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Alkali exchange between hornblende and melt: a temperature-sensitive reaction

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Abstract

Alkali exchange between the A site of hornblende and a coexisting melt may be described by the following reaction:

$$\text{Na (hornblende)} + \text{K (melt)} \rightleftarrows \text{K (hornblende)} + \text{Na (melt)}$$

The equilibrium constant of this reaction is:

$$K_D\,(\text{eq}) = \left[\frac{X_K}{X_{Na}}\right]_{\text{hbl}} \times \left[\frac{X_{Na}}{X_K}\right]_{\text{melt}}$$

where X_K and X_{Na} are mole fractions of K_2O and Na_2O in the hornblende and melt.

The value of this distribution coefficient has been calculated for 24 coexisting hornblende–melt pairs produced by partial melting of three basalts at $P_{H_2O} \simeq P_{total} = 5$ kbar, under controlled oxygen fugacity, at temperatures ranging from 700 to 1045°C. In calculating the observed distribution coefficient (K_D), values used for X_K and X_{Na} were the cation proportions of K and Na per 23 oxygens for hornblende, and moles of K and Na per 100 g of melt. When plotted against reciprocal temperature, K_D shows a strong positive temperature-dependence, describable by the equation $\ln K_D = (-4258/T) + 3.25$.

The anticipated effects on K_D of varying pressure and water activity, at constant temperature, are small. The exchange is not affected by variations of Na_2O and K_2O in the bulk composition or in the melt. The distribution coefficient is affected by changes in composition of the hornblende insofar as the changes affect the size of the A site, but this effect can be calibrated by taking into account variations in the cell volume of the hornblende.

Accordingly, this exchange reaction would seem to be a possible geothermometer for appropriate samples. Given the alkali contents of hornblende and a coexisting melt, and the cell volume of the hornblende, the temperature at which they equilibrated is determinable to approximately ±50°C.

Introduction

This paper is concerned with the exchange of Na and K between a silicate melt and the A site of coexisting hornblende, as described by the following equation:

$$\text{Na(hornblende)} + \text{K(melt)} \rightleftarrows \text{K(hornblende)} + \text{Na(melt)} \quad (1)$$

The data on which the discussion is based were obtained by detailed study of the compositions of phases produced in several rocks of basaltic composition at 700–1045°C and $P_{H_2O} \simeq P_{total} = 5$ kbar (Helz, 1973, 1976). The crystalline assemblages are dominated by hornblende±plagioclase below 850°C and by hornblende±augite+olivine above 850°C. A quenched silicate melt was present in all assemblages analyzed.

The compositional data include analyses of 24 coexisting hornblende–melt pairs, the equilibration temperatures of which cover the entire temperature interval (700–1045°C). The hornblendes (Helz, 1973) range over a large part of the compositional field reported for igneous hornblendes (Deer *et al.*, 1963). The melts (Helz, 1976) are mostly quartzofeldspathic but cover a fairly wide range of K_2O, Na_2O, and CaO contents. The range of temperatures over which hornblende and liquid coexist in the present set of

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data would be difficult to duplicate even in a fairly elaborate "simple" system involving end-member amphiboles.

Experimental and analytical methods

The starting materials for the hydrothermal melting experiments described above were powders of a Picture Gorge tholeiite, the 1921 Kilauea olivine tholeiite, and the 1801 Hualalai alkali basalt, ground to <200 mesh. Their bulk compositions are shown in Table 1. Each charge contained, in addition to the basalt powder, enough water to produce a separate vapor phase at experimental *P* and *T*. Oxygen fugacity during the runs was controlled with either the quartz–fayalite–magnetite (QFM) or hematite–magnetite (HM) buffers. Run temperatures ranged from 678 to 1045°C at $P_{H_2O} \simeq P_{total} = 5$ kbar, but glass occurs in analyzable amounts from 700–1045°C only. Further details on the nature of the starting materials and the experimental methods used are given in Helz (1973).

The analyses were made on an ARL electron microprobe operated at 15 kV and a sample current of 0.01 μA. The Na_2O and K_2O contents, in weight percent, for hornblendes and melts are given in Table 2; most are from Helz (1973, 1976) and are reproduced here for convenience only. The estimated analytical uncertainties for Na_2O and K_2O in the hornblendes are ±5 percent of the amount present. The uncertainty in the alkali contents of the glasses is estimated to be ±0.1 weight percent absolute for K_2O and ±0.2 weight percent absolute for Na_2O. (This is about ±10 percent of the amount present in most cases.) These uncertainties are for purposes of comparison with other data; the internal precision of this data set appears to be considerably better. A description of the analytical procedures may be found in Helz (1973); special problems relating to the glass analyses (alkali determinations, quenching problems) are discussed in Helz (1976).

Table 1. Chemical analyses of basalts used as starting materials in these experiments

	Picture Gorge tholeiite	1921 Kilauea olivine tholeiite	1801 Hualalai alkali basalt
SiO_2	50.71	49.11	46.53
TiO_2	1.70	2.51	2.41
Al_2O_3	14.48	12.74	14.91
Fe_2O_3	4.89	3.23	3.69
FeO	9.07	8.40	9.09
MnO	0.22	0.17	0.19
MgO	4.68	10.31	8.69
CaO	8.83	10.73	9.86
Na_2O	3.16	1.97	2.98
K_2O	0.77	0.49	0.97
P_2O_5	0.36	0.27	0.31
Sum	98.87	99.93	99.63

Cell parameters for 18 analyzed hornblendes are given in Table 3. These were made by least-squares refinement of X-ray powder diffraction data, following the method of Appleman and Evans (1973). Most refinements involve 14–16 fixed-index peaks. However, certain high-temperature charges (1921-1015, 1921-1000, and 1921-930) contain enough augite to interfere with many of the smaller hornblende peaks. These refinements are based on 11–12 peaks only, and addition of other lines changes the cell parameters markedly. These three refinements are therefore not strictly comparable to the others, and are probably somewhat less accurate. Further details of the methods used here are given in Helz (1973). The errors given in the table are the standard errors as calculated by the program for the final refinement. The total uncertainty in the cell parameters is about twice the size of these standard errors.

Calculations and results

The equilibrium constant for the reaction described by equation 1 is:

$$K_D(\mathrm{eq}) = \left[\frac{X_K}{X_{Na}}\right]_{\mathrm{hbl}} \times \left[\frac{X_{Na}}{X_K}\right]_{\mathrm{melt}} \qquad (2)$$

where X_K and X_{Na} would be the mole fractions of K and Na in the hornblende and melt.

The quantities used for X_{Na} and X_K in hornblende were the proportions of Na and K in the A site of each hornblende, as taken from its structural formula. The structural formulas were calculated on the basis of 23 oxygens, with all iron as FeO. The amount of K^+ in the A site is equal to the K^+ in the structural formula, as K^+ cannot enter any other site in hornblende. Na may enter the A site or the M_4 site, however; to the extent that Na(M_4) is significant, it must be subtracted from total Na before Na(A), and hence K_D, can be calculated.

