Variations in the ratios $[Si_m]/[Al_m]$ and $[K_m]/[Ca_m]$ cause rotations in the two-feldspar tie-lines.

3. For rock series having similar ratios (see 2) Barth's equilibrium constant should predict relative temperatures reasonably, but a calculation has shown that comparison between a granite and a syenite with identical bulk feldspar composition yields relative temperatures which may be in error by 80°C.

4. Accurate calibration of the thermometer must await the evaluation of suitable experiments conducted under carefully controlled conditions, making possible the evaluation of the activity coefficients and possibly giving some indication of the nature of the species present in the melt.

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SUMMARY

A revised equilibrium constant for coexisting feldspars is suggested:

$$K_{3(p.t.)} = \left\{ \frac{[Ab^{Kf}][An^{Pl}]}{[Ab^{Pl}][Kf^{Kf}]} \right\}_{solid} \times \left\{ \frac{[K][Si]}{[Ca][Al]} \right\}_{melt}$$

It is shown that differences in the $[Si]/[Al]$ ratio and the $[K]/[Ca]$ ratio in the melt cause rotation of the tie-lines joining coexisting feldspars. While relative temperatures can be estimated in rock series with similar ratios, the comparison between syenitic and granitic rocks is not accurately measured. Accurate temperatures must await the evaluation of compositions and activity coefficients of the various phases from carefully controlled experiments.

RESUMO

O autor redefine a constante de equilibrio para os feldspatos coexistentes numa fusão para:

$$K_{3(p.t.)} = \left\{ \frac{[Ab^{Kf}][An^{Pl}]}{[Ab^{Pl}][Kf^{Kf}]} \right\}_{solid} \times \left\{ \frac{[K][Si]}{[Ca][Al]} \right\}_{fusão}$$

Mostra que as linhas que unem os feldspatos coexistentes sofrem rotação com a variação da razão $[Si]/[Al]$ e $[K]/[Ca]$ no magma. Enquanto temperaturas relativas podem ser estimadas a partir de séries de rochas com razões semelhantes, a comparação da temperatura de rochas graníticas e sieníticas só pode ser medida quando determinarmos, experimentalmente, a composição e os coeficientes de atividade nas várias fases.

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