Geology

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Marie C. Johnson, Malcolm J. Rutherford
Department of Geological Sciences, Brown University, Providence, Rhode Island 02912

ABSTRACT

A new geobarometer based on the Al content of igneous hornblendes in equilibrium with melt, fluid, biotite, quartz, sanidine, plagioclase, sphene, and magnetite or ilmenite has been calibrated experimentally. The calibration was performed by equilibrating the required phase assemblage over the pressure range 2–8 kbar at 740–780 °C, and then analyzing euhedral hornblendes in equilibrium with glass (melt). Experiments were performed on natural samples of both volcanic and plutonic rocks. Earlier empirical calibrations of this geobarometer relied on analyzing natural hornblendes from plutons with the required phase assemblage and inferring pressure from nearby metamorphic country rocks. The experimental calibration differs from the empirical calibrations, especially above 5 kbar, and shows that the Al content of hornblendes in equilibrium with the required phase assemblage is greater for a given total pressure than previously thought. The geobarometer's uncertainty is dramatically reduced. The derived equation is P (±0.5 kbar) = 3 –3.46 (±0.24) + 4.23 (±0.13) (Al^T). The geobarometer is applied to post–Bishop Tuff volcanic rocks from Long Valley caldera, California, and reveals that most rhyodacites in this complex erupted from depths of about 6 km. These eruptions occurred over 500 000 yr, suggesting that the rhyodacitic magma reservoir beneath Long Valley had reached a steady P (depth)-T state.

INTRODUCTION

Amphibole is a common igneous mineral in hydrous calc-alkalic magmas crystallized at depth. The chemistry of a crystallizing amphibole is sensitive to such intensive parameters as pressure, temperature, oxygen fugacity, and water fugacity (e.g., Helz, 1982; Spear, 1981; Wones, 1981). In most magmas, the thermodynamic degrees of fredom are too great to allow any one intensive parameter to control uniquely an aspect of amphibole chemistry. Hammarstrom and Zen (1986) and Hollister et al. (1987), however, have shown theoretically and empirically that in some near-solidus calc-alkalic plutons the aluminum content of amphibole is controlled solely by total pressure. Their discovery promises a reliable method of estimating the pressure of phenocryst equilibration and the depth of certain silicic metaluminous magmas. Because total pressure is one of the most difficult magmatic parameters to assess and few geobarometers exist that can be applied to igneous rocks, this discovery is especially significant.

Hammarstrom and Zen (1986) examined five calc-alkalic plutons that contained the common mineral assemblage horblende + biotite + plagioclase (An_{30}) + quartz + sanidine + sphene + ilmenite or magnetite $\pm$ epidote. Two of the plutons studied, the Mount Princeton and Pioneer batholiths, are believed to represent shallow-level intrusions. The other three plutons, Round Valley, Moth Bay, and Ecstall, are in the Mesozoic accreted terranes of the western Cordillera and contain igneous epidote. Citing experimental work concerning epidote stability (Naney, 1983), Hammarstrom and Zen (1986) argued that these plutons equilibrated at pressures of at least 8 kbar. Using these arguments and supporting evidence from nearby metamorphic assemblages, they divided the five plutons into a low-pressure and a high-pressure group. Hornblende rims in these plutons were analyzed, and aluminum content was observed to correlate linearly with estimated equilibration pressure.

$$P\,(\pm3\text{ kbar}) = -3.92 + 5.03\,(Al^T);$$
$$r^2 = 0.80. \qquad (1)$$

In this equation, P (pressure) is in kilobars, and Al^T is the total aluminum content ($Al^{IV} + Al^{VI}$) of hornblende based on a 23-oxygen structural formula.

Hollister et al. (1987) refined this calibration by analyzing hornblendes from additional plutons that had equilibrated in the 4–6 kbar range. These pressures were estimated primarily from the plagioclase-garnet-Al_2SiO_5-quartz equilibrium (Ghent, 1976) in adjacent metamorphic country rocks. An equation very similar to equation 1 was calculated from this more extensive data set, and the correlation coefficient was significantly improved, decreasing the uncertainty:

$$P\,(\pm1\text{ kbar}) = -4.76 + 5.64\,(Al^T);$$
$$r^2 = 0.97. \qquad (2)$$

Although the r^2 reported by Hollister et al. (1987) is good, it reflects only the scatter about the regressed line (the precision of the data). It does not reflect the accuracy of each individual data point. The plagioclase-garnet-Al_2SiO_5-quartz equilibrium was recently reevaluated and was shown to have a ±2.5 kbar uncertainty (McKenna and Hodges, 1988). Equations 1 and 2 relied on indirect estimates of total pressure; to make the aluminum-in-hornblende geobarometer as accurate as possible, experimental confirmation and calibration, where pressure is known directly, are needed.