As discussed by Stout (1972) it can be very difficult to assign a reasonable Na(M_4) value without having Fe_2O_3 and FeO in the hornblende determined separately; however, the problem is not severe for the hornblendes in the present data base. The structural formulas for these hornblendes, when calculated as described above, have summations for cations in the

Table 2. Alkali contents and distribution coefficients for coexisting hornblendes and melts

	Sample	Na_2O in hornblende	K_2O in hornblende	Na in hornblende	K in hornblende	Na_2O in melt	K_2O in melt	K_D	ln K_D
1.	PG-700	2.03	.62	.59	.12	3.7	3.7	.309	-1.17
2.	PG-750	2.66	.49	.62*	.094	3.7	1.8	.474	-0.747
3.	PG-825	2.45	.51	.72	.097	4.2	1.3	.662	-0.412
4.	PG-875	2.70	.48	.79	.092	4.2	1.1	.674	-0.394
5.	PG-930	2.73	.48	.79	.092	4.3	1.1	.691	-0.370
6.	PG-1000	2.72	.71	.80	.14	4.3	1.1	1.04	+0.037
7.	1921-700	1.45	.47	.41	.088	2.4	3.5	.223	-1.50
8.	1921-725	1.61	.50	.46	.093	2.4	2.4	.307	-1.18
9.	1921-750	1.65	.46	.47	.09	2.4**	2.0**	.350	-1.05
10.	1921-825	1.95	.52	.55	.097	2.5	1.2	.560	-0.580
11.	1921-875	2.10	.44	.60	.082	2.6	1.0	.540	-0.616
12.	1921-930	2.22	.40	.63	.075	2.7	.96	.509	-0.676
13.	1921-1000	2.30	.50	.67	.096	3.0	.89	.738	-0.304
14.	1921-1015	2.18	.53	.63	.10	3.2	.84	.920	-0.083
15.	1921-1045	1.97	.48	.56	.090	2.8	.71	.969	-0.031
16.	1921-HM-725	1.73	.48	.48	.089	2.6	2.4	.305	-1.19
17.	1921-HM-825	1.86	.45	.52	.083	3.0	1.4	.518	-0.657
18.	1921-HM-925	1.97†	.37†	.55	.068	3.4	1.07	.601	-0.510
19.	1801-725	2.77	.66	.59*	.13	4.4	3.7	.405	-0.904
20.	1801-825	2.59	.74	.75	.14	4.5	1.9	.671	-0.399
21.	1801-875	2.60	.69	.75	.13	4.5	1.8	.659	-0.417
22.	1801-930	2.57	.71	.74	.13	4.5	1.8	.667	-0.405
23.	1801-970	2.57	.66	.74	.13	4.6	1.8	.682	-0.383
24.	1801-1000	2.56	.83	.74	.16	5.0	1.7	.969	-0.031

*Na in hornblende corrected for Na(M_4).

**Values estimated by interpolation.

†Corrected analyses, significantly different from values reported in Helz (1973).

M_1, M_2, and M_3 sites falling in the range 4.96–5.14. As discussed in Helz (1973) this implies that the ferric iron contents of these hornblendes are quite low (<10 percent of the iron present). Therefore, although there is probably some ferric iron present in these amphiboles, it has been ignored in calculating K_D because (1) the Fe(M_4) contents (0.00–0.14) are barely significant analytically and (2) there is no reason to assume Fe(M_4) must be exactly zero (see Goldman and Rossman, 1977).

Table 3. Cell parameters of hornblendes

	Sample	a, Å	b, Å	c, Å	β	Vol., $Å^3$
1.	PG-750	9.859 ± 0.002	18.105 ± 0.004	5.310 ± 0.001	104°57' ± 1'	915.9 ± 0.2
2.	PG-825	9.864 ± 0.003	18.101 ± 0.009	5.315 ± 0.002	105°1' ± 2'	916.7 ± 0.3
3.	PG-930	9.862 ± 0.002	18.089 ± 0.007	5.310 ± 0.001	104°59' ± 1'	915.1 ± 0.2
4.	PG-1000	9.892 ± 0.003	18.085 ± 0.005	5.327 ± 0.002	105°13' ± 2'	919.7 ± 0.4
5.	1921-700	9.835 ± 0.005	18.100 ± 0.010	5.304 ± 0.002	104°51' ± 2'	912.5 ± 0.4
6.	1921-725	9.847 ± 0.002	18.085 ± 0.007	5.300 ± 0.002	104°54' ± 1'	912.0 ± 0.3
7.	1921-750	9.848 ± 0.003	18.058 ± 0.007	5.297 ± 0.001	104°52' ± 2'	910.4 ± 0.3
8.	1921-825	9.844 ± 0.004	18.071 ± 0.006	5.312 ± 0.001	105°2' ± 1'	912.5 ± 0.3
9.	1921-930	9.844 ± 0.002	18.064 ± 0.006	5.307 ± 0.001	105°0' ± 1'	911.4 ± 0.2
10.	1921-1000	9.867 ± 0.002	18.058 ± 0.008	5.316 ± 0.002	104°57' ± 2'	915.0 ± 0.3
11.	1921-1015	9.872 ± 0.005	18.079 ± 0.014	5.335 ± 0.004	105°8' ± 3'	919.1 ± 0.6
12.	1921-HM-725	9.854 ± 0.003	18.085 ± 0.008	5.306 ± 0.003	104°57' ± 2'	912.6 ± 0.4
13.	1921-HM-825	9.856 ± 0.003	18.050 ± 0.007	5.309 ± 0.001	105°3' ± 1'	912.3 ± 0.2
14.	1921-HM-925	9.853 ± 0.004	18.022 ± 0.013	5.316 ± 0.002	105°7' ± 3'	911.3 ± 0.5
15.	1801-725	9.861 ± 0.003	18.093 ± 0.008	5.304 ± 0.003	104°49' ± 2'	914.9 ± 0.4
16.	1801-825	9.872 ± 0.005	18.088 ± 0.010	5.318 ± 0.003	105°6' ± 3'	916.9 ± 0.6
17.	1801-930	9.866 ± 0.002	18.058 ± 0.006	5.309 ± 0.001	105°8' ± 1'	913.1 ± 0.2
18.	1801-1000	9.885 ± 0.003	18.098 ± 0.008	5.324 ± 0.002	104°58' ± 2'	920.1 ± 0.4

Therefore, $Na(M_4)$ has been calculated as 2.00 − Ca − $Fe(M_4)$. Most of the hornblendes contain $Na(M_4)$ values of 0.10 or less, which has been ignored as being analytically insignificant. For these hornblendes X_{Na} is equal to the total Na content of the hornblende, shown in Table 2. Two hornblendes (PG-750 and 1801-725) contain 0.17 and 0.24 $Na(M_4)$ respectively. For these two, X_{Na} = total Na − $Na(M_4)$ (see Table 2).

