The effects of temperature and f_{O_2} on the Al-in-hornblende barometer

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Abstract

The Al-in-hornblende barometer potentially offers a basis for estimating crystallization pressure for granitic batholiths. However, owing to the simplicity of its formulation, misuse of the barometer can occur. Many granitic intrusions are emplaced at conditions inconsistent with those of the existing experimental calibrations, including $f_{O_2} <$ NNO and/or variable to high temperature. The barometer is sensitive to variations in both f_{O_2} and temperature: low f_{O_2} can cause calculated pressures to be high by a factor of two or more, and the effect of temperature is up to 2 kbar per 100 °C, depending on total Al abundance.

Batholiths emplaced at elevated temperature and portions of plutons that crystallized below H_2O saturation yield artificially high pressures relative to near-solidus experiments conducted at H_2O saturation. Al-in-hornblende pressures within the tonalitic Mount Stuart batholith of Washington, for example, define a 1–4 kbar domal structure that is exaggerated by emplacement crystallization temperatures that range from 620 to 760 °C. Pressure correlates with temperature ($r^2 = 0.86$), indicating that temperature-sensitive edenite exchange has greatly influenced observed pressure variations. Data for other plutons also exhibit a marked positive correlation between temperature and hornblende pressure. If corrections are not made for temperature, such large apparent pressure variations can lead to overly high estimates of pluton thickness and tilt in addition to invalid tectonic interpretations.

Using experimental data at ~675 °C (Schmidt, 1992) and at ~760 °C (Johnson and Rutherford, 1989), a revised expression for the barometer incorporating the effect of temperature is $P (\pm 0.6 \text{ kbar}) = 4.76\text{Al} - 3.01 - \{[T (°C) - 675]/85\} \times \{0.530\text{Al} + 0.005294[T (°C) - 675]\}$. For a pluton emplaced at 100 °C above wet-solidus temperatures, this reformulation of the barometer lowers derived pressures by 1.3 to >2 kbar at typical crustal pressures. For the Mount Stuart batholith, consideration of temperature yields revised pressures that are in agreement with pressures obtained from wall rocks and eliminates much of the apparent domal structure.

Low-f_{O_2} granites have amphibole Fe/(Fe + Mg) ratios that exceed the typical 0.40–0.65 range used in most experimental and empirical calibrations. Examples from anorogenic granitic batholiths of mid-Proterozoic age yield pressures that are too high by a factor of two to three in comparison with pressures obtained from adjacent metamorphic assemblages. Hornblende in these granites not only has high Fe/(Fe + Mg) but also low ratios of Fe^{3+} to Fe^{2+}. The anomalously high Al in Fe-rich, Fe^{3+}-poor hornblende is inferred to be the result of increased [6]Al occupancy of the M2 site not buffered by the Mg and Fe^{3+} abundances typical of amphiboles in calc-alkaline and other high-f_{O_2} plutonic rocks.

Introduction

The initial empirical formulation of the Al-in-hornblende barometer (Hammarstrom and Zen, 1986; Hollister et al., 1987) was based on pressures determined in adjacent aureole rocks. The barometer has subsequently been experimentally calibrated for the assemblage quartz + alkali feldspar + plagioclase + hornblende + biotite + iron titanium oxide + titanite + melt + fluid (Johnson and Rutherford, 1989; Thomas and Ernst, 1990; Schmidt, 1992). All calibrations are summarized in Figure 1. The empirical calibrations (Hammarstrom and Zen, 1986; Hollister et al., 1987) and the experimental calibration conducted at near H_2O-saturated solidus temperatures (Schmidt, 1992) are similar, whereas the experimental calibrations conducted at elevated temperatures (Johnson and Rutherford, 1989; Thomas and Ernst, 1990) record higher Al_{tot} in hornblende at the same pressure largely because of increased [4]Al. The Schmidt (1992) calibration was determined over a temperature range of 655–700 °C at 2.5–13 kbar. The two high-temperature calibrations employed different approaches. The Johnson and Ruth-
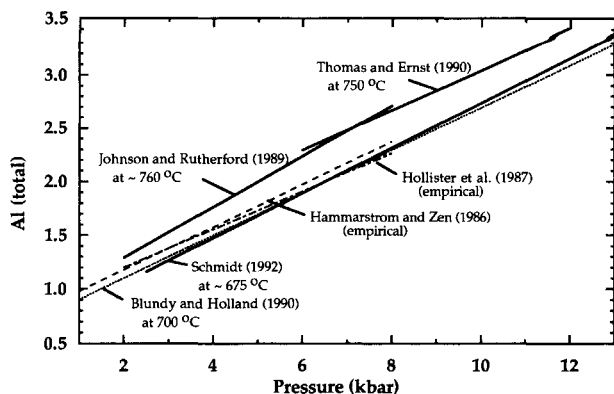
Fig. 1. Summary of empirical and experimental calibrations of the Al-in-hornblende barometer.

erford (1989) experiments used variable CO_2-H_2O fluids to achieve 2–8 kbar, near-solidus conditions over a temperature range of 720–780 °C, whereas Thomas and Ernst (1990) used a pure H_2O fluid at 6–12 kbar with a constant hypersolidus temperature of 750 °C. As shown in Figure 1, the two latter calibrations are similar at 6–8 kbar.

Both widely used and criticized (see Blundy and Holland, 1990, and comments by Poli and Schmidt, 1992; Hammarstrom and Zen, 1992; Rutherford and Johnson, 1992), the Al-in-hornblende barometer often provides the only means of constraining the emplacement depth of granitic plutons. Present formulations utilize the Al content of hornblende alone because the controlling reaction, one that buffers the tschermakite component, is uncertain. One such reaction is the pressure-sensitive H_2O-conservative reaction involving the formation of the Tschermak (Tsch) component, $Ca_2(Mg,Fe)_3^{[6]}Al_2Si_6^{[4]}Al_2$-$O_{22}(OH)_2$. First suggested by Hollister et al. (1987), this reaction is: 2 quartz + 2 anorthite + biotite = orthoclase + Tschermak, which causes amphibole to change in composition by the exchange vector $Si + R^{2+} = {}^{[4]}Al + {}^{[6]}Al$. This reaction has never been experimentally calibrated. Other reactions also affect Al in hornblende, such as the temperature-sensitive, edenite-forming reaction albite + tremolite = 4 quartz + edenite, which utilizes the exchange mechanism $Si + {}^{[A]}\square = {}^{[4]}Al + {}^{[A]}(K + Na)$. Additional important variables include temperature-sensitive substitutions involving Ti, such as $Ti + R^{2+} = 2^{[6]}Al$ and $Ti + {}^{[4]}Al = {}^{[6]}Al + Si$, and f_{O_2}-controlled Fe^{2+}-Fe^{3+} variations allowing operation of the exchange vector $Fe^{3+} = {}^{[6]}Al$.

