

# Amphibole composition in tonalite as a function of pressure: an experimental calibration of the Al-in-hornblende barometer

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**Abstract.** The Al-in-hornblende barometer, which correlates  $Al^{tot}$  content of magmatic hornblende linearly with crystallization pressure of intrusion (Hammarstrom and Zen 1986), has been calibrated experimentally under water-saturated conditions at pressures of 2.5–13 kbar and temperatures of 700–655°C. Equilibration of the assemblage hornblende-biotite-plagioclase-orthoclase-quartz-sphene-Fe-Ti-oxide-melt-vapor from a natural tonalite 15–20° above its wet solidus results in hornblende compositions which can be fit by the equation:

$$P(\pm 0.6 \text{ kbar}) = -3.01 + 4.76 Al_{hb}^{tot} \quad r^2 = 0.99,$$

where  $Al^{tot}$  is the total Al content of hornblende in atoms per formula unit (apfu).  $Al^{tot}$  increase with pressure can be ascribed mainly to a *tschermak*-exchange ( $t\bar{k}$ ,  $Mg_{-1}Al^VI Si_{-1}Al^{IV}$ ) accompanied by minor *plagioclase*-substitution ( $pl$ ,  $Ca_{-1}Na^{M(4)}Al_{-1}^{IV}Si$ ). This experimental calibration agrees well with empirical field calibrations, wherein pressures are estimated by contact-aureole barometry, confirming that contact-aureole pressures and pressures calculated by the Al-in-hornblende barometer are essentially identical. This calibration is also consistent with the previous experimental calibration by Johnson and Rutherford (1989b) which was accomplished at higher temperatures, stabilizing the required buffer assemblage by use of mixed  $H_2O$ - $CO_2$  fluids. The latter calibration yields higher  $Al^{tot}$  content in hornblendes at corresponding pressures, this can be ascribed to increased *edenite*-exchange ( $ed$ ,  $\square_{-1}^A Na^A Si_{-1} Al^{IV}$ ) at elevated temperatures. The comparison of both experimental calibrations shows the important influence of the fluid composition, which affects the solidus temperature, on equilibration of hornblende in the buffering phase assemblage.

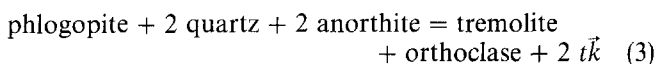
of intermediate calcalkaline plutons can be estimated by hornblende composition. In this geobarometer pressure correlates linearly with  $Al^{tot}$  content of hornblende (Fig. 1) buffered by a nine-phase assemblage (Hammarstrom and Zen 1986). By enlarging the calibration data set, Hollister et al. (1987) found a similar correlation (Eq. 2) with apparently reduced error.

$$P(\pm 3 \text{ kbar}) = -3.92 + 5.03 Al^{tot} \quad r^2 = 0.80 \quad (1)$$

$$P(\pm 1 \text{ kbar}) = -4.76 + 5.64 Al^{tot} \quad r^2 = 0.97 \quad (2)$$

Both empirical calibrations are based on pressures derived from contact-aureole geobarometry, and the given errors represent the scatter of hornblende data.

The theoretical basis of the Al-in-hornblende barometer is the phase rule. A tonalite or an amphibole-bearing granodiorite, or any similar amphibole-bearing rocks, can be described in a ten component system  $SiO_2 - TiO_2 - Al_2O_3 - Fe_2O_3 - FeO - MgO - CaO - Na_2O - K_2O - H_2O$ . A tonalite composed of nine phases (hornblende + biotite + plagioclase + orthoclase + quartz + sphene + Fe-Ti-oxide + melt + fluid phase) is therefore a trivariant system. The three degrees of freedom can be taken as the three intensive variables oxygen fugacity, temperature, and pressure. If oxygen fugacity is buffered by a second Fe-Ti-oxide or epidote, and temperature is close to the nearly isothermal solidus (presence of granitic melt), then effectively the only unconstrained variable is pressure. Pressure can be correlated to the major compositional variation observed in the minerals of tonalite, which is the  $Al^{tot}$  content of hornblende (Hammarstrom and Zen 1986). The  $Al^{tot}$  variation is ascribed mainly to a *tschermak*-exchange for which a possible buffer reaction is

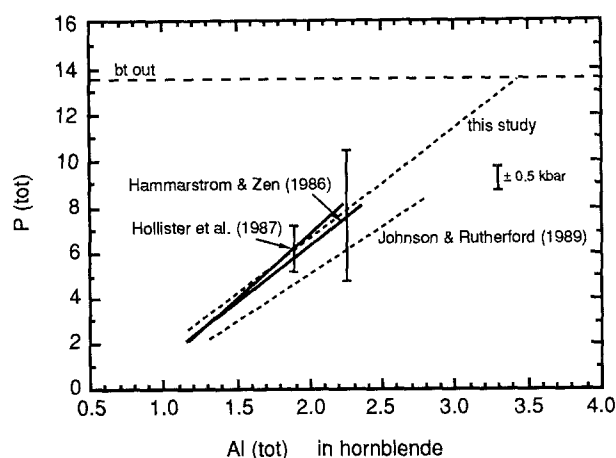


(Hammarstrom and Zen 1986; Hollister et al. 1987; Reusser 1987).