For the melt, X_{Na} and X_K in equation 2 were taken as the mole proportions of Na or K per 100 g of melt. This in effect assumes that all sites in the melt occupied by alkalies are equivalent.

With these values, the quantity on the right side of equation 2 was calculated for the 24 hornblende–melt pairs, and is designated K_D in this paper. K_D is an observed distribution coefficient; it equals the equilibrium constant [K_D (eq)] if the experimental assemblages have indeed equilibrated.

The results are shown in Figure 1: ln K_D increases from −1.3± to 0.0 as temperature increases from 700 to 1045°C. If one wishes to fit all of these points to a single line, the best least-squares fit is:

$$\ln K_D = (-4258/T) + 3.25 \qquad (3)$$

This is the dashed line in Figure 1.

Two alternative methods of calculating X_{Na} and K_D have also been tried. The first involves correcting total Na for $Na(M_4)$ in all hornblendes. The effect of this is to shift the array of points in Figure 1 up slightly. The least-squares linear fit in this case is:

$$\ln K_D = (-4039/T) + 3.10 \qquad (4)$$

Second, one can estimate the maximum effect on K_D of Fe_2O_3 in hornblende by equating $Fe(M_4)$ to zero, and then calculating X_{Na} = total Na − $Na(M_4)$. This shifts the points up still further, those at high temperatures (930°–1045°C) being more strongly affected than the low-temperature ones. The resulting least-squares linear fit is:

$$\ln K_D = (-4566/T) + 3.71 \qquad (5)$$

Note that in this case the slope is appreciably steeper than in equations 3 and 4. The effect of ignoring ferric iron in the hornblendes of the data base is thus to underestimate the actual dependence of K_D on temperature.

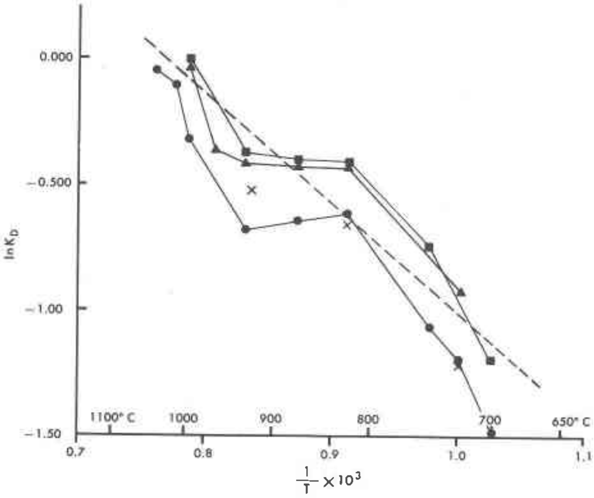

Fig. 1. The distribution coefficient for the exchange of K and Na between hornblende and melt, as ln K_D, plotted against reciprocal temperature. The dashed line fitting the data has the equation ln $K_D = (-4258/T) + 3.25$. It appears in Figs. 4, 5, and 7 as a solid line. Circles = 1921 hornblende–melt pairs; crosses = 1921-HM pairs; squares = Picture Gorge pairs; triangles = 1801 pairs. These symbols are the same in Figs. 1–3.

Discussion

The data of Figure 1 show that reaction 1 is very strongly temperature-dependent. At low temperatures potassium is concentrated in the melt relative to hornblende, but as temperature increases to 1050°C the distribution coefficient approaches one. It is not clear from the present data whether K_D will continue to increase as temperature increases further, with hornblende becoming enriched in K relative to the melt, or whether the distribution of alkalies will be random (K_D = 1) at all higher temperatures.

The question arises as to why this exchange reaction should be so temperature-dependent. There are two factors which may contribute. The first is that there may be intrinsic differences in structure between hornblende and liquid, which lead to differential changes in the alkali sites in each phase as temperature increases. To evaluate this effect we would need values for the enthalpies of the melt and the hornblendes, and the enthalpy of fusion of the hornblende; this information is not available.

In addition, non-ideal mixing of alkalies within either hornblende or melt would add to the overall entropy of the reaction. The work of Burnham (1975) suggests that mixing of K and Na in these quartzofeldspathic melts may be ideal. However, because of the large size difference between K^+ and Na^+, solid-solution series involving the substitution K $\rightleftarrows$ Na frequently have substantial positive volumes of mixing or a miscibility gap in the middle of the series. This is seen in the micas (Eugster *et al.*, 1972;

Blencoe, 1977) and feldspars (Tuttle and Bowen, 1958; Orville, 1967).

The hornblende structure is apparently less susceptible to collapse as Na^+ substitutes for K^+: at least, no excess volume effects were observed in the (K,Na) richterite series (Huebner and Papike, 1970). However, in hornblende the A site is distorted in shape. Because of this distortion, and the large difference in ionic radius, Na^+ and K^+ occupy slightly different positions in the A site (Papike *et al.*, 1969). The presence of two different A sites will increase the entropy of the exchange reaction by adding a configurational entropy term; however, since neither this nor the first effect can be evaluated rigorously, the relative importance of the two is unknown.

Whatever the precise reason for the strong temperature-dependence of this reaction, it may be possible to use it as an empirically-based geothermometer, without complete thermodynamic analysis. Most other silicate exchange reactions which have been proposed as geothermometers involve the exchange of Mg and Fe between two crystalline phases. Another, the plagioclase geothermometer, involves exchange of Na^+ and Ca^{2+}, balanced by Si^{4+} and Al^{3+}, between feldspar and liquid. Reaction 1 is simpler than these reactions for several reasons:

(1) Both Na and K are of fixed valence, unlike iron. Thus changes in oxidation state have no direct effect on K_D; electron microprobe analyses of hornblende and melt can often be used to calculate K_D, either directly or with minor corrections, without a separate determination of multiple valence states.

(2) Na and K are much more similar chemically than Fe and Mg, as measured by, *e.g.*, their electronegativities.

(3) Only one crystalline site is involved in the exchange: the 12-fold A site in hornblende. Most other proposed geothermometers involve either multiple sites in one or both phases, or coupled substitutions.

Nevertheless, in spite of these simplifying factors, it seems probable from Figure 1 that other factors besides temperature control K_D. Two complexities are immediately apparent:

(1) The shapes of the curves connecting hornblende–melt pairs from each bulk composition are S-shaped, suggesting that temperature-dependence is not linear.

(2) The curves for different basalt compositions are displaced from each other, implying that a compositional effect of some sort influences K_D at constant temperature.

Therefore, before reaction 1 can be considered useable as a geothermemeter, we must know what other factors besides temperature are affecting K_D and whether their effects can be calibrated. Possible factors include: variations in melt composition and hornblende composition; pressure; and water activity.

Compositional effects

As noted above, there is some compositional control on K_D: at constant temperature K_D (PG) $\geq$ K_D (1801) $>$ K_D (1921). However, for these three basalt compositions, this is a second-order effect, only slightly larger than the 11–16 percent uncertainty in K_D, related to the analytical uncertainties in Na_2O and K_2O.