We report here a series of experiments designed to test and calibrate the proposed geobarometer in the pressure range 2–8 kbar. Most experiments were performed on a glassy (40% phenocrysts) sample of the Fish Canyon Tuff, San Juan Mountains, Colorado. A few additional experiments were performed on a Round Valley pluton, Idaho, sample and a Long Valley, California, moat rhyolite sample. All phases required by the geobarometer are stable in the first two samples; sphene is absent or rare in the Long Valley sample. The new experimental data confirm the linear relation between aluminum in hornblende and total pressure, but yield a different equation for the regressed line.

As an example of the geobarometer's utility, the new calibration is applied to hornblendes in the post–Bishop Tuff volcanic rocks in Long Valley caldera, California. Several eruptions in this area, spanning 500 000 yr, contain the assemblage required for geobarometry. This fortuity allows a unique opportunity to trace the history of a magma system through time.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES
Experimental Techniques

Natural samples of two volcanic rocks (Fish Canyon Tuff, Long Valley moat rhyolite) and one plutonic (Round Valley) rock were chosen for experiments (Table 1). Hornblende rims in equilibrium with matrix glass in the Fish Canyon Tuff and Long Valley samples have low Al_2O_3 content (7 to 8 wt%), whereas hornblendes in the Round Valley sample have high Al_2O_3 content (13 wt%; Hammarstrom and Zen, 1986). All rocks were crushed and ground to a fine, homogeneous powder.

Experiments were performed between 2 and 8 kbar at temperatures of 720–780 °C and H_2O/CO_2 fluid ratios between 50/50 and

25/75. Oxygen fugacity was buffered in all experiments by either $MnO-Mn_3O_4$ (MNO), Ni-NiO (NNO), or andradite-magnetite-quartz-hedenbergite (AMQH) in crimped tubes adjacent to the sample. AMQH is an oxygen buffer about two log units above the NNO buffer at 750 °C (Liou, 1974; Gustafson, 1974). All experiments were water-undersaturated but contained an excess volatile phase. Water in the vapor phase was diluted by CO_2 added as $Ag_2C_2O_4$ held in a separate open tube. High-pressure ($\geqslant 5$ kbar) experiments were run in an internally heated pressure vessel. Low-temperature (<760 °C) experiments up to 5 kbar were run in Rene-41 cold seal vessels. All run temperatures are accurate to ±5°; pressures to ±20 bar. Experiments in the internally heated vessel were pressurized with Ar and in the Rene vessels with water.

Most experiments were performed as melting experiments; unfused starting material was brought directly to run temperature. A few crystallization experiments were performed in which the charge was first held at high temperature for 8–12 h and then slowly cooled ($10°-2°/h$) to final temperature. Products of high-pressure experiments were rerun at lower pressures in order to reverse the approach to equilibrium. Charges were held for 48–100 h at final temperature and then isobarically quenched. Chips of the quenched charge were mounted and made into polished thin sections that were examined in transmitted and reflected light prior to analysis.

Analytical Techniques

Polished thin sections were analyzed by using a fully automated Cameca Camebax (Tm) electron microprobe. Experimental glass analyses were obtained by using a 15 kV accelerating voltage and a 10 nA beam current. The beam size was set to 10 μm. In order to limit Na loss, Na peak counts were collected in five sequential 2 s intervals, and then the zero-time intercept was obtained by extrapolation from a linear regression of peak counts vs. time. Natural glasses were used as standards for major elements.

TABLE 1. STARTING BULK COMPOSITIONS

	Fish Canyon Tuff	LV 12	Round Valley pluton*
SiO_2	64.40	75.46	65.20
TiO_2	0.60	0.10	0.41
Al_2O_3	16.98	13.17	18.60
FeO	4.26†	0.94†	2.80
Fe_2O_3	–	–	0.52
MgO	1.11	0.14	1.10
CaO	3.62	1.44	5.50
Na_2O	4.04	3.50	5.00
K_2O	4.06	5.18	0.96
MnO	0.11	0.08	0.08
P_2O_5	n.d.	n.d.	0.17
Total	99.18	100.00	100.34

Note: n.d. = not determined.
* from Hammarstrom and Zen (1986).
† All iron as FeO.