Hollister et al. (1987) emphasized that for pressures in the range of  $\approx 2$ –15 kbar the solidus of water-saturated tonalite is approximately independent of temperature

## Introduction

Since Hammarstrom and Zen (1986) proposed the empirical Al-in-hornblende barometer (Eq. 1), solidus pressures



**Fig. 1.**  $\text{Al}^{\text{tot}}$  in hornblende as function of pressure. Lines of all calibrations, in which hornblende is in equilibrium with biotite + plagioclase + orthoclase + quartz + sphene + Fe-Ti-oxide + melt + vapor, are drawn for the pressure range of each calibration. *Solid lines* are the field calibrations by Hammarstrom and Zen (1986) and Hollister et al. (1987), *error bars* are  $\pm 3$  kbar and  $\pm 1$  kbar respectively. *Dotted lines* are the experimental calibrations with errors of  $\pm 0.5$  kbar and  $\pm 0.6$  kbar

[2.5 kbar, 685°C; 6 kbar, 650°C; 15 kbar, 630°C; Piwinski (1968); Lambert and Wyllie (1974); Whitney (1975); Huang and Wyllie (1986)]. A premise of the Al-in-hornblende barometer is that the temperature of hornblende equilibration was in the vicinity of the solidus (and therefore approximately constant for the investigated pressure range) because hornblende is expected to equilibrate as long as melt is present, and because orthoclase is only stable close to the solidus. In any case fluid-saturation of melts, which is questionable at temperatures far above the solidus, certainly occurs on the solidus, as far as anhydrous mafic phases such as garnet or clinopyroxene are unstable.

The requirements of a low-variance assemblage being present limit the application of the Al-in-hornblende barometer, but also offer the advantages that: (1) because hornblende equilibrates in the presence of melt close to the solidus, the solidification depth of an intrusion, or the equilibrium pressure of a magma chamber before eruption potentially is defined by the Al-in-hornblende barometer; (2) the application of the Al-in-hornblende barometer does not require the use of – up to now – inadequate activity models for hornblende.

The present study is intended: (1) to calibrate experimentally the Al-in-hornblende barometer under water-saturated conditions; (2) to reduce the uncertainty of empirical field calibrations; (3) to give further information on the exchange vectors acting in hornblende; (4) to show by comparison with the work of Johnson and Rutherford (1989a, b) the importance of temperature and  $X_{\text{CO}_2}$  in the fluid phase for the Al-in-hornblende barometer.

## Experimental procedure

### Starting material

A Bregaglia tonalite (REF-PR, Reusser 1987) which equilibrated at  $\approx 6$  kbar (using the Hammarstrom and Zen calibration 1986) and

**Table 1.** Starting material bulk compositions (wt%). Tonalite: REF-PR (Reusser 1987), granodiorite: AU7 (Ulmer 1982)

	Tonalite	Granodiorite
$\text{SiO}_2$	58.95	66.66
$\text{TiO}_2$	0.71	0.40
$\text{Al}_2\text{O}_3$	16.80	15.92
$\text{Fe}_2\text{O}_3$	2.36	1.81
FeO	3.75	1.65
MnO	0.11	0.11
MgO	3.15	1.58
CaO	6.48	4.43
$\text{Na}_2\text{O}$	2.83	2.49
$\text{K}_2\text{O}$	2.42	2.63
$\text{P}_2\text{O}_5$	0.23	0.12
$\text{H}_2\text{O}$	1.11	0.79
Total:	98.93	98.66

an amphibole-bearing granodiorite (AU 7, Ulmer 1982) from the Adamello intrusion were used for the experiments (Table 1). The samples were ground to a grain size of  $< 10 \mu\text{m}$ . 4 wt% of a metamorphic high-alumina amphibole (PJ8, 17.0 wt%  $\text{Al}_2\text{O}_3$ , Table 3) was added to test equilibration of amphibole rims. For runs at  $P < 7.0$  kbar an additional 4 wt% of a tschermakitic tremolite (TR4, 5.0 wt%  $\text{Al}_2\text{O}_3$ , Table 3) was added so that the equilibrium Al content was bracketed in most runs. Temperature-reversals were not possible due to the amount of melt necessary to permit reaction.

### Experimental techniques

Experiments at  $P > 7.0$  kbar were carried out with a single stage 22 mm diameter piston cylinder with a NaCl assembly similar to that of Mirwald et al. (1975). The top piston was electrically isolated from the bomb by celluloid tape. A pyrophyllite ring, which includes at its top a graphite disc, was located immediately below the piston to prevent salt extrusion. The chromel-alumel thermocouple was held by a crushable alumina tubing, its welding point was covered by an alundum-based cement. The assembly shows 3.5% friction calibrated against Jd-Ab-Qz at 600°C (Hays and Bell 1973). Pressure in the salt cell is assumed to be accurate to  $\pm 0.4$  bar (Holland 1980; Jenkins et al. 1985). The large diameter of the piston cylinder permitted simultaneous loading of three different bulk compositions (quartz-diorite or tonalite + glass, tonalite, amphibole-bearing granodiorite) in each experiment. Three 2.3 mm O.D.  $\text{Ag}_{50}\text{Pd}_{50}$  capsules, no longer than 4 mm were packed together with a nickel-bunsenite buffer and water in a 5.4 mm O.D. Au capsule. The presence of both buffer phases was controlled after each experiment. During the experiments the maximum distance from thermocouple to the sample did not exceed 4 mm. Temperature is believed to be accurate within  $\pm 5^\circ$ .