Hornblende and melt both vary in composition throughout the temperature range involved (700–1045°C); furthermore, many other phases are present in each assemblage, so the number of potential variables may appear to be very large. However, from the form of reaction 1, it can be seen that K_D is affected only by the relative energies associated with the A site in hornblende and the alkali sites in the melt. Thus compositional control of K_D must correlate with changes in hornblende composition or melt composition. As melt composition changes, other phases may become stable (*e.g.*, plagioclase, augite). However, K_D will be affected only to the extent that melt structure changes as melt composition changes: the presence or absence of other phases will not affect K_D directly.

It is helpful, in resolving what compositional factors are controlling K_D, that the variation of K_D *vs.* $1/T$ is nonlinear, because most oxide components in hornblende and liquid do vary linearly with temperature in these experiments (Helz, 1973, 1976). Neither the shape of these curves nor their sequence (PG $\geq$ 1801 $>$ 1921) can be explained by variations in Na_2O or K_2O in the bulk compositions of hornblendes or the melts, for example. The compositional parameter whose behavior as a function of temperature most resembles that of K_D is the Mg/(Mg + Fe) ratio of hornblende, shown in Figure 2. When one compares Figures 1 and 2, it appears that K_D is inversely related to variations in Mg/(Mg + Fe) in hornblende. In particular, the dip in K_D values between 875–970°C coincides with the peak Mg/(Mg + Fe) values in these hornblendes. However, other aspects of hornblende composition besides the Mg/(Mg + Fe) ratio must also be affecting K_D. For ex-

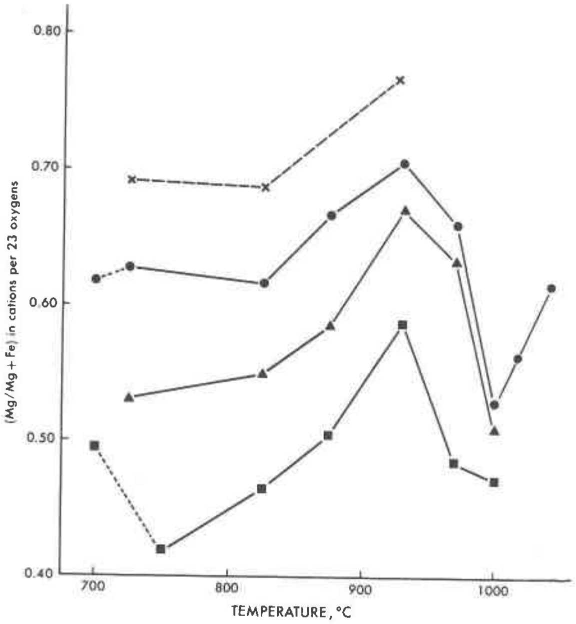

Fig. 2. Mg/(Mg+Fe) in hornblende *vs.* temperature. Large dashes connect 1921-HM data. Small dashes are used as in Fig. 7 (Helz, 1973, p. 275).

ample, hornblendes having higher [2Ti + Al(VI)] contents tend to have lower K_D values, for a given Mg/(Mg + Fe) ratio [compare the 1921-1000 and 1801-1000 hornblende K_D values *vs.* their compositions (Helz, 1973)].

Thus K_D is affected by variations in hornblende compositions, and furthermore there is no one compositional parameter to which all of the observed variation in K_D can be related. However, perhaps the most important difference between the Na^+ and K^+ ions is size. Therefore it seems reasonable to hypothesize that variation in hornblende composition at constant temperature affects K_D because it affects the size of the A site: more magnesian hornblendes or hornblendes with higher concentration of +3 and +4 cations in the octahedral sites tend to have smaller unit cells, overall. The smaller unit cells would tend, other things being equal, to favor Na^+ rather than K^+ in the A site.

In order to test this hypothesis, cell parameters were obtained for 18 experimentally-produced hornblendes. The correlation between the volume of the unit cells and K_D, at constant temperature, is quite good. Figure 3 shows the data of Figure 1, with the cell volumes from Table 2 beside the K_D values of the corresponding hornblendes, plus one data point from Table 5. The superimposed contours show the way K_D varies with temperature at constant cell volume. This contouring suggests that one can calibrate the effect of hornblende composition on K_D in terms of the volume of the unit cell; that is, the combination of a K_D value and the cell volume of the hornblende uniquely determines the temperature at which the particular hornblende–melt pair coexists.

Estimated effects of pressure and water activity on K_D

If the melt is more compressible than hornblende, the larger cation (K^+) will be enriched in hornblende as pressure increases, shifting equation 1 to the right and increasing K_D. The equation describing the effect of a change in pressure on the molar free energy ($\Delta\overline{G}$) of a reaction at constant temperature is:

$$\frac{\partial \Delta \overline{G}}{\partial P} = \Delta \overline{V} \qquad (6)$$

where $\Delta\overline{V}$ is the change in molar volume of the reaction. For equation 1, the change in molar volume can be written:

$$\Delta\overline{V} = (\overline{V}_{\mathrm{K\,hbl}} - \overline{V}_{\mathrm{Na\,hbl}}) - (\overline{V}_{\mathrm{K\,melt}} - \overline{V}_{\mathrm{Na\,melt}}) \qquad (7)$$

Although ideally one would like to know the effect of an infinitesimal change in K/Na on $\overline{V}$ for complex hornblendes or melts otherwise constant in composition, such information is not available. However, molar volumes are available for certain end-member compositions: Na-richterite and K-richterite (Hueb-

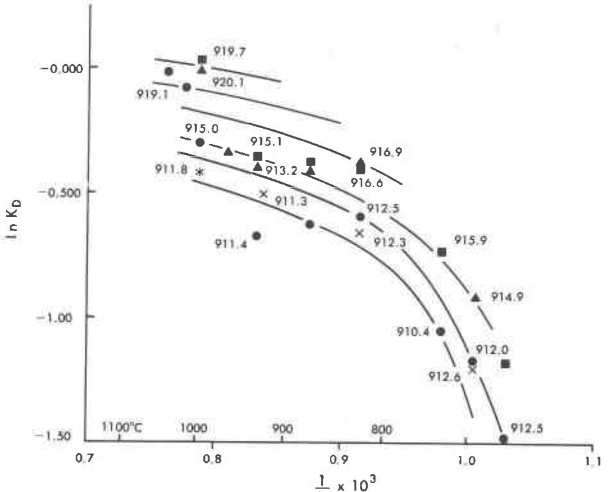

Fig. 3. Compositional data from Fig. 1. The numbers beside some of the points are the volumes of the hornblende unit cells, taken from Table 3. The contours indicate the approximate variation of K_D with temperature at constant cell volume. The asterisk denotes a hornblende–melt pair produced in the 1921 basalt at 1000°C, 8 kbar (Table 5, Col. 3), with its cell volume of 911.8A^3.