It has been common practice to apply the barometer to restricted assemblages and plagioclase compositions ($\sim An_{25-35}$). From consideration of the above tschermakite-forming reaction, it is apparent that high plagioclase anorthite content (outside the range of An = 25–35) or low potassium feldspar orthoclase activities can increase total Al in hornblende independent of pressure. Likewise, temperature can greatly increase $^{[4]}Al$ in hornblende at constant pressure by operation of the edenite-forming ex-

change mechanism (Spear, 1981; Blundy and Holland, 1990). In contrast, an increase in Ti can lead to a decrease in total Al by lowering the $^{[6]}Al$ by the first Ti-substitution mechanism noted above. Many arc-related plutons crystallize at elevated f_{O_2} (magnetite series of Ishihara, 1977), whereas anorogenic plutons are often emplaced at low f_{O_2} (Anderson, 1983). Low f_{O_2} decreases the Mg/Fe and Fe^{3+}/Fe^{2+} ratios in hornblende (Czamanske et al., 1981) and, as shown below, increases Al substitution. The ±1 kbar precision of the Hollister et al. (1987) calibration and the high precision of the experimental calibrations (Johnson and Rutherford, 1989; Thomas and Ernst, 1990; Schmidt, 1992) encourage the expectation of successful application. However, the assumption that many or most granitic plutons were emplaced on or near a H_2O-saturated solidus may be unjustified. Likewise, f_{O_2} is often not determined. Our goal is to evaluate where the barometer, in its present form, fails to yield accurate pressures and to determine whether the failure is due to an incomplete buffering assemblage, elevated temperature, or low f_{O_2}.

In all cases, we have normalized amphibole compositions to 13 cations and calculated Fe^{2+} and Fe^{3+} by charge balance. Cosca et al. (1991) demonstrated that only the 13-cation procedure (and not normalizations involving 15 cations or 23 O atoms) closely predicts site occupancies for amphiboles in which FeO and Fe_2O_3 were determined by titration. It also offers a reasonable estimation of Fe^{2+} and Fe^{3+}. The chosen normalization scheme does not significantly affect calculated Al_{tot} or pressure but it does affect calculated $^{[4]}Al$ and $^{[6]}Al$, and this can change calculated temperatures. For the Blundy and Holland (1990) plagioclase + hornblende thermometer used in this study, the effect, however, is minor (~15 °C).

EFFECT OF TEMPERATURE ON Al-IN-HORNBLENDE BAROMETRY

Recent use of the hornblende barometer to determine pressure has been widespread, including the studies of Vyhnal et al. (1991), Ghent et al. (1991), and Anderson et al. (1992). These three investigations determined temperature and tested their results against pressures derived from other barometers applied to rocks of the same pluton or in adjacent contact metamorphic rocks. However, many other recent studies have failed to evaluate critically hornblende-based pressures against other barometers and have ignored the effects of temperature.

A common assumption with the current formulation of the hornblende barometer is that plutons crystallize near a H_2O-saturated solidus. Experiments by Johnson and Rutherford (1989) achieved high solidus temperatures in the presence of a mixed CO_2-H_2O fluid. Temperature estimates for many granitic plutons are well above that of a H_2O-saturated solidus near 650 °C, presumably because of either the presence of a mixed fluid or fluid undersaturation. Examples include the Liberty Hill granite at 725 °C (Speer, 1987), the Axtel quartz diorite at 770 °C (Anderson et al., 1988), the Bald Rock granite at 773 °C (Vyhnal et al., 1991), the Wooley Creek batholith at >800 °C (Barnes,

TABLE 1. Average composition of coexisting plagioclase and hornblende (rims) and thermobarometry from the Mount Stuart batholith

Sample	x (km)*	y (km)*	Ab,Pl	Si,Hbl	[4]Al,Hbl	[6]Al,Hbl	P_1 (kbar)	T_1 (°C)	P_2 (kbar)	T_2 (°C)
e91-2b	−8.3	27.5	0.640	6.713	1.287	0.260	4.4 ± 0.5	741 ± 12	3.1 ± 0.5	760 ± 17
w91-8	−9.8	24.9	0.667	6.680	1.320	0.203	4.2 ± 0.7	742 ± 17	3.0 ± 0.6	761 ± 26
w91-1	−17.8	24.3	0.688	6.901	1.099	0.155	3.0 ± 0.5	708 ± 13	2.6 ± 0.4	714 ± 15
e91-15	23.9	9.9	0.675	6.998	1.002	0.203	2.7 ± 0.1	694 ± 07	2.5 ± 0.2	697 ± 08
IC-1	22.0	5.2	0.636	6.849	1.151	0.185	3.4 ± 0.6	728 ± 23	2.6 ± 0.1	739 ± 33
IC-7	12.8	12.1	0.640	7.091	0.909	0.258	2.5 ± 0.4	684 ± 12	2.5 ± 0.3	685 ± 13
93sw-4	−1.9	12.6	0.688	6.950	1.050	0.140	2.7 ± 0.4	702 ± 06	2.4 ± 0.4	706 ± 07
SP-1	−4.1	34.6	0.635	7.262	0.738	0.326	2.1 ± 0.5	651 ± 17	2.2 ± 0.5	650 ± 18
93se-6	9.2	14.3	0.680	7.148	0.852	0.197	2.0 ± 0.1	669 ± 08	2.0 ± 0.1	669 ± 09
ms-181	21.3	1.1	0.717	7.095	0.905	0.133	1.9 ± 0.2	674 ± 13	1.9 ± 0.2	674 ± 15
SP-8a	−3.2	31.8	0.654	7.322	0.678	0.321	1.7 ± 0.3	636 ± 11	1.9 ± 0.3	634 ± 11
427	9.3	0.0	0.690	7.074	0.926	0.104	1.9 ± 0.5	685 ± 18	1.8 ± 0.4	686 ± 20
93se-9	6.4	8.4	0.717	7.124	0.877	0.110	1.7 ± 0.4	670 ± 20	1.7 ± 0.3	670 ± 21
SP-8b	−3.2	31.8	0.654	7.309	0.692	0.225	1.4 ± 0.1	644 ± 15	1.5 ± 0.1	643 ± 15
e91-14	−3.0	34.6	0.685	7.307	0.693	0.220	1.3 ± 1.0	638 ± 27	1.5 ± 1.2	637 ± 30
93sw-14	−13.4	19.4	0.720	7.166	0.834	0.092	1.4 ± 0.6	664 ± 29	1.5 ± 0.6	663 ± 30
329b	−13.0	35.7	0.590	7.340	0.660	0.224	1.2 ± 0.5	653 ± 17	1.3 ± 0.4	652 ± 18
w91-6a	−11.9	23.7	0.597	7.355	0.645	0.174	0.9 ± 0.3	652 ± 17	1.0 ± 0.4	650 ± 17
93sw-2	−12.6	28.3	0.680	7.309	0.691	0.118	0.8 ± 0.4	645 ± 07	0.9 ± 0.4	644 ± 07
304-1	−6.4	8.6	0.705	7.244	0.756	0.047	0.8 ± 0.4	656 ± 09	0.9 ± 0.3	655 ± 10
93sw-9	−10.5	19.6	0.677	7.337	0.663	0.088	0.6 ± 0.4	642 ± 24	0.7 ± 0.5	641 ± 24
93se-12a	−10.7	31.8	0.680	7.405	0.595	0.150	0.5 ± 0.2	624 ± 09	0.6 ± 0.2	623 ± 09
93sw-6	−3.1	10.9	0.671	7.315	0.685	0.027	0.4 ± 0.2	651 ± 09	0.5 ± 0.2	651 ± 09

Note: P_1 from Schmidt (1992) calibration; P_2 from this study; T based on Blundy and Holland (1990) at specified pressure. P_2 and T_2 solved by iteration. Averages are for multiple analyses of four to nine pairs per sample; uncertainty in P and T represents 1σ precision error.
* Sample location relative to coordinates 121° E and 47.5° N, in kilometers with positive values east or north, respectively, and negative values west or south, respectively.