Experiments with  $P < 7.0$  kbar were performed in Nimonic cold-seal vessels pressurized with argon. Oxygen fugacity was buffered at NNO (nickel-nickel oxide) by double-capsule techniques. Pressure was measured with a Heise-gauge which is accurate to  $\pm 20$  bars,  $T$  is within  $\pm 3^\circ$ .

All experiments were carried out as crystallization experiments at  $P_{\text{tot}} = P_{\text{H}_2\text{O}}$  with 15–18 wt%  $\text{H}_2\text{O}$ . Temperature was held at  $\geq 720^\circ\text{C}$  for more than 30 h and slowly reduced ( $< 5^\circ/\text{h}$ ) to a temperature 15–20°C above the solidus, where the experiment was held for more than 280 h (Table 2). Oxygen fugacity was buffered to  $\text{N}^{\text{I}}\text{NO}$  because most tonalites contain magnetite ( $\pm$  ilmenite), which define an  $f_{\text{O}_2}$  above QFM (quartz-fayalite-magnetite) and below HM (hematite-magnetite). Variation of  $f_{\text{O}_2}$  within this range was found to have no effect on  $\text{Al}_{\text{hb1}}^{\text{tot}}$  by Johnson and Rutherford (1989). Experiments were considered to be technically successful when the gold capsule contained water at the end of a run.

**Table 2.** Run conditions

Run	$P_{H_2O}$ (kbar)	$T_i \rightarrow T_{eq}$ (°C)	Hours $T_{eq}$	Starting material	Seeds	Run products of tonalite
R14	16.0	650	427	To, Gd	PJ8, Alm	Amp, phe, ep, plag, qz, gar, sph, apa, op, melt?
R08	14.0	800 → 645	309	To, Gd	–	Amp, phe, ep, plag, qz, op, melt
R26	14.0	650	360	To, Gd	PJ8, Alm	Amp, phe, ep, plag, qz, apa, op, melt
R10	13.0	750 → 655	313	To, Gd, Dio	PJ8	Amp, bt, ep, plag, qz, or, sph, apa, op, melt
R13	11.5	750 → 655	295	To, Gd, Dio	PJ8	Amp, bt, ep, plag, qz, or, sph, apa, op, melt
R07	9.5	725 → 655	296	To	–	Amp, bt, ep, plag, qz, sph, apa, op, melt
R12	7.5	750 → 655	280	To, Gd, Dio	PJ8	Amp, bt, ep, plag, qz, or, sph, apa, op, melt
R28	6.0	720 → 665	480	To, ToG, Gd	PJ8, TR4	Amp, bt, ep, plag, qz, sph, apa, op, melt
R29	4.5	720 → 680	500	To, ToG, Gd	PJ8, TR4	Amp, bt, plag, qz, or, sph, apa, op, melt
R30	3.5	730 → 690	504	To, ToG, Gd	PJ8, TR4	Amp, bt, plag, qz, or, sph, apa, op, melt
R31	2.5	750 → 700	504	To, ToG, Gd	PJ8, TR4	Amp, bt, plag, qz, or, sph, op, melt

All runs water saturated and buffered at NNO (nickel-nickel oxide). Granodiorite shows the same run products except for absence of epidote, and presence of orthoclase also at 6.0 and 7.5 kbar. *To*, tonalite REF-PR; *ToG*, 50% REF-PR + 50% synthetic glass of same composition; *Gd*, granodiorite AU7; *Dio*, quartzdiorite. *PJ8*, high alumina amphibole; *TR4*, tschermakitic tremolite; *Alm*, synthetic almandine. *Amp*, amphibole; *bt*, biotite; *phe*, phengite; *plag*, plagioclase; *qz*, quartz; *or*, orthoclase; *gar*, garnet; *sph*, sphene; *apa*, apatite; *op*, opaques.  $T_i$ , initial temperature;  $T_{eq}$ , equilibrium temperature

### Analytical methods, normalisation and nomenclature

A Cameca SX50 microprobe with 5 crystal spectrometers was used for analyses. To minimize the excitation volume the beam was set to 12 kV and 20 nA. A beam size of 2  $\mu$ m was used to prevent the electron beam from affecting the sample during the total counting time of 96 seconds. Twelve elements were measured with variable counting times of 10 s (Si, Al, Ca, Na, K), 24 s (Fe, Mn, Ti, Cr, Cl) and 48 s (F). Data were processed with PAP-correction (Pouchou and Pichoir 1984), which is an enhanced ZAF correction procedure. Amphibole rims grew to a maximum width of 10  $\mu$ m, and were clearly identifiable in electron-backscatter and X-ray-element-distribution images. For each experiment amphibole rims, always in contact with melt, including both amphibole seeds and tonalitic amphiboles were analyzed (Fig. 2).