TABLE 2. EXPERIMENTAL HORNBLENDES FOR Al-IN-HORNBLENDE GEOBAROMETER

Run:	68	78c	107	74	109	115	106	15a	17	129	120	119
P (kbar):	2	2	2	2	2.5	3	5	5	5	6.5	6.5	8.2
SiO_2	46.51	46.88	47.19	45.95	45.42	46.64	42.89	43.52	44.76	41.96	39.75	39.93
TiO_2	1.32	1.24	1.33	1.42	1.43	1.46	1.54	1.53	1.10	1.22	1.21	1.20
Al_2O_3	7.37	7.38	7.54	7.52	8.50	8.76	11.23	11.33	11.77	13.00	13.46	15.27
FeO†	11.88	12.31	13.44	12.69	15.09	14.39	16.05	10.50	4.69	17.91	20.45	19.79
Fe_2O_3†	2.80	1.76	1.02	1.50	1.22	1.13	2.12	1.26	2.87	2.08	1.86	0.36
MgO	14.54	14.24	14.27	13.95	12.49	13.54	10.56	14.85	17.86	8.81	6.16	7.11
CaO	11.64	11.56	11.46	11.68	11.30	11.50	11.60	11.21	11.29	11.59	11.59	11.25
Na_2O	1.56	1.29	1.56	1.57	1.47	1.53	1.64	2.08	1.83	1.52	1.39	1.53
K_2O	0.79	0.82	0.81	0.94	1.07	1.05	1.36	1.06	0.65	1.57	1.75	1.87
MnO	0.70	0.74	0.68	0.68	0.72	0.67	0.74	0.37	0.41	0.68	0.49	0.48
Total	99.10	98.22	99.30	97.90	98.71	100.67	99.73	97.71	97.23	100.34	98.11	98.78
Mg*	68.6	67.3	65.4	66.2	59.6	62.6	54.0	71.6	87.2	46.7	34.9	39.0
Cations per 23 oxygens												
Si	6.820	6.898	6.875	6.815	6.739	6.743	6.396	6.406	6.461	6.271	6.173	6.074
Al^{IV}	1.180	1.102	1.125	1.185	1.261	1.257	1.604	1.594	1.539	1.729	1.827	1.926
Ti	0.146	0.137	0.146	0.158	0.160	0.159	0.173	0.169	0.119	0.137	0.141	0.137
Al^{VI}	0.094	0.178	0.169	0.129	0.226	0.236	0.369	0.371	0.463	0.561	0.636	0.811
Fe^{2+}	1.769	1.712	1.751	1.742	2.011	1.864	2.242	1.434	0.882	2.474	2.875	2.558
Mg	3.178	3.123	3.099	3.084	2.762	2.918	2.347	3.258	3.843	1.963	1.426	1.612
Mn	0.087	0.092	0.084	0.085	0.090	0.082	0.093	0.046	0.050	0.086	0.064	0.062
Ca	1.829	1.822	1.789	1.856	1.796	1.781	1.853	1.768	1.746	1.856	1.928	1.833
Na	0.444	0.368	0.441	0.451	0.423	0.429	0.474	0.594	0.512	0.440	0.419	0.451
K	0.148	0.154	0.151	0.178	0.203	0.194	0.259	0.199	0.120	0.299	0.347	0.363

† Ferrous and ferric iron calculated on the basis of 15 cations.

Major-element mineral analyses were obtained by using a 15 kV accelerating voltage, 15 nA beam current, and a focused beam. Mineral standards were used in the calibration procedure.

Only analyses of euhedral hornblende rims in contact with melt were used to calibrate the geobarometer. Structural formulas for all hornblendes were calculated on the basis of 23 oxygens (modified after Helz, 1979) and 15 cations (after Robinson et al., 1982). The 23-oxygen formula assumes that all iron is ferrous, whereas the 15-cation formula calculates ferrous and ferric iron by charge balance.

RESULTS

The objective of this study was to equilibrate the phase assemblage melt + fluid + quartz + sanidine + plagioclase (An$_{30}$) + hornblende + biotite + sphene + ilmenite or magnetite required for geobarometry over a 2–8 kbar pressure range. Experiments were considered successful if all the required phases were present and euhedral hornblendes were clearly in contact with melt. Melt must be present to reduce the thermodynamic degrees of freedom sufficiently to allow total pressure to control Al in coexisting hornblendes (Hammarstrom and Zen, 1986). More practically, melt is needed to allow diffusion-controlled hornblende recrystallizaton to occur on the time scale of laboratory experiments. Quartz and sanidine were the most difficult minerals to nucleate in crystallization experiments and the first minerals to disappear in melting experiments. A few low-pressure experiments in which quartz and/or sanidine could not be identified in the run products were still considered successful because the coexisting melt contained >75 wt% SiO_2 and >5 wt% K_2O

(anhydrous). These melts are considered to be close to quartz and sanidine saturation based on comparison with quartz- and sanidine-saturated melt compositions.