1987), and the granodiorite of the Russian Peak complex at 870 °C (Cotkin and Medaris, 1993). Dacitic and rhyolitic volcanic deposits have yielded temperature estimates as high or even higher (Hildreth, 1981; Whitney and Stormer, 1985; Grunder and Mahood, 1988). Several of these examples contain the full buffering assemblage for Al-in-hornblende barometry.

Plutons can also have considerable internal variation in crystallization temperature. One example is the Mount Stuart batholith of the northern Washington Cascades. The batholith and enclosing metamorphic rocks contain several mineral assemblages enabling application of a variety of thermometers and barometers. The batholith is a calcic, ilmenite-series, Mg-rich intrusion ranging from two-pyroxene diorite to hornblende + biotite tonalite and peraluminous granodiorite (Anderson, 1992; Anderson and Paterson, 1991). The diorite of the Mount Stuart batholith, although too low in quartz to allow use of the Al-in-hornblende barometer, contains assemblages that allow application of six cation-exchange thermometers. Estimated temperatures for the diorites average >850 °C. Tonalite forms the bulk of the batholith and, along with quartz diorite and granodiorite, has assemblages appropriate for comparison of five thermometers, including clinopyroxene + biotite (Perchuck et al., 1985), clinopyroxene + hornblende (Kretz and Jen, 1978), clinopyroxene + ilmenite (Bishop, 1980), plagioclase + hornblende (Blundy and Holland, 1990), and, in peraluminous rocks, garnet + biotite (Ferry and Spear, 1978; Ganguly and Saxena, 1984). Over the restricted whole-rock silica range of 60–68 wt% SiO_2, temperature estimates by these thermometers are relatively uniform but also indicate that

portions of the batholith were emplaced under much hotter conditions (740–780 °C) relative to the lower temperature (620–680 °C) portions that generally occur near the margin (Table 1). Intrasample precision error on these temperature estimates varies from ±7 to ±33 °C, hence we regard the range of solidus temperature as significant and a potential reflection of variable H_2O undersaturation. Some rocks of the batholith (e.g., tonalite) do not contain potassium feldspar or titanite and thus lack the full buffering assemblage of the hornblende barometer. However, several samples contain the full assemblage, and such samples, combined with well-constrained temperature estimates, provide an ideal case where internal variations in temperature and mineral assemblage can be utilized in a test of the hornblende barometer.

In addition to the hornblende barometer, two other barometers are applicable in the Mount Stuart igneous rocks, including garnet + hornblende + plagioclase + quartz (Kohn and Spear, 1990) and garnet + plagioclase + biotite + muscovite (Ghent and Stout, 1981; Hodges and Crowley, 1985). Two-thirds of the batholith is in contact with pelitic schists, which are amenable to thermobarometry (Evans and Berti, 1986; Bendixen et al., 1991). Although the northeastern region of the batholith and adjacent country rocks have undergone a postemplacement, kyanite-forming event (Evans and Berti, 1986; Paterson et al., 1994), the metamorphism is generally not detectable within the batholith.

Hornblende rims in contact with quartz from the tonalite of the batholith span a wide range in composition (Fig. 2). Al-poor subsolidus amphiboles, easily identified by their patchy texture, are not widespread and have been
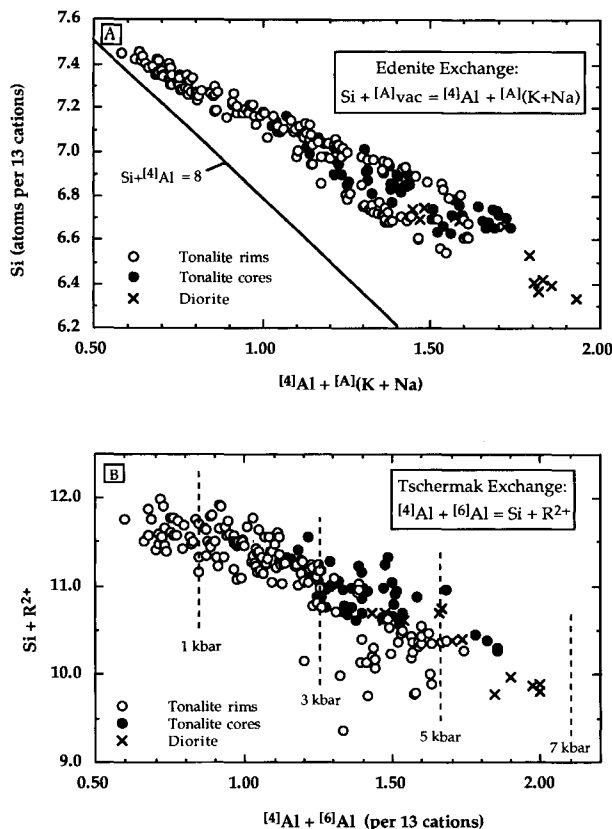
Fig. 2.   Hornblende core and rim compositions of the Mount Stuart batholith per 13 cations: (A) Si vs. $^{[4]}$Al + $^{[A]}$(K + Na) and (B) Si + R^{2+} vs. $^{[4]}$Al + $^{[6]}$Al.

omitted. Figure 2A and 2B show hornblende compositions plotted in formats to test the role of edenite and Tschermak exchange, respectively. Clearly both exchange mechanisms are important in these rocks. On the basis of the data portrayed in Figure 2A and using the experimental calibration of Schmidt (1992), the amphibole rims indicate pressures ranging from <1 to over 4 kbar. These apparent pressures yield a domal isobaric pattern for the batholith with higher pressures (greater depth) in the core and lower pressures along the margins. The low pressures range to an apparent 0.5 kbar, far below the 2 kbar lower limit of experimental calibration. Using data for one side of the batholith, Ague and Brandon (1992) observed part of this pressure variation and used the data to make tilt corrections on paleomagnetic data, assuming that the entire batholith had uniform tilt in one direction.