Amphibole compositions were normalized by assuming: (1) fixed  $Fe^{3+}/(Fe^{3+} + Fe^{2+})$  ratio of 0.30 and 23 oxygens (Table 3, calculations); (2)  $\Sigma$  cations – Ca – Na – K = 13. The  $Fe^{3+}/(Fe^{3+} + Fe^{2+})$  of 0.30 is based on Mössbauer-spectroscopy analyses of hornblendes from the tonalite starting material (Reusser 1987). An  $Fe^{3+}/(Fe^{3+} + Fe^{2+})$  of 0.2, as suggested by Clowe et al. (1988), would not effect the  $Al^{tot}$  content of amphiboles. Only amphibole compositions which result in similar formulas from both normalisation (1) and (2) were considered valid.

Even if, according to Leake (1978), experimental amphiboles are magnesio hornblende (2.5–7.5, 14.0 kbar), tschermakitic hornblende and ferroan pargasitic hornblende (7.5–9.5 kbar), tschermakite (11.5–13.0 kbar), and magnesio kataphorite (16.0 kbar), the term hornblende is employed for all amphiboles used for calibration or application of the Al-in-hornblende barometer. Exchange vectors in the text are always *emphasized*.

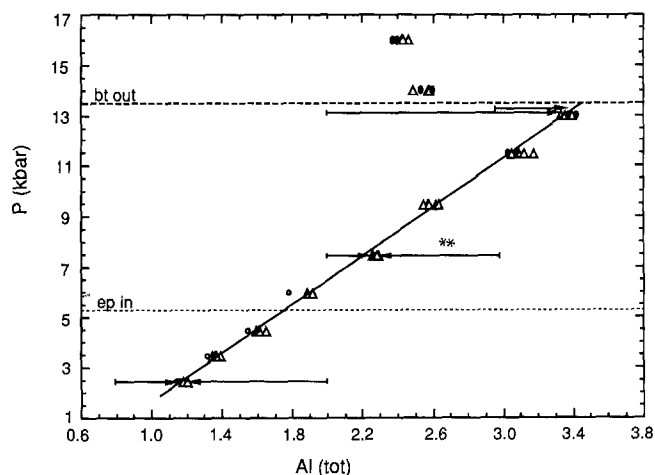
## Results

### $Al^{tot}$ calibration

The nine-phase assemblage hornblende + biotite + plagioclase + orthoclase + quartz + sphene + magnetite + melt +  $H_2O$  was equilibrated in the pressure range 2.5–13 kbar at temperatures 15–20°C above the solidus (Table 2). The requirements of the Al-in-hornblende barometer were fulfilled, except for the occasional absence of orthoclase. In the granodiorite orthoclase was present in all experiments from 2.5 to 13 kbar, but it was not always present in the tonalite (i.e. at 6.0 and 9.5 kbar) from the same experiment. However, because the  $Al^{tot}$  content of hornblende was essentially the same in both bulk compositions of any given experiment, and because of melt compositions high in orthoclase component, it is assumed that the melts in the tonalite at 6.0 and 9.5 kbar were nearly saturated with respect to orthoclase.

Amphibole rims were analyzed (Table 3) and found to have the same composition in both amphibole seeds and in the tonalite hornblende. The total Al content varies linearly with pressure in the range from 2.5 to 13 kbar (Figs 1, 2). Linear regression of the data points from eight different pressures yields

$$P(\pm 0.6 \text{ kbar}) = -3.01 + 4.76 Al^{tot} \quad r^2 = 0.99 \quad (4)$$



**Fig. 2.**  $Al^{tot}$  in amphiboles vs pressure. Amphiboles are equilibrated just above the water-saturated solidus. Arrows indicate the development of hornblende rims from initial amphibole composition at three selected pressures. Data points for each pressure include rims from low-alumina amphibole seeds (open circles, TR4), from high-alumina amphibole seeds (filled circles (crosses in Figs. 3, 4): PJ8) and from tonalite hornblende (triangles). The stars represent an experiment in which the conditions of Johnson and Rutherford's calibration were reproduced. Note that above 13 kbar biotite is not stable and therefore the buffering reaction for  $Al^{tot}$  changes