Table 4. K_D values for some hornblende–melt pairs produced in other experimental studies

	Starting Material	Pressure (kb)	Temperature (°C)	X_{H_2O}	Buffer Used	K_D	ln K_D
Holloway and Burnham (1972)	1921 Kilauea olivine tholeiite	4.90	875	0.60	NNO	.719	-.330
		5.20	999	9.57	NNO	.395*	-.929
Green and Ringwood (1968)	synthetic quartz tholeiite	9	920	?	None	.571	-.560
		9	960	?	None	.551	-.596
		9	1040	?	None	.281	-1.269
Cawthorn *et al.* (1973)	alkali basalt	5	1001	1.0	NNO	.759	-.276
	basaltic andesite	5	961	1.0	NNO	1.206	+.187
Allen *et al.*** (1975)	Mt. Hood andesite	13	900	1.0	NNO	.813*	-.207
		13	920	1.0	HM	.709*	-.344
Mysen and Boettcher (1975)	spinel lherzolite (B)	15	1050	1.0	HM	.787*	-.239
	garnet lherzolite (D)	15	1100	1.0	None	.689	-.372

*Indicates amphiboles for which K_D is sensitive to assumed Fe^{+2}/Fe^{+3} ratio.

**The glass analyses presented by Allen *et al.* have very low Na_2O contents, probably because of volatilization of Na_2O under the probe beam. The alkali contents of these were reconstructed approximately by calculating modes and determining alkalies by difference, using phase and bulk compositions presented by Allen *et al.* and the methods described in Helz (1976).

ner and Papike, 1970) and $NaAlSi_3O_8$ glass and $KAlSi_3O_8$ glass (Robie and Waldbaum, 1968). Putting these values in equation 6 gives:

$$\Delta\overline{V} = (277.48\text{–}273.93) - (116.5\text{–}110.1)$$

$$= -2.85 \text{ cm}^3/\text{mole}$$

With this value for $\Delta\overline{V}$, the effect on K_D at a given temperature may be calculated using the equation

$$\frac{d \ln K}{dP} = \frac{\Delta\overline{V}}{RT} \tag{8}$$

Assuming $\Delta\overline{V}$ is -2.85 cm³, and $T = 1300°K$, the change in ln K is 0.027 per kilobar. A pressure increase of 5 kbar, for example, would shift the line in Figure 1 up 0.14 log units. Alternatively, if one used the line in Figure 1 for hornblendes actually formed at 10 kbar, the estimated temperatures would be about 60° too high. Since the uncertainty in the microprobe analyses produces an uncertainty of ±40–50° in temperature, it will probably be difficult to see the effect of pressure on K_D unless very large pressure contrasts are involved.

The molar volumes used for the melts are those of the dry glasses at STP; these are not the same as the volumes would be for hydrous melts at T and P. However, unless K-bearing glasses behave differently from Na-bearing glasses as T, P, and H_2O content change, the difference between the molar volumes of the two should be of the same sign and order of magnitude as that obtained here. Let us further assume that variations in a_{H_2O} have no effect on the crystal structure of hornblende, so long as a_{H_2O} is high enough to stabilize hornblende. If this is true, variation in a_{H_2O} will affect equation 1 only to the extent that it either changes the relative compressibilities of hornblende and melt or changes the way K and Na mix in the melt. Such effects are likely to be small for the range of a_{H_2O} values over which hornblende is stable.

These conclusions, that pressure should shift this exchange reaction to the right, and that this effect should be small, are in good agreement with the observations of Cawthorn (1976). Cawthorn reports that hornblendes in extrusive rocks tend to be somewhat more sodic, relative to bulk-rock composition, than hornblendes from intrusive rocks, but the effect is barely visible given the scatter in the data. A shift in this same direction[1] was observed by Nicholls

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[1] Both Cawthorn (1976) and Nicholls (1974) calculated the ratio

$$\left[\frac{X_{Na}}{X_K}\right]_{hbl} \Big/ \left[\frac{X_{Na}}{X_K}\right]_{melt}$$

which is $1/K_D$ as defined in this paper.

Table 5. Chemical analyses, structural formulas (23 oxygens) and cell parameters for hornblendes, with alkali contents of coexisting melts and distribution coefficients for hornblende–melt pairs, from experimental charges provided by J. R. Holloway

	1	2	3	4	5
Starting material	1921	1921 glass	1921	1921	San Carlos
Pressure, kb	5.10	4.95	7.80	7.96	5
Temperature, °C	1001	999	955	1050	1000
X_{H_2O}	.57	.57	.57	.60	1.0
SiO_2	41.7	43.6	42.4	40.1	40.2
TiO_2	3.46	2.82	2.77	5.23	3.35
Al_2O_3	12.6	12.4	12.3	14.1	11.4
FeO	12.3	12.2	13.0	14.9	11.5
MnO	.14	.18	.16	.17	.10
MgO	13.6	14.3	12.9	11.1	14.7
CaO	10.8	9.94	11.6	9.37	11.9
Na_2O	2.25	2.10	2.11	2.19	2.63
K_2O	.51	.47	.52	.47	1.21
Sum	97.4	98.0	97.8	97.6	97.0
Si }8.00	6.162	6.346	6.261	5.966	6.030
Aliv	1.838	1.654	1.739	2.034	1.970
Alvi	.357	.473	.402	.406	.052
Ti	.385	.309	.308	.585	.378
Fe^{++}	1.520	1.485	1.606	1.854	1.441
Mn	.018	.022	.020	.022	.013
Mg	2.995	3.102	2.839	2.461	3.283
Sum	5.275	5.391	5.174	5.359	5.167
Ca	1.710	1.550	1.836	1.494	1.915
Na	.645	.593	.604	.632	.765
K	.096	.087	.098	.089	.232
Sum	2.451	2.230	2.538	2.218	2.912
a,Å	9.803 ±0.003	9.820 ±0.002	9.851 ±0.004		
b,Å	18.074 ±0.013	18.067 ±0.007	18.054 ±0.012		
c,Å	5.303 ±0.008	5.308 ±0.002	5.314 ±0.003		
β	104°47′ ±3′	104°50′ ±2′	105°1′ ±3′		
volume,$Å^3$	908.4 ±0.9	910.3 ±0.3	911.8 ±0.5		
Alkalies in coexisting melt:					
Na_2O	2.4	2.9	3.0	3.4	7.6
K_2O	1.2	1.2	1.1	1.0	3.8
K_D	.453	.541	.667	.728	.923
ln K_D	-.792	-.615	-.404	-.317	-.080

(1974), but he reported it to be large. The small effect calculated above assumes hornblende composition is constant except for K/Na. As discussed above, K_D is affected by other changes in hornblende composition, which might occur as pressure increases. Such pressure-induced changes in other aspects of hornblende composition might contribute to the large pressure effect reported by Nicholls (1974), and may be present in Cawthorn's data as well.