The percentage of melt was controlled carefully in each experiment in order to crystallize the required assemblage and to have sufficient melt present to attain equilibrium. With changes in total pressure, only small adjustments in temperature and H_2O/CO_2 fluid ratio were required to control the percentage of melt within these limits. For example, all experiments on the Fish Canyon Tuff sample were run between 740 and 780 °C and H_2O/CO_2 fluid ratios of 50/50 or less. The essentially isothermal conditions over a pressure range of 2 to 8 kbar reflect the nearly vertical P-T phase boundaries (Hollister et al., 1987).

Hornblende rims were analyzed in 12 successful experiments, and their compositions were recalculated on the basis of 23 oxygens (Table 2). The total aluminum content of these hornblendes varies linearly with total pressure (Fig. 1). Experimental reversals were obtained at most pressures; i.e., conditions were investigated in which the final Al content was both greater and less than the starting Al content, as indicated by the arrows in Figure 1. The experimental data define a trend that depends more strongly on total pressure than does the previous calibration (Hollister et al., 1987; Fig. 1). A linear regression of the experimental data points yields

$$P = -3.46 \ (\pm 0.24) + 4.23 \ (\pm 0.13) \ (Al^T);$$
$$r^2 = 0.99 \tag{3}$$

The standard deviation for the entire data set is 0.22 kbar. Although Hollister et al. (1987) re-

Figure 1. Total Al in experimental hornblendes in equilibrium with melt, fluid, quartz, sanidine, plagioclase, biotite, sphene, and magnetite or ilmenite plotted as function of total pressure. Total aluminum was calculated assuming 23-oxygen structural formula. Arrowheads indicate direction of approach to equilibrium; different types of arrows indicate different oxygen buffers. Line through data points represents linear regression of data. Dashed lines are 95% confidence intervals. Line labeled "Hollister et al." (1987) is empirical calibration reported by them.

Figure 2. Al^{IV} and Al^{VI}, calculated assuming 23-oxygen structural formula, in experimental hornblendes plotted as function of total pressure. Lines through data sets are based on linear regressions of data.
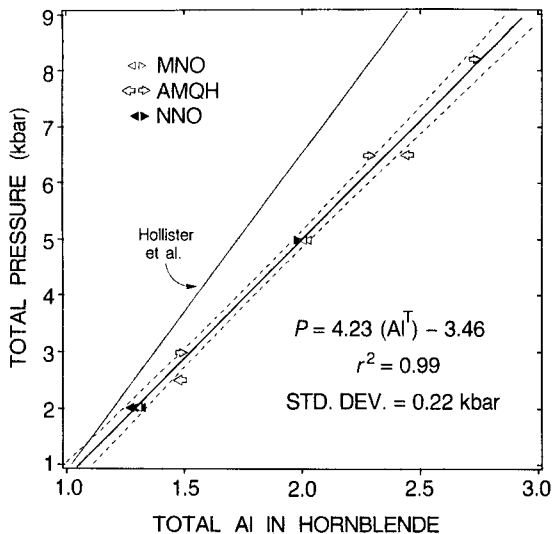
ported a similar r^2, equation 3 marks a significant improvement. Unlike the earlier works, the experimental calibration does not rely on indirectly estimating total pressure. Total pressure was controlled and is accurately known in each experiment. Hence, the uncertainty of each individual data point is greatly reduced. The uncertainty associated with applying this calibration to a given rock depends on the specific Al^T content of the hornblendes as indicated by the 95% confidence limits (dashed lines in Fig. 1). The maximum error is ±0.6 kbar at 8 kbar and slightly less (±0.5 kbar) at lower pressures.

The data were regressed in terms of the 23-oxygen hornblende formula to facilitate comparison with the previous calibrations. At the oxygen fugacities investigated in this study, 10%–20% of the iron in a hornblende may be ferric (Clowe et al., 1988); the 23-oxygen formula assumes all iron is ferrous. However, the calculated total aluminum content in each hornblende is independent of the ferric/ferrous ratio. A change in the ferric/ferrous ratio slightly affects how Al is partitioned between Al^{IV} and Al^{VI} in the structural formula but does not affect Al^T. In fact, regressing the experimental data by using the 15-cation structural formula that calculates ferric/ferrous ratios by charge balance also yields equation 3.

