The aluminum content of hornblende in calc-alkaline granitic rocks: A mineralogic barometer calibrated experimentally to 12 kbars*

WARREN M. THOMAS and W. G. ERNST[1]

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024-1567, U.S.A.

Abstract—Partial melting experiments on a natural hornblende-bearing tonalite have been conducted in a piston-cylinder apparatus in order to determine the total aluminum content of hornblende in equilibrium with quartz + K-feldspar + plagioclase + biotite + epidote + sphene + Fe-Ti oxide + melt + fluid at 750°C as a function of pressure in the range 6–12 kbar. A hornblende of similar composition to that in the tonalite itself, but possessing a higher aluminum content, was added to the starting material. In runs of one week duration, rims formed on both types of hornblende grains, with the compositions converging from initially different values in the two hornblende populations.

Using this technique, a calibration for the total Al content of hornblende as a function of aqueous fluid pressure at a constant, near solidus temperature was derived: $P (\pm 1.0 \text{ kbar}) = -6.23 + 5.34 \text{ Al}^T$. The pressures calculated from this equation are appropriate for granitoid melts crystallizing at approximately 750°C. They agree well with a previous experimental calibration, but are too low by more than a kbar when extrapolated to low pressures.

INTRODUCTION

DETERMINATION of the pressure of crystallization of calc-alkaline plutons has historically been difficult; most efforts have relied largely on constraints gleaned from appropriate mineral assemblages, if any, in the contact aureole. HAMMARSTROM and ZEN (1986) and HOLLISTER et al. (1987) empirically calibrated an approximately temperature-independent barometer based on the Al content of hornblende coexisting with quartz + K-feldspar + plagioclase + biotite + sphene + Fe-Ti oxide (+ melt) in calc-alkaline granitoids. In practical terms, the nearly isothermal nature of the solidus at middle and deep continental crustal levels allows Al^T in the amphibole to be employed as a mineralogic barometer. RUTTER and WYLLIE (1988) published a note describing agreement with this naturally-calibrated barometer of three experimentally altered hornblende compositions in a tonalite, but under vapor-absent conditions and with garnet in the subsolidus assemblage. JOHNSON and RUTHERFORD (1988, 1989) have recently calibrated this barometer with reversed experiments in the pressure range 2 to 8 kbars using natural starting material and an internally heated gas apparatus.

The purpose of the present study was to calibrate experimentally this hornblende barometer at higher aqueous fluid pressures using a piston-cylinder apparatus. The basic approach to the problem was to melt partially a natural hornblende-bearing tonalite to which a second, chemically similar but more aluminous hornblende had been added, and to

measure convergence in rim compositions of the two hornblendes as a function of pressure.

STARTING MATERIAL

The starting material for the experiments was a tonalite from the Late Cretaceous Josephine Mountain Intrusion from the San Gabriel Mountains, California. The mineral assemblage of this sample is quartz, plagioclase, K-feldspar, hornblende, biotite, epidote, magnetite, sphene, and zircon; the rock is fresh and unaltered. Because the amount of alkali feldspar is somewhat variable from sample to sample, 10 wt% natural orthoclase of composition $\text{Or}_{95}\text{Ab}_{05}\text{An}_{00}$ was added to the crushed sample to insure its presence in each experimental charge. The natural granitic material was lightly crushed to a maximum grain size of 0.1 mm, but was not sieved to avoid eliminating minerals which might be preferentially represented in the finer-grained fractions. For most of the critical experiments, the starting material was altered by adding a second hornblende similar to that in the tonalite and crushed to the same grain size. This introduced hornblende, which has a higher aluminum content and lower total iron content than that of the indigenous hornblende, is from a high-pressure garnet hornblendite from Santa Catalina Island, California (SORENSEN, 1988; JACOBSON and SORENSEN, 1986). Although the coexisting mineral assemblage of this rock consists primarily of garnet + zoisite, it was chosen in order to obtain a hornblende with a very high aluminum content to contrast with that from the tonalite. The two hornblendes are easily distinguished in the experimental charges, both optically and by the compositions of their cores. The hornblende from the tonalite is slightly zoned, and inasmuch as spatial relationships