Comparison with other experimental data

There are relatively few other experimentally-produced hornblende–melt pairs for which analyses are reported in the literature; data for some of these are summarized in Table 4. The distribution coefficients in Table 4 were calculated using the same conventions observed in Table 2 and Figures 1 and 3, that is, all iron in the hornblende was taken as FeO, and Na(M_4) was corrected for only where it exceeded 0.10 cations per 23 oxygens. The results are plotted with my data in Figure 4.

These 11 additional hornblende–melt pairs were produced in a variety of bulk compositions, at temperatures ranging from 875°–1100°C, and pressures of 5 to 15 kbar. Nine have K_D values which fall within the range of K_D values observed in the present study, or only slightly outside, while two have K_D's much lower than those of any pairs produced in this study. When one considers the analytical difficulties involved, plus the considerable variations in bulk composition, water activity, and oxygen fugacity among the different sets of experiments, this level of agreement between the various data sets is quite good. It confirms both the general accuracy of the analytical data, and the dominant role of temperature in controlling the value of K_D. By contrast, a pressure effect is not evident: hornblendes formed at 9–15 kbar are not systematically offset from those produced at 5 kbar. Some compositional effects can be seen in Figure 4, however. The three hornblendes from andesites all fall above the best-fit line for the basalt data, while two hornblendes from peridotites fall below it. This general pattern agrees with the evidence from the present study, that the single most important chemical variable controlling K_D is the Mg/Fe ratio of hornblende.

One of the two K_D values which fall well below the rest of the data in Figure 4 is for a hornblende–melt pair produced in the 1921 Kilauea basalt at 5 kbar, 1000°C (Holloway and Burnham, 1972). In order to determine why this one pair has such a low K_D value, Dr. J. R. Holloway provided four experimental charges from the set described by Holloway and Burnham (1972) for analysis. Data for these hornblende–melt pairs, plus data for a fifth charge made using the basanite from San Carlos, Arizona, are presented in Table 5. The analytical and X-ray methods used are the same as previously described. Two of these charges (Cols. 3 and 4, Table 5) were analyzed earlier (Holloway and Burnham, 1972); the others have not been analyzed before.

The results in Table 5 generally fit well with the data from Table 2. Most hornblende–melt pairs from the 1921 Kilauea tholeiite plot together, and the pair from the San Carlos basanite plots with the data from the relatively iron- and alkali-rich Picture

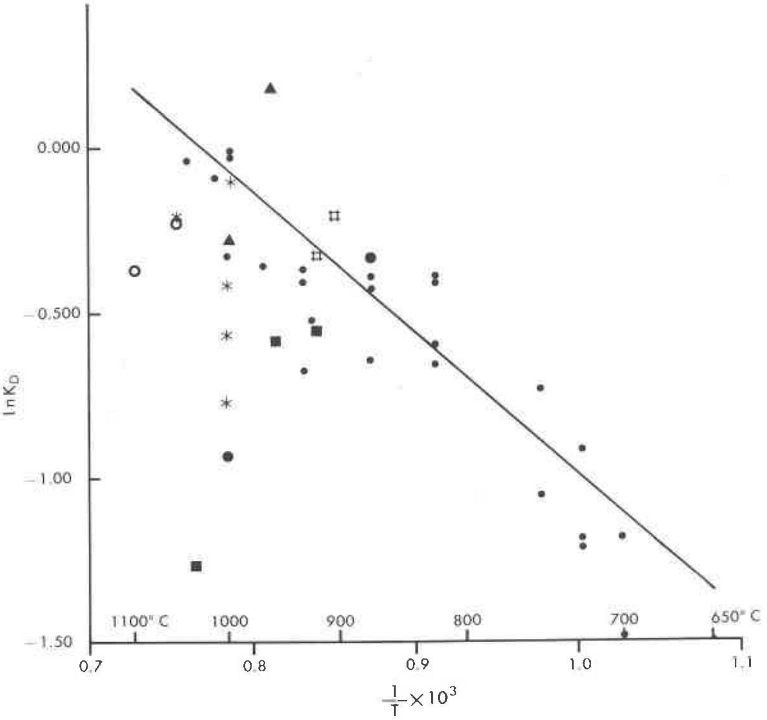

Fig. 4. Distribution coefficients calculated for hornblende–melt pairs from other experimental studies, superimposed on the data of Fig. 1 (indicated as small dots). Symbols for data from Table 4 are: solid circles = Holloway and Burnham (1972); solid squares = Green and Ringwood (1968); solid triangles = Cawthorn *et al.* (1973); open squares = Allen *et al.* (1975); open circles = Mysen and Boettcher (1975). Data points from Table 5 are indicated by asterisks.

Gorge and Hualalai basalts. Again, no pressure effect is evident in comparing data from 5 and 8 kbar runs.

However, there is a large range in K_D values for hornblende–melt pairs produced in the 1921 Kilauea tholeiite at 1000°C. This variation cannot be the result of changes in bulk composition: it must be produced by variations in hornblende and/or melt composition. The hornblendes having K_D values falling below the general distribution of data all have relatively high Mg/Fe ratios, plus moderate to high Ti + Al(VI) contents. Therefore, they would be expected to have relatively small cell volumes and low K_D values, as previously hypothesized.

The cell refinements in Table 5 confirm this hypothesis of the correlation between hornblende composition, cell volume, and K_D. In fact there is a very good correlation between K_D and cell volume for all six hornblendes produced at 1000°C for which cell parameters are available (Table 5, Cols. 1, 2, 3; plus the 1921-1000, 1801-1000 and PG-1000 hornblendes from Tables 2 and 3). The new data thus confirm the importance of the cell volume of hornblende as a secondary control on K_D at constant temperature.

Another factor may contribute to the relatively low K_D's observed for the hornblendes in Cols. 1 and 2 of Table 5, however. Because of their low CaO contents they contain appreciable Fe or Na in the M_4 site, and hence K_D is very much dependent on the (unknown) Fe_2O_3 content of the hornblende. This brings up the question of the extent to which one can do without a separate Fe_2O_3 determination in calculating K_D. There are several categories of hornblendes for which the amount of Fe_2O_3 will have relatively little effect on K_D. They are:

(1) hornblendes in which the M_4 site is filled with Ca (Ca = 1.8 or more);

(2) hornblendes in which Fe(M_4) is small (≤ 0.10) even when the structural formula is calculated with all iron as FeO;

(3) hornblendes in which the sum Ca+Na+K is equal to or greater than 3.00 (*i.e.*, the M_4 and A sites are completely filled with these three cations).

For hornblendes in these categories, it is not necessary to know the ferric iron content in order to calculate K_D; a microprobe analysis is sufficient.