Nonlinear descriptions of the data in Figure 1 were briefly considered. None of these possibilities resulted in improved correlation coefficients or reduced standard error of estimates. The linear fit is preferred because it has the highest r_2, is the most simple to apply, and is the fit chosen previously (Hammarstrom and Zen, 1986; Hollister et al., 1987).

A few experiments failed to stabilize the required phase assemblage. Most commonly, these experiments lacked quartz and had low-SiO_2 coexisting glasses. The lack of quartz and the low-silica glasses resulted from too much melting, or not enough crystallization; the percentage

of melt needed to be reduced by decreasing either the temperature or the H_2O/CO_2 fluid ratio. In every case, hornblendes that were in equilibrium with all the required phases except quartz had higher aluminum contents than hornblendes equilibrated at the same pressure with all the required phases including quartz. Hence, the validity of the geobarometer critically depends upon hornblende being in equilibrium with quartz. If quartz is not present, the activity of SiO_2 is less than maximum, and the aluminum content of coexisting hornblende is a function of both pressure and melt SiO_2 activity (see also Hollister et al., 1987). In that the coexisting melt is dominated by SiO_2 and Al_2O_3, a decrease in melt SiO_2 activity is likely to be accompanied by an increase in melt Al_2O_3 activity; increasing Al_2O_3 activity will be mirrored by an increase in the Al content of coexisting hornblendes. Therefore, hornblendes not in equilibrium with quartz will yield anomalously high pressures if equation 3 is applied. For example, in a 5 kbar experiment in which all required phases crystallized except quartz, hornblende rims average 13.03 wt% Al_2O_3 or 2.29 Al^T. Equation 3 would imply a pressure of 6.2 kbar, a 1.2 kbar overestimate.

In the experimental hornblendes, TiO_2, CaO, Na_2O, K_2O, and MnO do not vary systematically with increasing pressure, whereas both Al^{IV} and Al^{VI} increase linearly (Table 2; Fig. 2). The increasing Al^{IV} and Al^{VI} content implies that a Tschermak-type substitution (Mg + Si $\rightleftharpoons$ Al^{VI} + Al^{IV}) is controlling the pressure-sensitive component of the hornblende. If a Tschermak substitution is the primary change occurring with increasing pressure, then the total change from 2 to 8 kbar in Al^{VI} should equal the total change in Al^{IV}. This change is about 0.8 atoms in both cases (Fig. 2), confirming the importance of the Tschermak substitution.

The experimental hornblendes have widely varying MgO, FeO, and Fe_2O_3 contents, reflect-
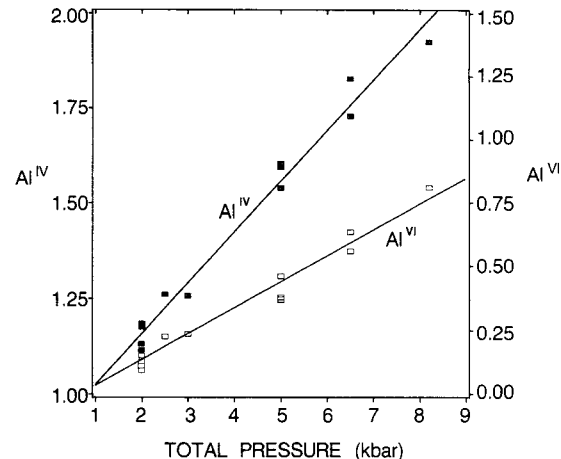
ing variations in oxygen fugacity (Table 2). At f_{O_2} values equal to or lower than NNO, it has been suggested that sphene may be unstable (Czamanske and Wones, 1973). However, sphene was present in all NNO runs used in this calibration; it tended to be an anhedral phase in these runs and was probably undergoing resorption.

DISCUSSION
Geobarometer

The experimental calibration of the Al-in-hornblende geobarometer differs significantly from previous empirical calibrations, especially in the 5–8 kbar region; hornblendes equilibrated at 5–8 kbar with the stipulated mineral assemblage contain much more aluminum than predicted by Hollister et al. (1987; Fig. 1). This new calibration indicates that the high-pressure plutons studied previously (Hammarstrom and Zen, 1986; Hollister et al., 1987) must have equilibrated at shallower depths than estimated from field evidence.