---

Table 1. Composition of starting material, in weight percent

Weight percent	Natural tonalite*	Added K-feldspar	Introduced hornblende	Starting material
SiO_2	57.2	64.81	42.84	56.7
TiO_2	0.78	0.02	0.58	0.69
Al_2O_3	18.0	18.15	17.59	18.0
Cr_2O_3	n.a.	0.04	0.29	0.06
FeO**	6.06	0.05	9.91	5.84
MnO	0.12	0.02	0.05	0.11
MgO	2.7	0.00	10.98	3.13
CaO	6.42	0.00	11.42	6.26
Na_2O	3.9	0.53	2.05	3.47
K_2O	1.89	16.55	0.56	3.07
P_2O_5	0.43	n.a.††	n.a.	0.36†
CO_2	0.28	n.a.	n.a.	0.23†
H_2O†	0.69	n.a.	n.a.	0.57†
Total	98.47	100.17	96.27	98.49†

* XRF analysis by A. Barth.
** All Fe reported as FeO.
† Minimum values.
†† Not analyzed (n.a.).

are partially lost through crushing, the zoning contributes to the uncertainty in original Al content of ± 0.05 (1σ) per 23-oxygen formula. The composition

of this modified starting material is given in Table 1. Chemical analyses and cation proportions of hornblendes are presented in Table 2. Except for Al and Fe content, the amphiboles employed in the experiments are closely comparable. Analyses are reported with all iron treated as ferrous, although they are compatible with ferric iron contents ranging from 5–20%. Changes in the estimated amount of ferric iron generally affects the calculated Al^T by less than 2% relative. This starting material was run in sealed capsules with 10 wt% distilled H_2O, enough to saturate the melt experimentally generated by partial fusion.

EXPERIMENTAL PROCEDURE

All experiments were conducted in a piston-cylinder apparatus at UCLA using the NaCl cell furnace assembly of BOETTCHER et al. (1981); no pressure corrections were deemed necessary. The press was calibrated employing the equilibrium albite = jadeite + quartz (JOHANNES et al. 1971); nominal pressure is considered accurate to 200 bars. Temperatures were measured with Pt-Pt$_{90}$Rh$_{10}$ thermocouples and are thought to be known to $\pm 5°C$.

All experiments were run in Pt or Ag capsules of 11.4 mm length and 2.79 mm o.d. Because as large a charge as possible was desired, these experiments were performed

Table 2. Compositions of original and experimental hornblendes (wt.%)

	Original		6 kbar		8 kbar		10 kbar		12 kbar	
	A*	B*	A	B	A	B	A	B	A	B
SiO_2	44.12	42.84	40.66	41.86	39.44	40.33	38.68	38.71	39.00	39.40
TiO_2	1.24	0.58	0.76	0.98	1.16	1.64	0.87	1.01	0.61	0.65
Al_2O_3	9.68	17.59	13.26	12.81	15.02	14.55	16.82	14.72	20.00	19.61
Cr_2O_3	0.02	0.29	0.08	0.11	0.00	0.00	0.05	0.02	0.00	0.07
FeO†	17.72	9.91	15.44	13.78	18.11	18.47	16.74	16.66	17.06	16.30
MnO	0.54	0.05	0.40	0.30	0.36	0.24	0.33	0.27	0.20	0.24
MgO	10.48	10.98	9.28	11.18	7.90	8.15	8.57	8.48	6.34	6.66
CaO	11.76	11.42	11.88	11.96	11.45	11.50	11.34	11.31	10.86	11.04
Na_2O	1.39	2.05	1.47	1.53	1.92	1.76	1.95	1.93	2.08	2.13
K_2O	1.07	0.56	1.92	1.75	1.58	1.70	1.77	1.56	1.78	1.72
Total	98.02	96.27	95.15	96.26	96.94	98.34	97.12	94.67	97.93	97.82