As discussed earlier, the hornblendes of Table 2 fall mostly in categories 1 and 2. (The exceptions are the 1921-1015 and 1921-1045 hornblendes.) In Table

5, those in Cols. 1, 2, and 4 are sensitive to assumed Fe_2O_3 content, as are the four hornblendes marked by asterisks in Table 4. The effect of recalculating K_D with some ferric iron in all hornblendes would be to raise K_D for these hornblendes relative to the K_D values for the other hornblendes in Figure 4. In no case does this shift weaken any of the conclusions drawn above; in some instances it would strengthen them.

In summary, experimental data from other sources are in good agreement with the results of this study. The exchange of Na and K between hornblende and liquid is controlled chiefly by temperature. Pressure effects are not evident in the data in Figure 4. Secondary shifts in K_D are produced by variations in hornblende composition, but these can apparently be explained in terms of varying hornblende cell volume, and calibrated so that the combination of K_D and cell volume determines temperature uniquely. Finally, although for certain kinds of hornblendes one must know Fe_2O_3/FeO in order to calculate the A-site occupancy, there are many types of hornblendes for which a microprobe analysis will be sufficient.

Applications

It appears that the exchange reaction shown in equation 1 may have some promise as a geothermometer. Data needed to apply this geothermometer include analyses of hornblende and a coexisting liquid, and the cell volume of the hornblende. For hornblende–melt pairs with K_D values and cell volumes lying within the range of contours shown in Figure 3, it should be possible to determine the temperature of coexistence to perhaps ±50°C. Extrapolation of the data to higher temperatures or to larger or smaller cell volumes will introduce larger absolute uncertainties.

Natural assemblages to which this geothermometer might be most easily applied are those containing either (1) hornblende in contact with fresh glass or (2) hornblende phenocrysts in a more rapidly quenched groundmass. For natural samples, there may be additional sources of error beyond the uncertainties in the microprobe analyses and the cell refinement. These include such problems as (1) the presence of zoning in hornblende, (2) lack of direct contact between hornblende and glass, (3) post-quenching changes in glass or groundmass chemistry, and (4) in the absence of glass, difficulty in determining the composition of the groundmass, where it differs from the whole-rock composition.

This exchange reaction can also be used in other ways. Given a temperature, known or estimated, it can be used to test for equilibrium between a known hornblende and known melt composition, and thus perhaps to distinguish between xenocrystic and cognate hornblende. Alternatively, for a given temperature, the exchange reaction can be used to predict the K/Na ratio of the melt which would be in equilibrium with a particular hornblende at that temperature. This application might be particularly interesting for hornblendes from differentiated plutonic rock series, in which the succession of rock compositions may, because of crystal accumulation, differ somewhat from the liquid line of descent.

Two examples of the possible use of this exchange reaction follow.

Hornblende–glass pairs from Salt Lake Crater, Oahu

Figure 5 shows data on hornblende–glass pairs from two partially melted xenoliths from Salt Lake Crater, Oahu. All analyses were made using an ARL EMX electron microprobe operated at 15 kV, with a sample current of 0.01 μA. The conventions used in calculating hornblende structural formulas, K_D, *etc.* were identical to those used in Figure 1. Temperatures were calculated using equation 3, which was assumed to continue linearly above the present limits of the experimental data.

Xenolith RHSL-1 contains a primary assemblage of clinopyroxene > garnet > ilmenite, biotite, horn-

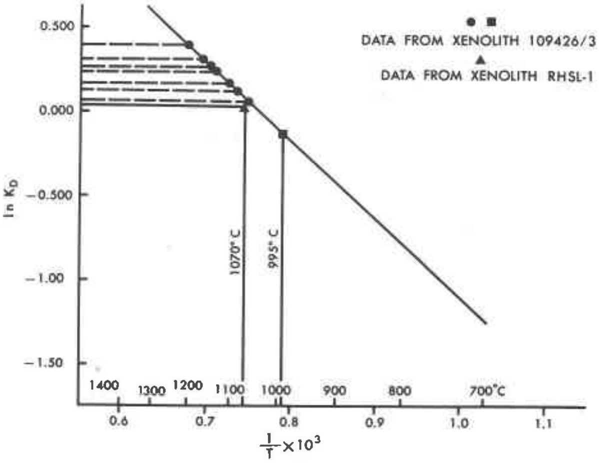

Fig. 5. Hornblende–melt distribution coefficients and oxide geothermometer data for assemblages in two xenoliths from Salt Lake Crater, Oahu, Hawaii. Vertical lines indicate the presence of a magnetite–ilmenite pair, giving the temperature shown; horizontal lines indicate the presence of a hornblende–melt pair. Only the assemblage from RHSL-1 contains all four phases.

blende, and pyrrhotite, with many interstitial pockets of melt. The melt pockets have second-generation minerals crystallizing from them. The data are from a single pocket, containing the assemblage hornblende, aluminous clinopyroxene, olivine, spinel, ilmenite, magnetite, and glass. The Fe-Ti oxide pair gives $T = 1070°C$, $\log f_{O_2} = -10.1$ (Buddington and Lindsley, 1964). The hornblende–melt alkali distribution ratio is $\ln K_D = 0.010$, giving a temperature of 1045°C, using equation 3 only. The two temperatures differ by only 25°C, which is quite good agreement considering that no cell volume correction can be made.

Xenolith 109426/3 contains the primary assemblage clinopyroxene = hornblende > orthopyroxene, garnet, ilmenite. It contains a few pockets and veinlets of glass plus secondary crystals, the glass being in contact with euhedral hornblende. In the center of the xenolith, as cut, is an area of texturally similar interstitial material, in which the glass has completely crystallized. This area contains a magnetite–ilmenite pair, whose compositions give $T = 995°C$, $\log f_{O_2} = -12.1$. The hornblende-glass assemblages contain ilmenite only, so no direct correlation between the oxide geothermometer and K_D can be made. However, the oxide pair probably records a near-solidus or subsolidus temperature: the glassy interstitial areas should have quenched from higher temperatures. The upper stability limit of hornblende is approximately 1160°C when $P_{H_2O} < P_{total}$ (Millhollen and Wyllie, 1974). Therefore, the maximum range of plausible K_D values for the hornblende–melt pairs in 109426/3 is fixed at both ends. Figure 5 shows that the K_D values, even without a cell volume correction, give temperatures in the range 1060°–1215°C, all well above the oxide temperature, and not significantly higher than the upper stability limit of hornblende as determined by Millhollen and Wyllie.

Figure 6 shows the apparent quenching temperature of the hornblende–melt pairs from xenolith 109426/3 plotted against the distance of each pair from the holocrystalline interstitial patch in the center of the cut. Apparent temperature rises steadily from the core to the present edge of the xenolith, where the xenolith is coated with the host nephelinite. This systematic variation suggests that the differences in temperature within this data set are significant and that they are recording differences in quenching rate, as the fastest quench should have occurred in the outermost part of the xenolith, while the interior cooled more slowly.