**Table 3.** Selected analyses of initial and experimental amphibole compositions (Ton. = tonalite amphibole)

P (kbar)	Experimental amphiboles										Ton. RPR	Amphibole seeds	
	2.5	3.5	4.5	6.0	7.5	9.5	11.5	13.0	14.0	16.0		PJ8	TR4
SiO <sub>2</sub>	47.59	46.11	46.00	45.44	44.90	42.63	42.56	40.52	45.06	47.56	42.33	41.86	55.70
TiO <sub>2</sub>	1.11	1.17	0.76	0.78	1.23	1.21	0.44	0.97	0.79	0.69	1.18	0.35	0.16
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.05	0.04	0.00	0.00	0.00	0.01	0.02	0.00	0.02	0.00	0.00	0.07
Al <sub>2</sub> O <sub>3</sub>	6.67	7.66	9.19	10.86	13.37	14.68	17.83	19.22	15.09	14.55	11.33	16.96	4.94
Fe <sub>2</sub> O <sub>3</sub>	5.40	5.39	5.74	5.02	5.07	5.22	4.85	5.48	4.73	4.47	6.09	5.93	0.10
FeO	11.34	11.31	12.05	10.55	10.65	10.96	10.18	11.50	9.94	9.38	12.80	12.46	0.22
MnO	0.36	0.43	0.24	0.20	0.40	0.23	0.56	0.19	0.24	0.19	0.46	0.17	0.06
MgO	12.49	11.38	10.23	10.82	10.18	9.02	8.86	6.86	9.42	8.80	9.77	7.51	23.15
CaO	10.89	11.40	10.85	11.47	10.00	10.30	10.74	9.57	8.83	6.76	11.85	10.46	13.69
Na <sub>2</sub> O	0.91	1.13	1.36	1.42	1.58	1.74	1.76	2.22	3.56	4.88	1.28	1.49	0.45
K <sub>2</sub> O	0.65	0.76	0.95	0.77	1.01	1.00	0.91	0.77	0.58	0.64	1.36	0.45	0.13
F	–	0.12	0.19	–	0.17	0.00	0.13	0.00	0.12	0.06	0.00	–	0.35
Cl	–	0.13	0.05	–	0.06	0.00	0.02	0.01	0.00	0.02	0.13	–	0.02
H <sub>2</sub> O	2.03	1.92	1.92	2.04	1.97	2.02	2.00	2.03	2.02	2.06	2.00	2.03	2.05
Total:	99.45	98.88	99.48	99.37	100.55	99.01	100.80	99.41	100.35	100.05	100.46	99.67	100.94
Si	7.011	6.876	6.825	6.691	6.521	6.323	6.160	5.988	6.511	6.818	6.330	6.187	7.514
Ti	0.122	0.131	0.085	0.087	0.134	0.135	0.048	0.107	0.086	0.074	0.133	0.039	0.016
Cr	0.000	0.006	0.005	0.000	0.000	0.000	0.001	0.002	0.000	0.002	0.000	0.000	0.008
Al <sup>IV</sup>	0.988	1.124	1.175	1.309	1.478	1.677	1.840	2.012	1.489	1.182	1.670	1.813	0.486
Al <sup>VI</sup>	0.169	0.223	0.432	0.576	0.811	0.888	1.202	1.337	1.081	1.276	0.327	1.141	0.299
Fe <sup>3+</sup>	0.599	0.605	0.641	0.557	0.554	0.583	0.528	0.609	0.515	0.482	0.686	0.660	0.010
Fe <sup>2+</sup>	1.398	1.411	1.496	1.299	1.293	1.359	1.233	1.421	1.201	1.125	1.600	1.540	0.025
Mn	0.045	0.054	0.030	0.025	0.049	0.029	0.069	0.024	0.029	0.023	0.058	0.021	0.007
Mg	2.743	2.530	2.262	2.374	2.203	1.994	1.911	1.510	2.029	1.880	2.178	1.654	4.655
Ca	1.719	1.821	1.726	1.810	1.555	1.637	1.665	1.515	1.368	1.038	1.899	1.656	1.978
Na <sup>M4</sup>	0.204	0.180	0.274	0.190	0.394	0.363	0.324	0.467	0.632	0.962	0.101	0.288	0.002
Na <sup>A</sup>	0.056	0.146	0.118	0.216	0.052	0.136	0.169	0.170	0.366	0.395	0.270	0.139	0.116
K	0.123	0.145	0.180	0.145	0.186	0.189	0.168	0.146	0.108	0.117	0.259	0.085	0.022
F	–	0.056	0.089	–	0.080	0.000	0.060	0.000	0.055	0.027	0.000	–	0.149
Cl	–	0.032	0.012	–	0.016	0.000	0.005	0.003	0.000	0.005	0.032	–	0.005
OH	2.000	1.912	1.899	2.000	1.904	2.000	1.935	1.997	1.945	1.968	1.968	2.000	1.846
Fe <sup>M4</sup>	0.078	0.000	0.000	0.000	0.051	0.000	0.012	0.018	0.000	0.000	0.000	0.055	0.020
X <sub>Mg</sub>	0.662	0.642	0.602	0.646	0.630	0.595	0.608	0.515	0.628	0.626	0.576	0.518	0.995

All runs water-saturated and buffered at NNO. Amphiboles are normalized for fixed Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>) ratio of 0.30 and 23 oxygen pfu (see text).  $X_{Mg} = Mg/(Mg + Fe^{2+})$

Standard deviation of the entire data set is  $\pm 0.19$  kbar ( $2\sigma$ ). The unexpectedly high squared correlation coefficient of  $r^2 = 0.99$  was also obtained by Johnson and Rutherford (1989b) in their experimental calibration. Even with natural data, Hollister et al. (1987) found a high correlation coefficient of  $r^2 = 0.97$  by regression of hornblende analyses from nine different plutons. The experimental calibration yields also good correlations for Al<sup>IV</sup> and Al<sup>VI</sup>, and systematic variations for Ca, Na, and for the Fe-Mg ratio, but not for other chemical parameters such as K, Ti, Mn, F, Cl.