Cations per 23 oxygens

Si	6.64	6.26	6.30	6.34	6.07	6.11	5.90	6.07	5.86	5.91
Al^T	1.72	3.03	2.42	2.29	2.72	2.60	3.03	2.72	3.54	3.47
Al^{IV}	1.36	1.74	1.70	1.66	1.93	1.89	2.10	1.93	2.14	2.09
Al^{VI}	0.36	1.29	0.72	0.63	0.79	0.71	0.93	0.79	1.40	1.38
Ti	0.14	0.06	0.09	0.11	0.13	0.19	0.10	0.12	0.07	0.07
Cr	0.00	0.03	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.01
Fe^{2+}	2.23	1.21	2.00	1.75	2.33	2.34	2.14	2.18	2.14	2.04
Mn	0.07	0.01	0.05	0.04	0.05	0.03	0.04	0.04	0.02	0.03
Mg	2.35	2.39	2.14	2.52	1.81	1.84	1.95	1.98	1.42	1.49
Ca	1.90	1.79	1.97	1.94	1.89	1.87	1.86	1.90	1.75	1.78
Na	0.41	0.58	0.44	0.45	0.57	0.52	0.58	0.59	0.61	0.62
K	0.21	0.10	0.38	0.34	0.31	0.33	0.34	0.31	0.34	0.33

* A = indigenous hornblende; B = introduced hornblende.
† All Fe reported as FeO.

unbuffered with regard to oxygen; f_{O_2} imposed by the furnace assembly and press is between Ni-NiO and hematite-magnetite buffers, as corroborated by running charges of those assemblages at the conditions of the experiments. Moreover, JOHNSON and RUTHERFORD (1988, 1989) stated that they found a minimal effect in their experiments by variation of oxygen fugacity between the Ni-NiO and the $MnO-Mn_3O_4$ buffers. No evidence was found in any of the runs of oxidation or reduction of Fe in the charges.

All experiments were of one week duration. Initially, a variety of temperatures were used, ranging from 650 to 900°C, but the final critical experiments were conducted exclusively at 750°C to increase reaction rates. Experiments were performed at pressures of 6, 8, 10, and 12 kbars, with one 2-kbar experiment conducted hydrothermally in a cold-seal pressure vessel.

At the conclusion of each experiment, the capsule was mounted on a glass slide, and ground and polished for the electron microprobe. Even small degrees of partial melting caused the sample to cohere and behave like a typical rock in the thin-sectioning process. Each experimental product was examined optically and subsequently with the electron microprobe. Amphiboles were chemically analyzed using a Cameca Camebax microprobe employing 15 kv accelerating voltage, 10 nanoamp sample current and a 1 μm beam diameter. ZAF corrections were applied and major elements are considered accurate to 1–2% relative, and minor elements to 2–10% relative.

Zoned amphiboles were analyzed—and portrayed in Fig. 1—for only those well-constrained runs in which all starting phases were present in addition to melt at the conclusion of the experiments.