We have tested hornblende pressures in several areas of the Mount Stuart batholith using contact metamorphic pressures of Bendixen et al. (1991), Paterson et al. (1994), and Anderson (unpublished manuscript). Three examples are shown in Figure 3 for an area where the batholith occurs in two large lobes separated by a half-kilometer wide screen of contact metamorphosed pelitic schist. Using the garnet + aluminosilicate + silica + plagioclase

(GASP) barometer, Bendixen (in Paterson et al., 1994) calculated a rim-based pressure of 3.2 ± 0.3 kbar using the calibration of Koziol and Newton (1988). The ±0.3 kbar error is an estimate of analytical precision based on multiple analyses of adjacent mineral rims and does not include the large value of uncertainty of ±2.5 kbar for GASP barometry concluded by McKenna and Hodges (1988). These Mount Stuart area metamorphic rocks exhibit other indications of low pressure associated with batholith emplacement, including the well-recognized restriction of andalusite (overprinted by sillimanite in this region) to the contact aureole and the occurrence of cordierite + potassium feldspar (Evans and Berti, 1986; Paterson et al., 1994). In comparison with that derived from the country rocks, an igneous sample from the western side of the metamorphic screen yields hornblende rim pressures (Schmidt, 1992, calibration) of 4.2 ± 0.7 kbar (Fig. 3A), and a sample from the eastern side yields hornblende rim pressures of 4.4 ± 0.5 kbar (Fig. 3B). Both of these rocks are quartz diorites (60.8 and 61.1 wt% SiO$_2$, respectively), and their crystallization temperatures are measured at ~740 ± 17 °C using the plagioclase + hornblende thermometer of Blundy and Holland (1990) at pressure derived from the Al-in-hornblende barometer. The eastern locality also contains garnet + two mica granodiorite, and the thermobarometry for that sample (Fig. 3C) indicates lower crystallization temperatures potentially appropriate for wetter, peraluminous magma. Calculated core and rim pressures are variable, but compositions taken on the outer portions of feldspar and garnet rims yield pressures comparable to that derived from the contact aureole in this vicinity of the batholith. Although the discrepancy is not large, we conclude that igneous hornblende barometry for these samples is yielding pressures that are slightly high (by ~1 kbar) but still within the range of overall uncertainty.

The Blundy and Holland (1990) thermometer yields temperatures similar to those derived from other thermometers applicable to quartz diorite, tonalite, and granodiorite and is the only one that can be used widely throughout the batholith. We have also utilized the Holland and Blundy (1994) calibration of the hornblende + plagioclase thermometer but have found it to be too sensitive to the $^{[A]}$Na-site occupancy of hornblende to yield precise intrasample estimates of temperature unless one arbitrarily imposes a constant Fe^{3+}/Fe^{2+} ratio. Imposing a constant hornblende Fe^{3+}/Fe^{2+} ratio is appropriate only for intrusions that crystallize at relatively constant levels of oxidation. As reported by Anderson and Paterson (1991), the diorite-to-granodiorite series of the Mount Stuart batholith crystallized along a reducing trend, from above the Ni-NiO buffer to below the QFM buffer, involving over nine orders of magnitude change in f_{O_2}. Rim compositions of adjacent hornblende (on quartz) and plagioclase were used to calculate average solidus temperature and pressure (Schmidt, 1992, calibration) for each sample (Table 1). The resulting P-T data (Fig. 4) have a correlation coefficient of 0.856 over a temperature range of
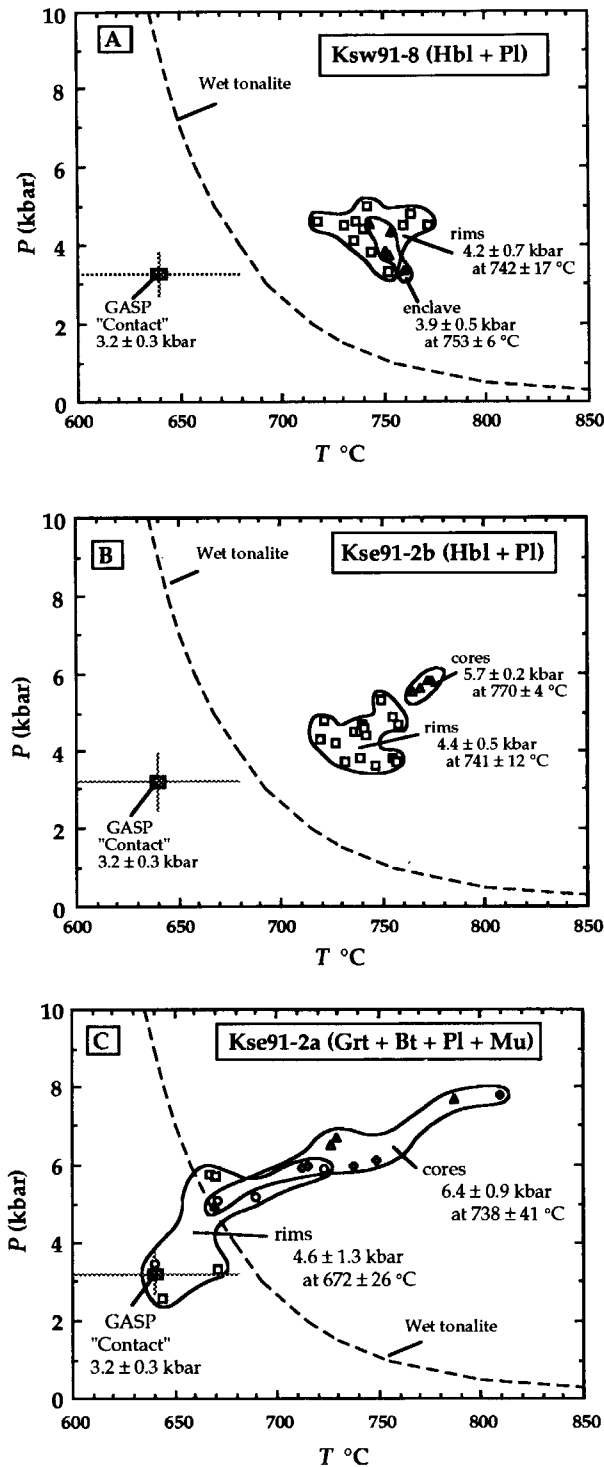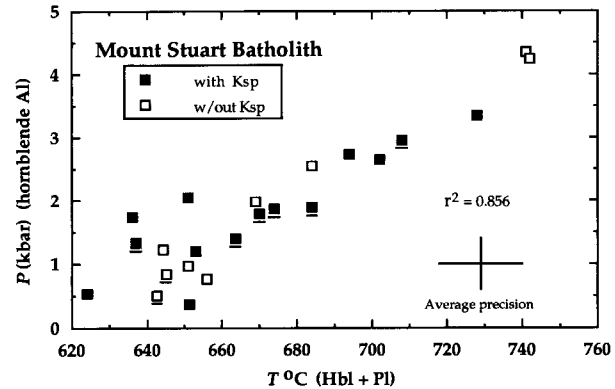
Fig. 4. Average pressure (Schmidt, 1992) and temperature (Blundy and Holland, 1990) for 23 localities within the Mount Stuart batholith. Samples with and without potassium feldspar (solid and open squares, respectively) and those having titanite (underlined symbols) are noted. Determinations at $P < 2.5$ kbar are outside the range of experimental calibration.