#### Tschermak-exchange

The simplest expression for  $t\bar{k}$ -substitution is  $Mg_{-1}Al^{VI}Al^{IV}Si_{-1}$ . To include all *tschermak*-type substitutions on the octahedral sites of amphibole, it is necessary to extend the previous expression to  $(Mg, Fe^{2+}, Mn^{2+})_{-1}(Fe^{3+}, Al^{VI})Al^{IV}Si_{-1}$  and to correct for  $t\bar{i}$ -substitution ( $t\bar{i} = Ti^{VI}Mg^{VI}Al_{-2}^{VI}$ ) which removes 2 Al<sup>VI</sup> for each Ti in the formula unit.

The octahedral vs tetrahedral alumina (Eq. 5) and the  $(2Ti + Fe^{3+} + Al^{VI})$  vs Al<sup>IV</sup> (Eq. 6) are regressed using

least-squares fits, regressions of Al<sup>IV</sup>, Al<sup>VI</sup>, and  $(2Ti + Fe^{3+} + Al^{VI})$  vs pressure are plotted in Fig. 3. The small deviation of the slope (Eq. 6) from the ideal value of one demonstrates that more than 80% of alumina is incorporated through a *tschermak*-substitution into the amphibole structure. The intercepts, much closer to the ideal value of zero in Eq. 6 than in Eq. 5 show the important contributions of Fe<sup>3+</sup> and Ti to the *tschermak*-exchange.

$$Al^{VI} = -1.07 + 1.21Al^{IV} \quad r^2 = 0.88 \quad (5)$$

$$2Ti + Fe^{3+} + Al^{VI} = -0.11 + 1.12Al^{IV} \quad r^2 = 0.91 \quad (6)$$

With high Al<sup>tot</sup>,  $t\bar{k}$ -substitution becomes selective with respect to Mg – Fe<sup>2+</sup> and Al – Fe<sup>3+</sup>. This selectivity results because Mg is preferentially replaced by Al, whereas the Fe<sup>tot</sup> content of the hornblendes do not vary particularly. As a consequence, Mg/(Mg + Fe<sup>tot</sup>) is negatively correlated with pressure, a behavior which can also be inferred from the data of Johnson and Rutherford (1989b).

Above 13 kbar biotite and orthoclase are no longer stable and equilibrium (3) no longer buffers  $t\bar{k}$ -exchange; therefore at this pressure amphibole composition differs

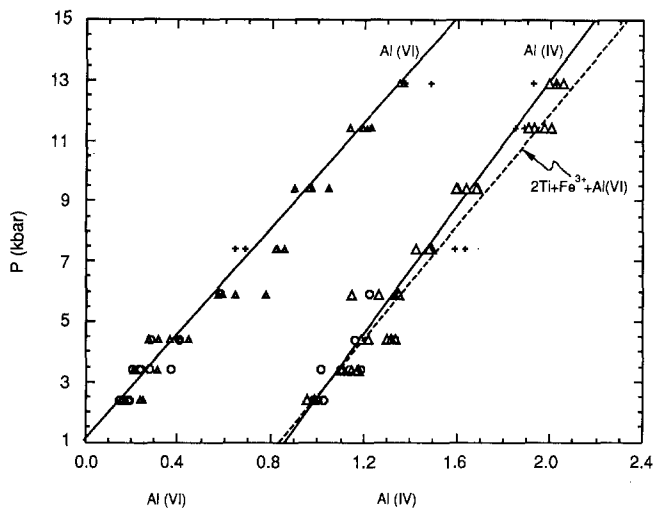


Fig. 3.  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$  of experimental hornblendes (symbols as in Fig. 2), linear regression for data from 2.5 to 13 kbar, normalized for 23 oxygens and  $\text{Fe}^{2+}/\text{Fe}^{\text{tot}} = 0.30$ . Dotted line represents regression for  $(2\text{Ti} + \text{Fe}^{3+} + \text{Al}^{\text{VI}})$  vs pressure. Linear regressions of data normalized to 23 oxygens with  $\text{Fe}^{3+}/\text{Fe}^{\text{tot}} = 0.20$  shows approximately the same slopes and correlation coefficients, whereas normalization with  $\Sigma$  cations-Ca-Na-K = 13 results in significantly lower correlation coefficients for Eqs. 5, 6 and an increased slope of Eq. 6 with respect to Eq. 5

significantly from the trend between 2.5 and 13 kbar. Results obtained above 13 kbar and analyses of possible buffer reactions for amphibole will be presented elsewhere.