RESULTS

In all experiments, melt was generated and rims of distinctive composition up to 30 μm wide were produced on hornblendes in the charge. In most cases, the change in composition appeared texturally to have been accomplished by diffusional modification of the original grain rim; in a few samples, overgrowths were observed, as evidenced by euhedral rims in contact with melt. In all cases, the rims exhibited compositions with allowed amphibole stoichiometries. The cores retained their original compositions; thus the two populations of hornblendes were readily distinguished. The total aluminum content in the indigenous hornblende was altered from an original value of 1.72(5) per 23-oxygen formula unit to a rim maximum of 3.54; for the introduced hornblende, the original value of 3.03(3) changed to a minimum of 2.29 and a maximum of 3.47. The aluminum content of the rims is a clear function of pressure, with the higher values associated with higher pressures, as seen in the empirical and earlier experimental calibrations. Note also that, although the two initial amphiboles possessed contrasting Fe as well as Al contents, Table 2 demonstrates that experimentally produced rim compositions are sensibly identical—hence chemical equilibration is indicated.
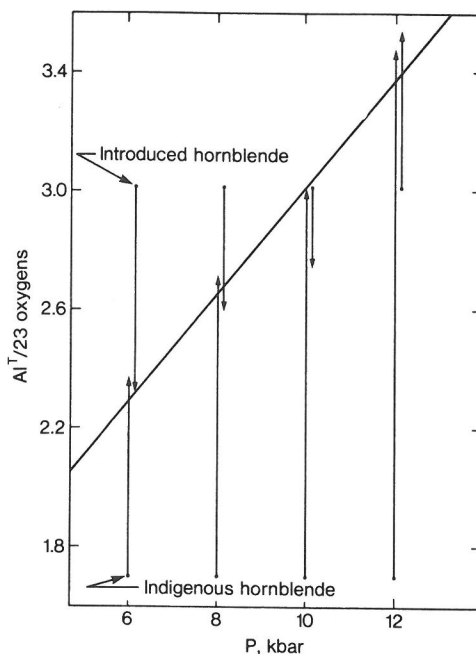

FIG. 1. Plot of the change in total Al of hornblende rims as a function of pressure in one week runs at 750°C. The base of the arrows represents the average initial Al^T of the indigenous and introduced hornblende and the heads of the arrow the *most extreme* values in the re-equilibrated rims. The line plotted represents a linear least squares fit to the midpoints between the heads of the arrows. Note that at 12 kbars, the compositions of both hornblendes have become more aluminum rich than the starting materials.

The results of the new experiments at 750°C are summarized in Fig. 1. Note that for each pressure, the base of the arrows represents the average Al content of cores for the two types of hornblendes, with the head of the arrows corresponding to the *most extreme* rim value in the runs for that pressure. In each case, excepting at 12 kbar, the aluminum compositions of the two hornblendes have converged; indeed, because the extreme values have been plotted, the compositions appear to have "passed" each other. Assuming that the one-sigma error in the formula numbers is 1%, the compositions of the runs overlap within 2σ at 6 and 8 kbar. The compositions of the hornblendes represented by the arrowheads in Fig. 1 are included in Table 2. Fitting a line to the midpoints between the arrowheads for 6, 8, 10 and 12 kbars yields a calibration of