Fig. 3. Comparison of igneous thermobarometry and contact metamorphic barometry for two localities within the Mount Stuart batholith using (A and B) hornblende + plagioclase (Schmidt, 1992, and Blundy and Holland, 1990, calibrations) and (C) garnet + plagioclase + biotite + muscovite (Ghent and Stout, 1981, and Ganguly and Saxena, 1984, calibrations) on the basis of coexisting rim and adjacent core compositions.

620–760 °C. Our data come from 23 rocks, but not all contain potassium feldspar and magmatic titanite. The role of titanite remains unknown, but the lack of potassium feldspar ($a_{\text{orthoclase}} < 1$ in the melt) means that those calculated pressures are maximum values. However, we found no correlation between the presence or absence of these two phases and calculated pressure (Fig. 4). We conclude that although the $a_{\text{orthoclase}}$ and the a_{titanite} were less than unity in some samples, they either were at levels sufficiently close to saturation so as to preclude influencing Al content in hornblende or did not significantly affect the equilibria. The two quartz diorites depicted in Figure 3 have temperatures at the high end of the above correlation. These and other high-temperature samples (mostly tonalite) come from the interior of the batholith where pegmatites are infrequent and clinopyroxene persists as a magmatic phase.

The imperfect correspondence of Al-in-hornblende and metamorphic pressure, the range and correlation of calculated solidus temperature and pressure (Fig. 3), and the evidence for a significant amount of edenite exchange (Fig. 2A) suggest that the Al content of hornblende is, in part, a reflection of another variable, specifically temperature. The range in solidus temperature is beyond that expected for H_2O-saturated quartz diorite and tonalite (observed silica range = 60–68 wt%) and is likely a reflection of variable magmatic H_2O content. Because some of the batholith samples contain hornblende with Al content lower than that calibrated for barometry, we now consider two other sets of data that yield a P-T trend similar to that of the Mount Stuart batholith.

A positive correlation between temperature and pressure derived from the Al-in-hornblende barometer was also founded by Vyhnal et al. (1991) and Ghent et al. (1991). Rocks in both studies have the full buffering assemblage and their P-T solutions (recalculated) range 3–6 kbar at 695–770 °C and 3–8 kbar at 690–780 °C, re-
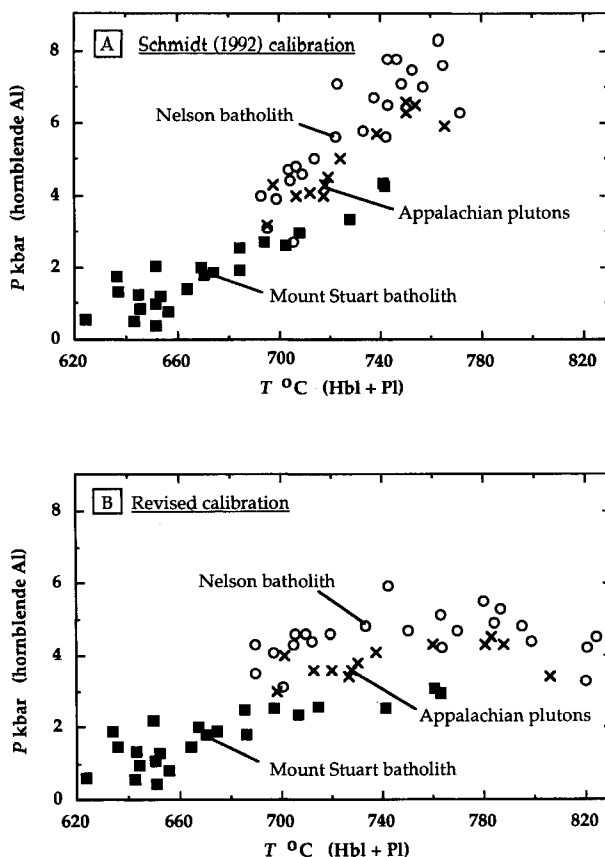
Fig. 5. Pressure and temperature for the Mount Stuart batholith (this study), the Nelson batholith of Ghent et al. (1991), and the Appalachian plutons of Vyhnal et al. (1991) recalculated to (A) Schmidt (1992) calibration and (B) the revised expression (see text). All temperatures are based on the plagioclase + hornblende thermometer (Blundy and Holland, 1990) at the calculated pressure.

spectively (Fig. 5A). This positive correlation is not due to the pressure dependence of the plagioclase hornblende thermometer. As calibrated by Blundy and Holland (1990), temperature is on average lowered, not increased, 15 °C per 1 kbar increase in pressure. Part of the apparent pressure variation may be due to H_2O-undersaturated solidus temperatures increasing the Al content of hornblende. Otherwise, such data will require that some crustal sections or plutons be highly tilted and overly thick, up to ~15 km in cases like the ones cited here. As is evident in Figure 5, plutons can crystallize over a wide range in temperature, far above that of the wet-granite solidus near 650 °C.

Available experimental data allow an expansion of the barometer's calibration to include a term that corrects for temperature. Since we are interested in applications over a 1–10 kbar range, we have utilized the experimental data of Johnson and Rutherford (1989) and Schmidt (1992). The Johnson and Rutherford (1989) and Schmidt (1992) calibrations are $P = 4.23Al_{tot} - 3.46$ and $P = 4.76Al_{tot} -$
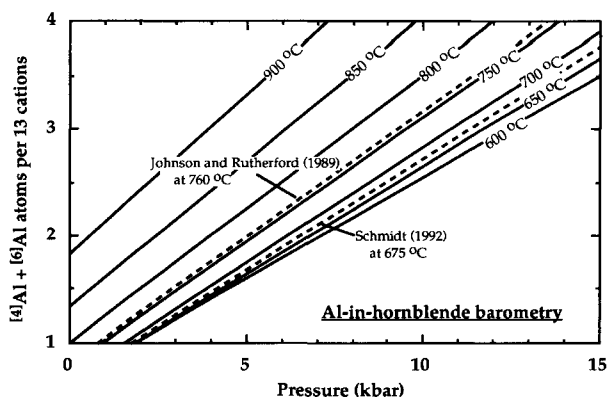

Fig. 6. Graphical expression of revised Al-in-hornblende barometer calibration. The calibrations of Johnson and Rutherford (1989) and Schmidt (1992) are shown for comparison.

3.01, respectively. Schmidt (1992) concluded that the two sets of experimental data were consistent and that the offset in Al at fixed pressure was due to the higher temperature used in the Johnson and Rutherford (1989) study. The two sets of experimental data can be combined into one expression if P, T, and hornblende Al are known. Neither of the two experiments was precisely isothermal, and we have used an average temperature of 675 °C for the Schmidt (1992) data and 760 °C for the Johnson and Rutherford (1989) data. The resulting equation is $P (\pm 0.6$ kbar$) = 4.76Al - 3.01 - \{[T (°C) - 675]/85\} \times \{0.530Al + 0.005294[T (°C) - 675]\}$. This expression yields pressures consistent with Schmidt (1992) and Johnson and Rutherford (1989) at the above respective temperatures. The depicted error (± 0.6 kbar) incorporates the largest 2σ regression error observed between the two data sets (both have very high squared-correlation coefficients near 0.99) but does not include error in temperature or analytical imprecision. Uncertainty in temperature of ± 50 °C, for example, leads through propagation to an additional average uncertainty of ± 0.8 kbar, and a 1% analytical error in Al contributes an additional error of ± 0.1 kbar. Figure 6 graphically depicts the new barometric expression and, for comparison, the calibration curves for the two sets of experiments from which it is derived.