The presence of stable, igneous epidote in the three high-pressure plutons is cited as the most convincing evidence of magmatic equilibration at a minimum of 8 kbar total pressure (Hammarstrom and Zen, 1986). This reasoning is based on an experimental study of granitic systems in which epidote was reported to be in equilibrium with melt at 8 kbar but not at 2 kbar. Pressures intermediate to 2 and 8 kbar were not investigated, and so the minimum pressure required for igneous epidote stability is unknown. Zen and Hammarstrom (1988) argued that igneous epidote implies pressures of at least 6 rather than 8 kbar. If the high-pressure epidote-bearing plutons studied by Hammarstrom and Zen (1986) and Hollister et al. (1987) equilibrated at 6 kbar, instead of the estimated 8 kbar, the empirical line would rotate to a slope much closer to the experimental line. Reported hornblende analyses (Hammarstrom and Zen,

1986) and the new experimental calibration indicate that the Round Valley pluton equilibrated at 7.3–7.5 kbar and the Ecstall pluton at 5.6–6.1 kbar. In contrast, the pressures estimated by using the empirical calibration (equation 2) are 9.7–10.0 kbar (Round Valley) and 7.5–8.1 kbar (Ecstall).

The pressure of igneous epidote in the natural high-pressure plutons and its absence in the experimental high-pressure runs cannot account for the discrepancy in hornblende Al content. The geobarometer works because the phase assemblage melt, fluid, quartz, sanidine, plagioclase, biotite, sphene, and ilmenite or magnetite buffers the Al content of coexisting hornblendes. By the phase rule, there are ten major oxide components and nine phases; the system is invariant at specified values of P, T, and f_{O_2} (Hammarstrom and Zen, 1986; Hollister et al., 1987). As long as the nine required phases are in equilibrium, the Al content of hornblende is fixed and it cannot be affected by the presence of any other phase, such as epidote.

One 10 kbar experiment with the phase assemblage required for geobarometry is reported from an experimental garnet tonalite study (Rutter and Wyllie, 1988). Electron-microprobe analysis of a hornblende rim from this experiment reveals an Al^T content of 2.60. This data point plots on the line calculated by Hollister et al. (1987), but the hornblende contains much less Al than would be predicted for 10 kbar by the new experimental calibration. Garnet is reported to be stable in this experiment. However, the presence of garnet, given that the hornblende is in equilibrium with all the required phases, cannot affect the Al content of the coexisting hornblendes. The significance of this data point is unknown because the experiment was not reversed. The hornblendes may not have reached equilibrium; they may have been approaching an Al content greater than 2.60.

Application to Long Valley Caldera Volcanic Rocks

The power of this Al-in-hornblende geobarometer is that it can be applied to appropriate plutonic or volcanic rocks to deduce the pressure of equilibration. For plutonic rocks, this pressure corresponds to intrusion depth. For porphyritic volcanic rocks, this pressure corresponds to the depth of the magma reservoir where phenocrysts and melt last equilibrated. For example, applying this geobarometer to the Fish Canyon Tuff indicates that the assemblage equilibrated in a magma chamber 8 km deep just prior to eruption (Johnson and Rutherford, 1989). The moat rhyolite and associated volcanic rocks in Long Valley caldera, California, are another example to which this geobarometer may be applied.

Long Valley caldera (17 by 32 km) was formed by catastrophic eruption of the Bishop Tuff at 0.7 Ma. Aphyric rhyolite was subse-

quently erupted (0.68–0.64 Ma) in the middle of the caldera floor accompanying and adding to a resurgent dome (Fig. 3). Resurgent doming was followed by crystal-rich rhyolite eruptions in the moat between the resurgent dome and the caldera walls. These crystal-rich units are collectively termed "moat rhyolite" (Bailey et al., 1976). They erupted in three successive pulses, each separated by 0.2 m.y., starting north of the dome at 0.5 Ma and progressing clockwise around the dome (Bailey et al., 1976). More recently, rhyodacites were erupted along the southwest caldera wall forming part of the Mono-Inyo Craters lineament. The most recent eruptions in this region occurred 600 yr ago and formed the flows and domes of the Inyo volcanic chain. Two independent magma systems were tapped during the Inyo chain eruptions, producing two distinct lava types designated coarsely porphyritic and finely porphyritic (Sampson and Cameron, 1987). Today, there continues to be geophysical evidence of an active magma chamber beneath parts of Long Valley caldera (i.e., Hill et al., 1985).