$$P\ (\pm 1.0\ \text{kbar}) = -6.23\ (\pm 0.07)$$
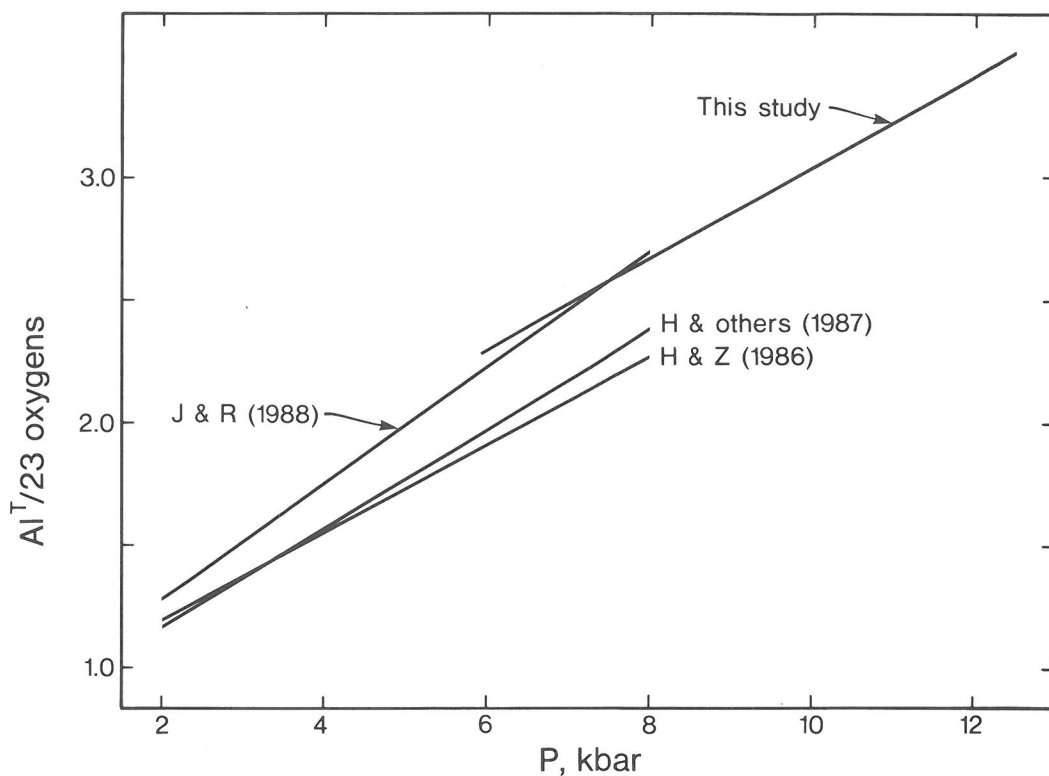$$+\ 5.34\ (\pm 0.40)(Al^T),\quad r^2 = 0.94.$$

FIG. 2. Comparison of calibration from this study with those from previous studies. Sources for curves are: H & Z (1987) = HAMMARSTROM and ZEN (1987); H & others (1988) = HOLLISTER and OTHERS (1988); and J & R (1988) = JOHNSON and RUTHERFORD (1988). Curves are shown only for the pressure range from which the particular calibration was derived.

A linear relationship was assumed, and the data fitted and errors calculated using the treatment of YORK (1969). Uncertainties in the slope and intercept quoted are one sigma. The stated uncertainty in the predicted pressure is a function of the aluminum content and varies, at the 95% confidence level, from ±0.72 kbar in the midrange of the calibration to ±1.33 at the upper extreme. An unweighted mean of ±1.0 kbar has been quoted in the equation above.

DISCUSSION

Comparisons of the calibrations derived from the data of this study with the results of the three previous studies are shown in Fig. 2. The curves are shown only for the pressure ranges from which the particular calibrations were derived. It can be seen that in the range in which they overlap, that is, from 6 to 8 kbars, the present calibration and that of JOHNSON and RUTHERFORD (1988, 1989) agree closely, yielding nearly identical pressures for a given

Al content, although the slopes are different. Both experimental calibrations predict a lower pressure for a given Al^T content than the empirical curves. At Al contents below the region of calibration of this study, pressures calculated from a linear extrapolation of our results are lower by 1–2 kbars than either the empirical calibrations or the JOHNSON and RUTHERFORD (1988, 1989) experiments. Hornblendes in the 2-kbar hydrothermal run showed no adjustment of rim compositions and thus cannot be used to constrain the low-pressure end of this calibration. Comparisons of the two experimental calibrations are given in Table 3.

Characterization of the synthetic rim composition is problematic, inasmuch as the rims are gradational over several tens of micrometers. The most extreme values were chosen inasmuch as these are invariably at the edge of the grain and thus in contact with the melt. If the mean compositions of the rims from the two amphiboles comprising a bracket were actually identical, but each with a dispersion of values around the mean, the choice of the most

Table 3. Comparison of barometers

Al^T/23 oxygens	This study	J and R*
1.5	1.8 kbar	2.9 kbar
2.0	4.5	5.0
2.5	7.1	7.1
3.0	9.8	9.2
3.5	12.5	11.4

* JOHNSON and RUTHERFORD (1988, 1989).