Our suggestion is that this expression be used until further work clearly establishes the barometric reaction with a calibration based on the compositions of all phases in the barometric assemblage. Although potentially applicable to high-temperature intrusions, the new expression probably should not be applied to plutons with temperatures much >800 °C because such conditions are far outside the range of experimental calibration and the full buffering assemblage may not be stable. The assumption that the crystallization temperature of plutons is near a wet, H_2O-saturated solidus remains unjustified until tested against well-characterized thermometers. Our choice of using the hornblende + plagioclase thermometer was based on comparison to five other thermometers. Its for-

mulation, however, has also been criticized (Poli and Schmidt, 1992). The point being made here is that hornblende barometry, as with all other barometers, cannot be utilized without concern for the effect of other intensive parameters. The barometer is temperature dependent, a fact recognized originally by Hammarstrom and Zen (1986). The effect increases with pressure and ranges from 1.3 to >2 kbar per 100 °C. For the Mount Stuart batholith samples shown in Figure 3, the 4.2 and 4.4 kbar pressures decrease to 2.9 ± 0.7 and 3.1 ± 0.5 kbar, respectively, which compare well with the 3.2 ± 0.3 kbar pressure determined from GASP contact aureole barometry. The overall domal pattern of hornblende pressures in the batholith is not eliminated but largely disappears with most pressures falling in the 1–3 kbar range. Revision of the P-T data of Vyhnal et al. (1991) and Ghent et al. (1991) also results in a much less striking range in pressure (Fig. 5B). Revised pressures for the Appalachian plutons of Vyhnal et al. (1991) range from 3 to 4 kbar and those for the Nelson batholith of Ghent et al. (1991) average near 5 kbar. Studies such as that by Vyhnal and McSween (1990), Ghent et al. (1991), Anderson et al. (1992), and Ague and Brandon (1992) have used observed pressure variations to determine tectonic history or the magnitude of postemplacement tilting. Revised pressures eliminating the effect of temperature will necessitate modified or different tectonic interpretations.

EFFECT OF f_{O_2} ON HORNBLENDE BAROMETRY OF ANOROGENIC GRANITES

Rapakivi granite intrusions were a widespread global phenomenon during the middle Proterozoic as part of an anorogenic trinity with anorthosite and charnockite (Anderson, 1983). Hundreds of these immense batholiths were emplaced across the North American continent between 1.0 and 1.5 Ga and most contain the full buffering assemblage required for Al-in-hornblende barometry. Their hornblende and other mafic silicate compositions and Fe-Ti mineralogy systematically shift across the continent, an apparent reflection of fundamental changes in the state of oxidation of their crustal source (Anderson and Morrison, 1992). Low-f_{O_2}, ilmenite-series granites occupy a huge swath from Laborador (Emslie and Stirling, 1993) through Wisconsin (Anderson, 1980) and into Wyoming (Fuhrman et al., 1988). These plutons have very Fe-rich mafic minerals, including hornblendes with Fe/(Fe + Mg) ratios of 0.82–0.99 (Fig. 7) similar to that of the whole rock.

Higher f_{O_2}, magnetite-series granites typify intrusions from the midcontinent through Colorado and into the southwestern United States. Their mineral assemblage (including potassium feldspar + magnetite) requires that biotite and hornblende Fe/(Fe + Mg) ratios are controlled by intensive parameters (Wones, 1981). Variations in temperature, f_{H_2O}, and total pressure are important, but it is f_{O_2} that by far exerts the strongest control on mafic silicate mineral chemistry. With increasing f_{O_2}, the Fe/(Fe + Mg) ratio of these silicates markedly decreases inde-
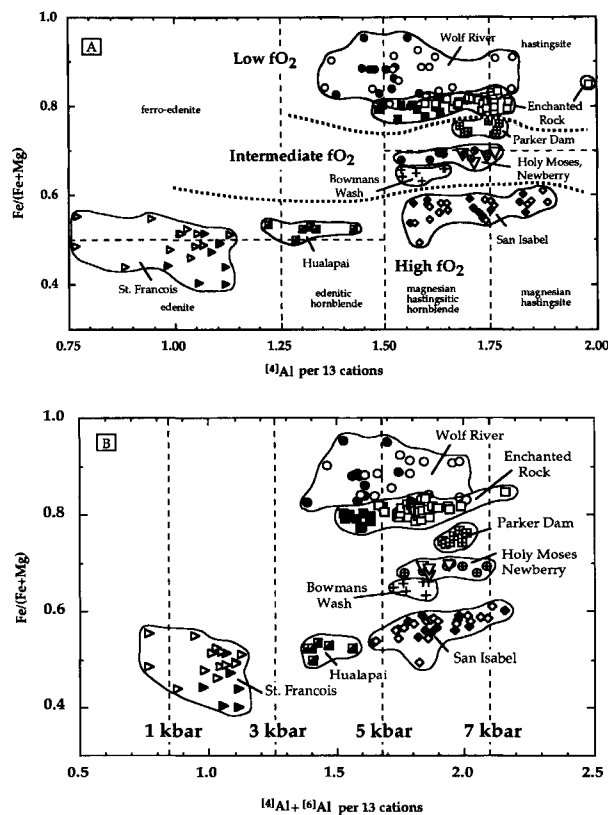

Fig. 7. Composition of hornblende from Proterozoic anorogenic granites of North America in terms of (A) Fe/(Fe + Mg) vs. [4]Al and (B) Fe/(Fe + Mg) vs. [4]Al + [6]Al. Dashed lines in A are classification divisions from Leake (1978). Isobars in B are based on the calibration of Schmidt (1992).

pendent of the Fe/Mg ratio of the whole rock. Amphibole occurring in this large group of granitoids ranges in composition from Fe rich (hastingsite) to more Mg rich (edenite) largely owing to considerable f_{O_2} variations (Fig. 7). The Enchanted Rock batholith in the Llano uplift of central Texas is magnetite series, yet has Fe-rich hornblende (Smith, 1993) because f_{O_2} was below QFM. The 1.4 Ga Parker Dam, Bowman's Wash, and Newberry plutons of California and the Holy Moses pluton of Arizona were emplaced at intermediate levels of f_{O_2} well above QFM (Anderson and Bender, 1989) and have hornblende with Fe/(Fe + Mg) ratios between 0.62 and 0.78. The highest f_{O_2} granites, all characterized by extensive aeromagnetic anomalies and an abundance of magnetite, include the Hualapai granite of western Arizona (Anderson and Bender, 1989), the San Isabel batholith of Colorado (Cullers et al., 1992), and the plutons of the Saint Francois Mountains of Missouri (Bickford and Anderson, 1993). The hornblende in these rocks has Fe/(Fe + Mg) ratios ranging from 0.40 to 0.61. Calculated f_{O_2} measured from the lowest f_{O_2}, ilmenite-series granite to the highest f_{O_2}, magnetite-series granite at a reference temperature of 720 °C, spans four orders of magnitude, from $10^{-17.4}$ to $10^{-13.2}$