#### M(4)- and A-sites

Because of the dependence of M(4)- and A-site-occupancy estimates on the normalization scheme used in determining amphibole formulas, the actual substitution mechanism must be deduced by considering coupled substitutions. The rate of  $\text{Al}^{\text{IV}}$  increase is slightly lower than the  $(2\text{Ti} + \text{Fe}^{3+} + \text{Al}^{\text{VI}})$  increase from 2.5 to 13 kbar (Eq. 6) as equal amounts of  $\text{Al}^{\text{IV}}$  and  $(2\text{Ti} + \text{Fe}^{3+} + \text{Al}^{\text{VI}})$  are incorporated by  $tk$ -exchange. This decrease coincides with: (1) a decrease of Ca content; (2) an increase of Na content (Fig. 4). These small, but significant, changes in amphibole chemistry reflect an increasing amount of *plagioclase*-exchange ( $\bar{pl} = \text{glaucophane} - tk$ ,  $\bar{gl} = \text{Ca}_{-1}\text{Na}^{\text{M(4)}}\text{Mg}_{-1}\text{Al}^{\text{VI}} = \text{Mg}_{-1}\text{Al}^{\text{VI}}\text{Si}_{-1}\text{Al}^{\text{IV}} + \text{Ca}_{-1}\text{Na}^{\text{M(4)}}\text{Al}^{\text{IV}}\text{Si}$ ), with the result that the increase in Na with pressure is mainly due to Ca replacement on the M(4)-site (Brown 1977; Spear 1980). If the decrease in Ca content was compensated by  $\text{Fe}^{2+}$ , the additional Na would necessarily occupy the A-site, and a relatively higher increase of  $\text{Al}^{\text{IV}}$  than  $(2\text{Ti} + \text{Fe}^{3+} + \text{Al}^{\text{VI}})$  would result, but this is not observed. Therefore variation of Ca and Na are best described by  $\bar{pl}$ -exchange on M(4)-site and an insignificant variation of A-site occupancy.

#### Discussion

Johnson and Rutherford (1989b) calibrated the Al-in-hornblende barometer (Eq. 7) using a mixed  $\text{CO}_2$ - $\text{H}_2\text{O}$ -fluid phase. The effect of a  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluid is to shift the

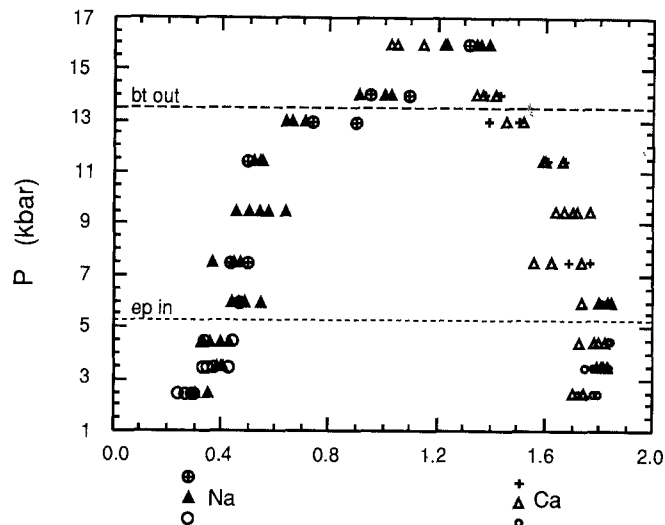


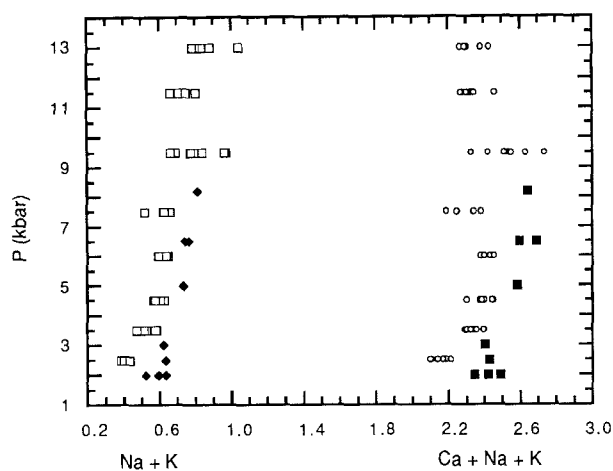
Fig. 4. Ca and Na content in experimental amphiboles vs pressure (symbols as in Fig. 2)

fluid-saturated solidus and the phase-stability-fields to higher temperatures (Swanson 1979; Bohlen et al. 1982 and references therein). Therefore, the Al-in-hornblende barometer phase assemblage was stable in Johnson and Rutherford's experiments at 780–740°C and pressures from 2 to 8 kbar.

$$P(\pm 0.5 \text{ kbar}) = -3.46 + 4.23\text{Al}^{\text{tot}} \quad r^2 = 0.99 \quad (7)$$

Eq. 7 describes the  $\text{Al}^{\text{tot}}$ -pressure relationship at temperatures approximately 90° higher than those for Eq. 4 and yields higher  $\text{Al}^{\text{tot}}$  at corresponding pressures ( $\Delta\text{Al}^{\text{tot}}_{2 \text{ kbar}} = +0.24 \text{ apfu}$ ,  $\Delta\text{Al}^{\text{tot}}_{8 \text{ kbar}} = +0.40 \text{ apfu}$ ), or lower pressures at corresponding  $\text{Al}^{\text{tot}}$  ( $\Delta P_{\text{Al}^{\text{tot}} = 1.3} = 1.1 \text{ kbar}$ ,  $\Delta P_{\text{Al}^{\text{tot}} = 2.7} = 2.1 \text{ kbar}$ ), respectively. The higher  $\text{Al}^{\text{tot}}$  in the hornblendes of Johnson and Rutherford coincides with increased alkalis (Fig. 5) which occupy the A-site since Ca contents are slightly higher in their calibration at  $\approx 750^\circ\text{C}$  than in this study at  $\approx 660^\circ\text{C}$ . Therefore the effect of higher temperatures is mainly to increase *edenite*-substitution (Spear 1981a; Graham and Navrotsky 1986). The requirements resulting from the theoretical basis of the Al-in-hornblende barometer were fulfilled for both the present experimental calibration at  $P_{\text{tot}} = P_{\text{H}_2\text{O}}$ , and that of Johnson and Rutherford at  $P_{\text{tot}} = P_{\text{CO}_2} + P_{\text{H}_2\text{O}}$ , but the different temperatures of calibration result in two different equations for  $\text{Al}^{\text{tot}}$  as a function of pressure.