Al-rich value for the indigenous hornblende and the least Al-rich value for the introduced hornblende would result in brackets that have apparently "passed" each other. Thus, this feature of the plot as presented may not necessarily imply disequilibrium. On the other hand, the indigenous hornblende was much closer to the composition in equilibrium with the melt than was introduced hornblende, and the latter may have initially adjusted to a more Al-poor, metastable composition. Inasmuch as all experiments in the present study were of the same duration, it cannot be determined from them if the introduced hornblende would have readjusted to more aluminous compositions with time.

Consideration of the compositions of experimentally produced amphibole rim compositions shows that both Al^{IV} and Al^{VI} increase with pressure. Fitting Al^{VI} against Al^{IV} for individual analyses in Table 2 results in the equation

$$Al^{VI} = -1.74 + 1.38Al^{IV}, \quad r^2 = 0.65,$$

suggesting that some of the variability in aluminum content is accounted for by a Tschermak type substitution, $R^{2+} + Si \rightleftarrows Al^{IV} + Al^{VI}$. Fitting the rim compositions of the indigenous hornblende and its average initial composition yield

$$Al^{VI} = -1.06 + 1.03Al^{IV}, \quad r^2 = 0.79.$$

The same treatment for rim and initial compositions of the introduced hornblende yields no significant correlation, suggesting that the introduced hornblende may be adjusting its composition by a different exchange mechanism.

In conclusion, results of the present study are consistent with the calibration of JOHNSON and RUTHERFORD (1988, 1989) and extend the experimental evidence for increasing aluminum content of hornblende as a function of pressure to 12 kbar.

REFERENCES

BOETTCHER A. L., WINDOM K. E., BOHLEN S. R. and LUTH R. W. (1981) Low-friction, anhydrous, low- to high-temperature furnace assembly for piston-cylinder apparatus. *Rev. Sci. Instr.* **52**, 1903–1904.

HAMMARSTROM J. M. and ZEN E-AN (1986) Aluminum in hornblende: an empirical geobarometer. *Amer. Mineral.* **71**, 1297–1313.

HOLLISTER L. S., GRISSOM G. C., PETERS E. K., STOWELL H. H. and SISSON V. B. (1987) Confirmation of the empirical correlation of aluminum in hornblende with pressure of solidification of calc-alkaline plutons. *Amer. Mineral.* **72**, 231–239.

JACOBSON C. E. and SORENSEN S. S. (1986) Amphibole compositions and metamorphic history of the Rand Schist and the greenschist unit of the Catalina Schist, southern California. *Contrib. Mineral. Petrol.* **92**, 308–315.

JOHANNES W., BELL P. M., MAO H. K., BOETTCHER A. L., CHIPMAN D. W., HAYS J. F., NEWTON R. C. and SEIFERT F. (1971) An interlaboratory comparison of piston-cylinder pressure calibration using the albite breakdown reaction. *Contr. Mineral. Petrol.* **32**, 24–38.

JOHNSON M. C. and RUTHERFORD M. J. (1988) Experimental calibration of an aluminum-in-hornblende geobarometer applicable to calc-alkaline rocks (abstr.) *EOS* **69**, 1511.

JOHNSON M. C. and RUTHERFORD M. J. (1989) Experimental calibration of the aluminum-in-hornblende geobarometer with application to Long Valley caldera (California) volcanic rocks. *Geology,* (In press).

RUTTER M. J. and WYLLIE P. J. (1988) Experimental calibration of hornblende as a proposed empirical geobarometer (abstr.). *EOS* **69**, 87.

SORENSEN S. S. (1988) Petrology of amphibolite facies mafic and ultramafic rocks from the Catalina Schist, southern California: metasomatism and migmatization in a subduction zone metamorphic setting. *J. Metamorphic Geol.* **6**, 405–435.

YORK D. (1969) Least squares fitting of a straight line with correlated errors. *Earth Planet. Sci. Lett.* **5**, 320–324.