Few quantitative total pressure estimates exist for any Long Valley volcanic units. An exception is the recent estimate for the Bishop Tuff magma based on dissolved H_2O and CO_2 contents in quartz melt inclusions. The magma is inferred to have equilibrated at pressures as low as 1.6 kbar (Anderson et al., 1989). Unfortunately, the Bishop Tuff lacks amphibole, so the hornblende geobarometer cannot be applied. However, several post–Bishop Tuff units, including all the moat rhyolite eruptions and the coarsely porphyritic unit of the Inyo chain, contain abundant euhedral amphibole and all other phases required for geobarometry except sphene.

The lack of sphene in these samples is likely to have a negligible effect on pressure estimates; the Long Valley hornblendes have TiO_2 content (~1.3 wt%) identical to the TiO_2 content of the hornblendes used in the experimental calibration. In several samples, two Fe-Ti oxides are stable instead of one Fe-Ti oxide and sphene. At a given temperature, the presence of two oxides buffers the TiO_2 content of the melt and coexisting hornblendes.

In essence, the phase assemblage required for geobarometry is stable in different Long Valley rhyodacites over almost 0.5 Ma, providing a unique opportunity to trace magma reservoir depths through time. To investigate these reservoir depths, samples were collected from each of the moat rhyolite eruption centers (Fig. 3). In addition, samples were obtained from Deer Mountain (a dome closely associated with the youngest moat rhyolite) and the coarsely porphyritic unit of the Glass Mountain flow, samples 16 and 17 in Figure 3. Thin sections were prepared and examined, and hornblende rims in equilibrium with matrix glass were analyzed by electron microprobe (Table 3).

The hornblendes in each thin section are euhedral and homogeneous in composition. The total range in Al_2O_3 for all six samples studied is 6.5–7.5 wt% (Table 3). Applying the Al-in-hornblende geobarometer to these data indicates that the moat rhyolite, Deer Mountain, and Glass Mountain samples erupted from very shallow (4–6 km) magma reservoirs (Table 3). Each pressure estimate has a 0.5 kbar calculated uncertainty based on the uncertainty associated with each given Al^T. However, the relative uncertainty for different samples is much smaller than 0.5 kbar because all the samples have the
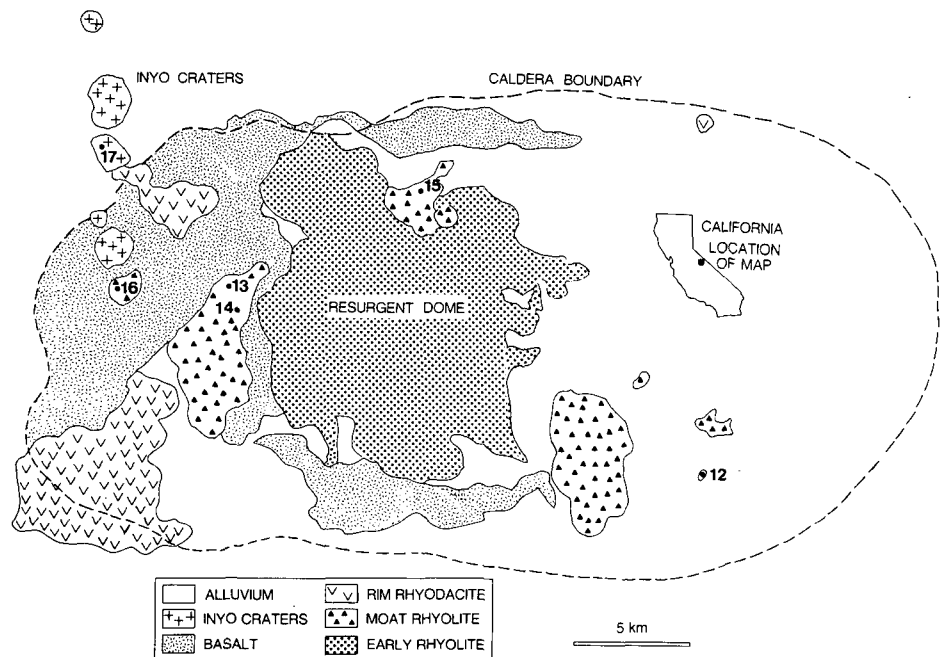

Figure 3. Generalized geologic map of Long Valley caldera (adapted from Sorey et al., 1978). Dots and numbers indicate sample locations referred to in text.