The  $\text{Al}^{\text{tot}}$  variation in hornblende crystallized in the specified assemblage of the Al-in-hornblende barometer was suggested to be the result of the *edenite*-buffer reaction (Blundy and Holland 1990), tremolite + albite = 4 quartz + edenite, which is a potential geothermometer (Shido and Miyashiro 1959; Engel and Engel 1962; Spear 1981a). This substantial criticism of the barometer is extensively discussed by the comments of Hammarstrom and Zen, Johnson and Rutherford, and Poli and Schmidt (all 1992) on Blundy and Holland (1990). Here it should be reemphasized that because of the isothermal character of both the present and Johnson and Rutherford's experimental calibrations, any temperature



**Fig. 5.** Total alkalis (Na + K) and Ca + Na + K of experimental hornblendes vs pressure (*open symbols*, this calibration; *full symbols*; Johnson and Rutherford 1989b). If the same amounts of  $\text{Fe}^{\text{M}(4)}$  are assumed in both experimental calibrations, Ca + Na + K gives a normalization-independent estimate of A-site occupancy

effect in each particular calibration is excluded a priori. The hornblende compositions obtained in each calibration show that: (1) the variation in A-site occupancy, which is the only unequivocal parameter in the amphibole formula to determine the amount of  $\text{ed}$ -substitution, is small (Table 3, Fig. 5; Table 2 Johnson and Rutherford 1989b); (2) the large  $\text{Al}^{\text{IV}}$  increase is related to an  $\text{Al}^{\text{VI}}$  increase of similar extent. Therefore the  $\text{Al}^{\text{tot}}$  variation in each particular calibration is mainly a result of  $\text{tk}$ -exchange, whereas the difference between the two experimental calibrations can be mainly explained by the mostly temperature dependent  $\text{ed}$ -exchange.

Thomas and Ernst (1990) report that in their experimental calibration of the Al-in-hornblende barometer (at  $750^\circ\text{C}$ , 6–12 kbar,  $P_{\text{H}_2\text{O}} = P_{\text{tot}}$ ) orthoclase and quartz occurred as stable phases. This does not agree with previous experimental work (Lambert and Wyllie 1974; Whitney 1975; Naney 1983; reviews by Wyllie 1977; and Green 1982). Perhaps either the large grain size (100  $\mu\text{m}$ ) used by Thomas and Ernst permitted metastable orthoclase and quartz to persist, or in the piston cylinder apparatus, thermal gradients (Leistner 1979), resulting from the long capsule lengths (11.4 mm) used by Thomas and Ernst, may have created conditions such that orthoclase and quartz were stable at the cold end of the capsules while amphibole compositions were measured at the hotter end. It seems unlikely that the assemblage needed to buffer  $\text{Al}^{\text{tot}}$  in hornblende could have been stable at  $750^\circ\text{C}$ , 6–12 kbar and the difficulties of calibration discussed by Thomas and Ernst may have been the result of disequilibrium within their capsules.

## Conclusions

The agreement of the field calibrations of the Al-in-hornblende barometer, for which pressures were estimated from the contact-aureole of the investigated plutons, and the present experimental calibration is strong evidence that in these types of intermediate granitoids: (1) hornblende equilibration continues until and ceases at the wet

solidus; (2) significant subsolidus reaction, which would cause a change in  $\text{Al}^{\text{tot}}$  content of hornblende and therefore a discordance of pressures calculated by contact-aureole and by Al-in-hornblende barometry, is of minor importance. Explicitly it should be noted, that the cessation of hornblende equilibration at the solidus cannot be explained by the lack of melt in the subsolidus range. Experimental studies (Apted and Liou 1983; Spear 1981b; D. Jenkins, personal communication) showed that amphibole in fluid-saturated systems is quite reactive also in the subsolidus range. The more probable explanation is that after solidification of the plutons the released fluid escaped rapidly and a “dry” unreactive system remained. The  $\text{Al}^{\text{tot}}$  content of fully buffered magmatic hornblende can be used to determine an intrusion depth within the pressure range from 2.5–13 kbar with a precision of  $\pm 0.6$  kbar. However the pressure calculated from hornblende composition is indirectly also a function of fluid composition as has been shown by comparison with the experiments of Johnson and Rutherford (1989b), and consequently any indications of a  $\text{CO}_2$ -bearing fluid should be carefully considered.

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