TABLE 2. Representative analyses of hornblende from anorogenic granites of North America

Pluton	Wolf River	Nain	Enchanted Rock	Parker Dam	Newberry	Holy Moses	Bowman's Wash	San Isabel	Hualapai	Saint Francois
Sample	GR-7	EC90	ERB-23	JP280	NY6b	Hp1b1	JP413	TG-87	HP-7	BSF-219
Specimen	h3	253	19	b13	e3	e3	b4	q7	e1	a1
SiO_2	40.32	39.72	41.22	39.77	40.39	39.96	42.04	40.86	44.04	47.28
TiO_2	1.10	1.40	1.48	0.79	1.62	1.27	1.43	0.48	0.52	1.32
Al_2O_3	9.62	10.39	8.67	10.90	10.00	10.06	10.30	11.32	7.82	5.78
FeO^*	28.23	28.46	28.40	26.69	24.04	23.36	22.39	21.91	19.46	17.78
MgO	3.62	3.18	3.51	4.69	6.29	6.43	7.31	7.71	9.89	10.86
MnO	0.65	0.19	0.79	0.58	0.62	0.88	0.41	0.88	0.97	0.98
CaO	10.77	10.82	10.75	11.25	11.33	11.41	11.32	11.19	10.60	9.95
Na_2O	1.49	1.28	1.61	1.58	1.40	1.84	1.83	1.58	2.04	1.70
K_2O	1.59	1.60	1.31	1.82	1.58	1.71	1.80	1.64	1.59	0.59
F	0.59	0.40	0.27	0.77	0.65	1.42	0.98	0.76	1.19	1.17
Cl	0.36	0.01	0.18	0.27	0.21	0.00	0.17	0.24	0.14	0.16
Fe_2O_3 calc	6.06	5.61	4.98	6.17	5.73	4.31	3.51	8.02	6.31	6.74
FeO_{calc}	22.78	23.41	23.92	21.14	18.89	19.48	19.24	14.69	13.79	11.71
H_2O_{calc}	1.52	1.69	1.72	1.48	1.56	1.23	1.46	1.54	1.37	1.41
O = F, Cl	0.33	0.17	0.15	0.39	0.32	0.60	0.45	0.37	0.53	0.53
Sum	100.14	99.53	100.25	100.82	99.93	99.41	101.34	100.55	99.73	99.12
Formula per 13 cations, tetrahedral site										
Si	6.390	6.318	6.518	6.228	6.295	6.286	6.413	6.240	6.697	7.067
[4]Al	1.610	1.682	1.482	1.772	1.705	1.714	1.587	1.760	1.303	0.933
Al_{tot}	1.797	1.948	1.616	2.012	1.837	1.866	1.852	2.039	1.401	1.019
M1, M2, M3 sites										
[6]Al	0.187	0.267	0.134	0.240	0.132	0.152	0.265	0.278	0.098	0.086
Ti	0.131	0.167	0.176	0.093	0.190	0.150	0.164	0.055	0.060	0.148
Fe^{3+}	0.722	0.672	0.593	0.727	0.672	0.511	0.402	0.922	0.722	0.759
Mg	0.854	0.754	0.828	1.095	1.462	1.507	1.662	1.755	2.242	2.420
Mn	0.087	0.026	0.105	0.077	0.081	0.117	0.053	0.114	0.125	0.124
Fe^{2+}	3.019	3.114	3.613	2.768	2.463	2.562	2.454	1.876	1.754	1.464
Sum	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
M4 site										
Ca	1.829	1.844	1.821	1.888	1.892	1.923	1.850	1.831	1.727	1.594
Na	0.171	0.156	0.179	0.112	0.108	0.077	0.150	0.169	0.273	0.406
Sum	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
A site										
Na	0.287	0.239	0.316	0.367	0.314	0.484	0.391	0.299	0.328	0.086
K	0.322	0.325	0.265	0.364	0.314	0.343	0.350	0.320	0.309	0.112
Sum	0.609	0.564	0.581	0.731	0.629	0.828	0.742	0.619	0.637	0.198
OH site										
OH	1.606	1.796	1.819	1.547	1.624	1.294	1.483	1.573	1.392	1.407
F	0.296	0.201	0.134	0.381	0.321	0.706	0.473	0.365	0.573	0.553
Cl	0.097	0.003	0.047	0.072	0.055	0.000	0.044	0.062	0.035	0.041
Sum	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Fe^{3+}/Fe_{tot}	0.193	0.177	0.158	0.208	0.214	0.166	0.141	0.329	0.292	0.341
$Fe_{tot}/(Fe_{tot} + Mg)$	0.814	0.834	0.819	0.762	0.682	0.671	0.632	0.615	0.525	0.479
Pressure	5.5	6.3	4.7	6.6	5.7	5.9	5.8	6.7	3.7	1.8
Reference	1	2	1	3	3	3	3	1	3	1

Note: pressure in kilobars from Schmidt (1992) calibration; references: 1 = Smith, this study; 2 = Emslie and Stirling (1993); 3 = Anderson and Bender (1989).
* Total Fe as FeO.

bars (Anderson and Morrison, 1992). Representative analyses of hornblende are given in Table 2.

Although too high in K_2O and Fe/Mg to be calc-alkaline, all the rocks contain the requisite mineral assemblage for hornblende barometry, including quartz, two feldspars, biotite, hornblende, Fe-Ti oxide, and titanite. Only the Enchanted Rock and Wolf River batholiths have plagioclase (An_{15-20} and An_{16-25}, respectively) that is outside the recommended An_{25-35} range, a feature that should cause lowering of hornblende Al and derived pressure. Many of these granites have textures and emplacement styles typical of epizonal plutons. Surrounding metamorphic rocks

generally yield pressures <4 kbar. Contact metamorphic rocks around granite and anorthosite intrusions in Labrador, for example, yield pressures of 3.5 ± 1.0 kbar (Berg, 1977; Emslie and Stirling, 1993). Older metamorphic rocks near the 1.49 Ga Wolf River batholith yield pressures of 1.5–3.8 kbar (Geiger and Guidotti, 1989), and fractionated granite minimum liquids in the batholith have compositions appropriate for pressures <1 kbar (Anderson, 1980). Plutons of the Saint Francois Mountains intrude coeval volcanic rocks of the complex and should therefore be shallow, with pressures <2 kbar. The Enchanted Rock batholith is part of a suite of 1.08 Ga granites that contact
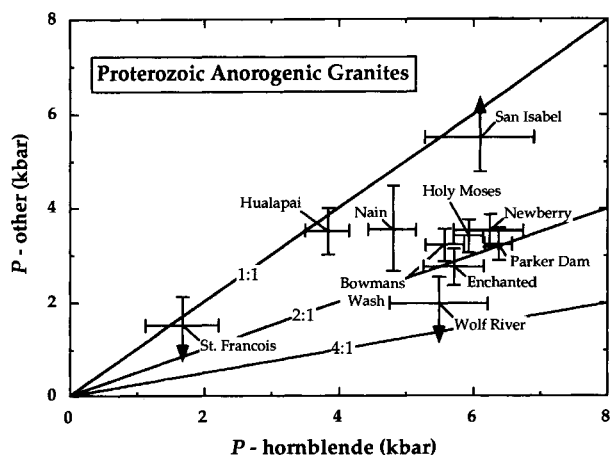
Fig. 8. Pressures derived from Al-in-hornblende barometry for Proterozoic anorogenic granites vs. pressures derived by other means (see text). Pressure limits are depicted except where uncertain (arrows).