The data from both xenoliths suggest that temperatures for the hornblende–melt reaction do indeed quench in, providing that the quench is fast enough to produce a glass. That is, although glasses may be altered deuterically or by weathering, there is no

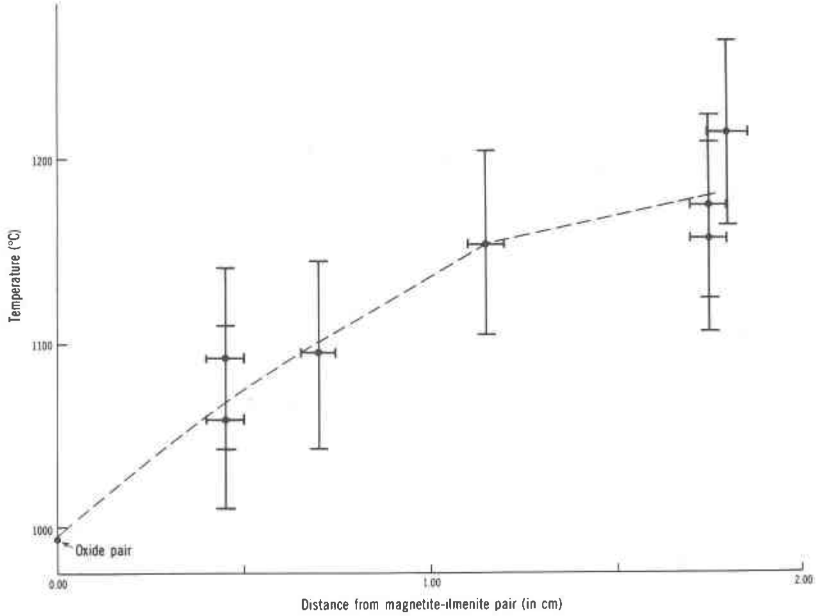

Fig. 6. Apparent temperatures for hornblende–melt pairs from xenolith 109426/3 plotted against distance of the pair from the subsolidus magnetite–ilmenite pair. Horizontal error bars indicate the uncertainty in the distance measurement. Vertical bars show the uncertainty in absolute temperature produced by analytical uncertainty and phase inhomogeneity. Relative compositions, and hence relative temperatures, are known much more precisely.

later exchange of alkalies between hornblende and glass merely because of physical proximity.

Hornblende-rock pairs from the Sierra Nevada

One of the few published studies which includes cell refinement data as well as rock and hornblende analyses is that of Dodge *et al.* (1968) on hornblendes from some of the granitic rocks of the central Sierra Nevada batholith. Although plutonic rocks are not ideal material to which to apply this exchange reaction, this data set offers a unique opportunity to illustrate the size of the cell-volume correction for hornblendes from felsic bulk compositions.

In calculating K_D and temperature values for these hornblende-rock pairs, the following conventions were used: (1) K and Na in the hornblende structural formulas given by Dodge *et al.* (1968) were used for X_K and X_{Na} in hornblende. (2) The K/Na of the melt was assumed to be that of the whole-rock analysis.[2] (3) K_D was then calculated and temperature estimated using equation 3, which corresponds to the straight line shown in Figure 7. (4) The "temperatures" were then corrected for hornblende compositional effects by moving to the appropriate cell-volume contour at constant K_D. (Note that some of the cell-volume contours shown in Fig. 7 have been extrapolated to lower temperatures.)

Two features of these results are particularly important:

(1) The cell volumes of the hornblendes from granitic rocks are systematically higher than those from basalts, as would be predicted from earlier discussion.

(2) The cell-volume correction is large.

The first feature confirms that the cell-volume correction will be necessary in applying this potential geothermometer to hornblendes from granitic compositions. The second suggests it would be desirable to supplement the data base of Tables 2 and 3 with data for hornblende-melt pairs from experiments on rocks with granodioritic compositions, in the range 700–850°C.

However, the present data base should be sufficient to make semiquantitative corrections for hornblendes from granitic rocks, as shown in Figure 7. When this is done for the Sierran samples, the temperatures are consistently lower than those calculated using equation 3, commonly 100–200°C lower. Also, the range in apparent temperatures is greatly reduced, from 1030–700°C to 780–670°C. Melting experiments on Sierran rocks (Piwinski and Wyllie, 1967) at $P_{total} = 2$ kbar suggest that melting begins at

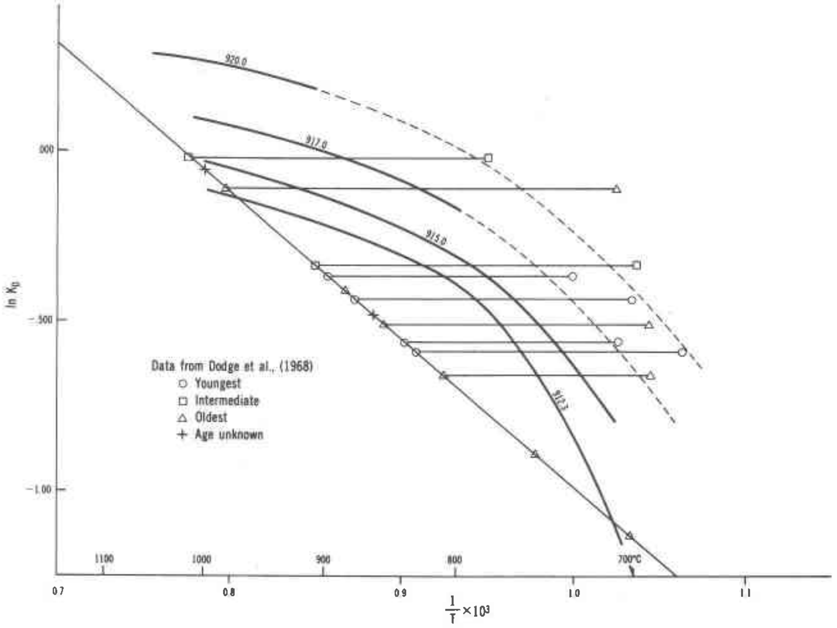

Fig. 7. Sodium–potassium distribution coefficients for hornblende–rock pairs of different ages from the Sierra Nevada batholith, showing effect of cell-volume correction on estimated temperature. Solid contours are from Fig. 3; dashed contours are extrapolations.

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[2] Most of these rocks have compositions near that of the granitic minimum-melting composition, so they cannot be very far from melt compositions.

675–705°C under those conditions, but that the rocks are completely melted only at 900–1000°C. Crystallization at lower water contents would not raise the solidus, unless another gas species (CO_2?) were present, but would raise the liquidus temperatures considerably. As noted above, the best estimates for hornblende–melt equilibration temperatures for the Sierran samples of Dodge *et al.* (1968) lie in the range 780–670°C. These temperatures, if they are even approximately correct, are near-solidus temperatures. This implies that the hornblendes now present in these rocks may not have compositions quenched in from near-liquidus conditions, but re-equilibrated with whatever melt was present until the rocks were mostly crystallized. This seems very reasonable for rocks produced by slow cooling at moderate confining pressures.

Acknowledgments

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