TABLE 3. LONG VALLEY VOLCANIC ROCKS

Sample no.†	Age (Ma)	Mg*†	Al₂O₃ wt%	Al T ‡	P ±0.5 (kbar)
15	0.5	50.58	6.53 ±0.25	1.162 ±0.048	1.5
12	0.3	56.44	6.36 ±0.23	1.115 ±0.047	1.3
13	0.1	42.71	7.31 ±0.35	1.304 ±0.073	2.1
14	0.1	42.73	7.16 ±0.30	1.298 ±0.056	2.0
16	0.1	51.79	7.35 ±0.20	1.289 ±0.034	2.0
17	600y	56.76	7.46 ±0.46	1.301 ±0.082	2.0

† All samples contain the required phase assemblage ± cpx, opx, zircon, and a second Fe–Ti oxide. Quartz is embayed in most samples. 15–Light brown, dense matrix with crystallites and some flow banding; clots of crystals, sperulitic glass; 10% phenocrysts. 12–Vesicular, flow-banded matrix; green hornblendes; 10% phenocrysts. 13–Vesicular, glassy matrix; dark brown hornblendes; several large, wormy, embayed plagioclase crystals; 15%–20% phenocrysts. 14–Glassy, colorless matrix; feldspar crystal clots; dark brown hornblendes; 20% phenocrysts. 16–Vesicular, flow–banded glassy matrix; crystal clots; several large, wormy, embayed plagioclases; plagioclase commonly has hornblende and biotite inclusions; exsolved Fe–Ti oxides; 15% phenocrysts. 17–Vesicular glassy matrix; crystal clots of plagioclase, hornblende, biotite; 15%–20% phenocrysts.

† Mg* = [Mg/Mg + Fe²⁺].

‡ Based on 23–oxygen structural formula.

same mineral assemblage and similar hornblende chemistries except for Al^T; the difference between 1.5 and 2.0 kbar (5 and 6 km) is real and significant. Samples 13 and 14 were collected from the same eruption center at sites 1 km apart. The analyzed hornblendes have very similar Mg* values (Mg* = Mg/Mg + Fe²⁺), total aluminum content, and estimated equilibration pressures. This similarity implies that the magma reservoir was homogeneous and/or well mixed just prior to eruption. It is possible, however, that magma from a range of depths could be present in different parts of a flow and could be identified by Al in hornblende.

The estimated shallow depths are similar to the depths calculated for the Bishop Tuff magma (Anderson et al., 1989). They also agree with geophysical evidence suggesting that a magma chamber, as shallow as 4–5 km in some areas, may be currently active beneath Long Valley (Hill et al., 1985). In addition the arcuate pattern of the moat rhyolite eruptions suggests that they erupted from shallow depth (Bacon, 1985). The similarity of total pressures over a 0.5 Ma span is remarkable (Table 3). It implies that the magmas beneath Long Valley rose to the same depth before each eruption cycle. The magma reservoirs appear to have reached a steady state.

The 1.5 and 1.3 kbar pressures inferred for the two oldest moat rhyolite eruptions are surprisingly low. In general, igneous hornblende is unstable below about 1.5 kbar because a minimum melt H₂O content is required to stabilize hornblende (Merzbacher and Eggler, 1984) and the rhyolite solidus (water-saturated) increases rapidly with decreasing pressure below 1.5 kbar. Further, as noted by Hollister et al. (1987), the

Al content of hornblende may become temperature as well as pressure sensitive below 2 kbar. To test whether hornblende was a liquidus phase at 1.5 kbar, an experiment on a powdered sample of LV 12 was run at 720 °C. Hornblende (6.5 wt% Al₂O₃) was found to coexist with melt and the other phases required for geobarometry. For this set of conditions, the Al content of the hornblendes seemed to be unaffected by the slight decrease in temperature.

The low pressures indicated by the Al-in-hornblende geobarometer for the oldest Long Valley rhyolites also strongly constrain the water fugacity in these magmas. To stabilize igneous amphibole in dacitic magmas, at least 5 wt% water in the coexisting melt is needed (Merzbacher and Eggler, 1984; Rutherford and Devine, 1988). If this is applied to rhyodacitic magmas, the presence of stable, euhedral hornblendes lacking oxide break-down rims in the Long Valley rhyolites requires at least 5 wt% water dissolved in the coexisting melt. The 1.5 and 1.3 kbar pressures imply that the coexisting melt must have been nearly water saturated to dissolve the required 5 wt% water.

In conclusion, the potential of the Al-in-hornblende geobarometer has been confirmed experimentally, and a relation between total pressure and Al^T based on experimental data has been derived. The importance of the geobarometer has been demonstrated by appying the geobarometer to the Long Valley magma system.

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