Fig. 9. Calculated $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratios for hornblende from Proterozoic anorogenic granites on the basis of 13 cations.

metamorphosed their host rocks at pressures $\leq 2.8 \pm 0.5$ kbar (Schwarze, 1990; Letargo and Lamb, 1992; W. Carlson, 1993 personal communication). Contact metamorphic pressures are not known for plutons in the southwestern United States, but they intrude a 1.7 Ga granulite terrane that has yielded pressures of 3.2 ± 0.2 kbar adjacent to the Parker Dam and Bowman's Wash plutons (Orrell and Anderson, 1987; Orrell, 1988) and 3.5 ± 0.5 kbar near the Hualapai, Holy Moses, and Newberry plutons (Thomas et al., 1988; Young et al., 1989). The only deep-seated anorogenic pluton known in North America is the San Isabel batholith, and it is the only one that contains magmatic epidote (Cullers et al., 1992). P-T conditions recorded in metamorphic rocks adjacent to the San Isabel batholith remain unstudied, but the presence of magmatic epidote suggests pressures in excess of 5 kbar (Zen and Hammarstrom, 1984; Liou, 1973; Schmidt, 1993).

Hornblende in most of these granites reveals a much different story. Using the Schmidt (1992) calibration, derived pressures are high and many are in the 5–6 kbar range. The failure of the hornblende barometer to yield pressures similar to those derived from adjacent metamorphic rocks or by other means is summarized in Figure 8. Many of the hornblende pressures are high by a factor of two or three times, despite the fact that all have compositions similar to those used in experimental and empirical calibrations of the barometer. Only three plutons yield predictable Al-in-hornblende pressures. Pressures for the Silvermine granite of the Saint Francois Mountains are 1.7 ± 0.6 kbar (this study), those for the Hualapai granite are 3.8 $\pm$ 0.3 kbar (Anderson and Bender, 1989), and those for the San Isabel granite are 6.1 ± 0.3 kbar (Cullers et al., 1992). Hornblende grains from these three plutons share a common attribute. They crystallized at high f_{O_2} and have Fe/(Fe + Mg) ratios between 0.4 and 0.6, the same range observed for hornblende crystallized
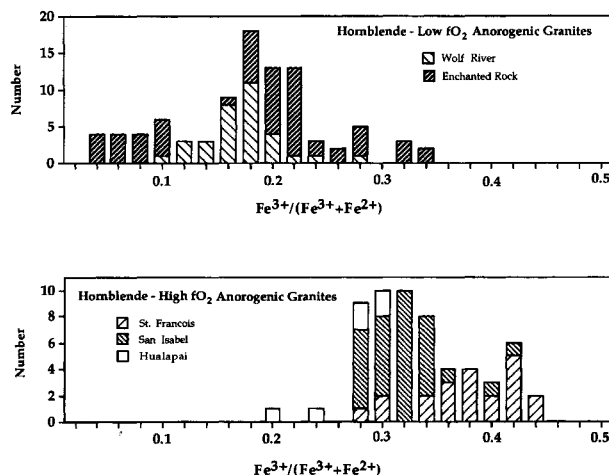
in most experimental calibrations. We infer that two factors other than temperature are the cause of the aluminous nature of hornblende and the high calculated pressures for the other anorogenic granites. One is the low Mg content of hornblende. In a study of natural tonalite, Schmidt (1993) confirmed that as Al_{tot} increased with pressure, Mg decreased far more than Fe^{2+}, and concluded that Tschermak substitution preferentially removes Mg from the M2 site instead of Fe. If some other parameter, such as f_{O_2}, imposes a continuous reaction that lowers Mg (relative to Fe^{2+}), this will also force Tschermak substitution. A second factor is low Fe^{3+} relative to total Fe. Calculated $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratios in these grains of hornblende, based on 13 cations and charge balance, are shown in Figure 9. This figure also serves as an independent test of the 13-cation normalization scheme to estimate Fe^{3+} and Fe^{2+} reliably. Our definition of low vs. high f_{O_2} comes from calculation of this intensive parameter on the basis of Fe-Ti oxide and mafic silicate compositions. The estimated $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratios for hornblende of these different granites are distinct, and it seems apparent, as might be expected, that differing levels of f_{O_2} in these two suites has led to different Fe^{3+} and Fe^{2+} abundances, which are also detected by calculation. The unusually high Al_{tot} in hornblendes from low f_{O_2} granites indicates significant Fe^{3+}-$^{[6]}Al$ exchange. Clearly, the aluminous hornblendes in these Fe-rich, low-f_{O_2} granites are not amenable to application of the hornblende barometer because none of the calibrations have employed hornblendes with Fe/(Fe + Mg) above 0.65 or have been conducted at f_{O_2} near or below QFM.

CONCLUSION

The status of hornblende barometry remains preliminary until the full barometric reaction is established and experimentally calibrated using the compositions of all minerals and not just hornblende. In its present form, it

lacks the sophistication found in many barometers, such as those calibrated for metamorphic rocks, and must be used judiciously. Temperature and f_{O_2} are parameters that petrologists need to evaluate prior to application of the barometer. Temperature can greatly increase [4]Al in hornblende, and high-temperature plutons will contain hornblende with increased total Al solely because of temperature. Without temperature control, hornblende barometry can yield overinflated estimates of pluton thickness and tilt. The lack of a complete Tschermak-buffering assemblage can also be critical. The absence of potassium feldspar and titanite does not appear to significantly affect pressure determinations, but pressures from such samples should be thoroughly evaluated by testing the barometric results against other barometers. Other factors can influence calculated pressure. The role of f_{O_2} is fundamentally important. The fact that a rock is of magnetite series is insufficient information because magnetite-bearing granites can also form under low-f_{O_2} conditions. The Fe^{3+} and Fe^{2+} of hornblendes should be determined either by chemical analysis or calculation. From our study, a limiting $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratio is ~0.25 (or 0.20 as suggested by Schmidt, 1992, for less Fe-rich hornblendes) and any amphibole with lower Fe^{3+} contents should not be utilized for hornblende barometry as presently calibrated. Likewise, hornblende $Fe_{tot}/(Fe_{tot} + Mg)$ ratios should be in the range of 0.40–0.65.

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