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Confirmation of the empirical correlation of Al in hornblende with pressure of solidification of calc-alkaline plutons

L. S. HOLLISTER, G. C. GRISSOM, E. K. PETERS, H. H. STOWELL, V. B. SISSON
Department of Geological and Geophysical Sciences, Princeton University,
Princeton, New Jersey 08544, U.S.A.

ABSTRACT

We have tested the proposed hornblende geobarometer of Hammarstrom and Zen (1985) by analyzing and averaging only rim compositions of hornblende from plutons for which we have independently determined pressures of intrusion from the metamorphic country rocks. Over a range in pressure of 2–8 kbar, the average hornblende rim content of Al at nine localities correlates linearly with pressure. The data points fall within error on the linear relation proposed by Hammarstrom and Zen (1986), which was based primarily on data near 2 and 8 kbar. Our results confirm that the relation is valid for intermediate pressures (4–6 kbar), and the addition of our intermediate-pressure data reduces the error in pressure determined from the Al content of hornblende from ±3 kbar, proposed by Hammarstrom and Zen (1986), to ±1 kbar, provided due caution is exercised in sample selection. The geobarometer works because calc-alkaline plutons seem to be bivariant at the end of crystallization and because the temperature of solidification is fairly pressure insensitive above 2 kbar.

INTRODUCTION

Hammarstrom and Zen (1983, 1985, 1986) proposed an empirical correlation between the estimated pressures of crystallization of calc-alkaline plutons and the total Al content of hornblende. The correlation is described by the linear relationship.

$$P\ (\pm 3\ \text{kbar}) = -3.92 + 5.03\text{Al}_\text{T}$$

where P is pressure in kilobars, and Al_T is total number of cations of Al per formula unit based on 23 oxygens. Should this proposed geobarometer prove to be valid, it would be extremely useful in unraveling the tectonic histories of orogenic belts, in which hornblende-bearing calc-alkaline plutons occur in voluminous amounts.

Most of the data on which the geobarometer is based come from samples that crystallized at 1.5–3 and 7–10 kbar (Hammarstrom and Zen, 1986). Relatively few data come from plutons that crystallized at intermediate pressures (4–6 kbar). Furthermore, knowledge of variation of hornblende compositions across single plutons is limited, and not all the hornblende analyses on which the calibration is based can be argued to be for hornblende that crystallized with all the phases in the rock plus melt.

The present study examines data collected for the purpose of constraining the geobarometer in the 4–6-kbar range, to determine the range of composition of hornblende across two plutons that solidified at different pressures, and to relate core-to-rim differences in components in hornblende to factors controlling its composition in calc-alkaline magma. Finally, the geobarometer is applied to additional melts that solidified at pressures from 2–3 and 7–8 kbar, based on metamorphic mineral assemblages in the adjacent country rock.

We conclude that pressures of solidification of calc-alkaline plutons can be estimated to ±1 kbar, in the pressure range 2–8 kbar, based on the Al content of hornblende rims, in association with quartz, plagioclase, orthoclase, biotite, magnetite, and titanite. Using our data alone, the calibration curve (Fig. 1) is insignificantly different in slope and position from that of Hammarstrom and Zen (1986).

CONDITIONS FOR APPLICATION OF THE GEOBAROMETER

Hornblende composition is known to vary significantly with rock composition and with pressure and temperature. Besides Hammarstrom and Zen (1986), papers that have emphasized factors controlling hornblende composition include Helz (1982), Spear (1981), Laird and Albee (1981), Wones and Gilbert (1982), and Raase (1974). Although general statements of pressure-temperature conditions can be made from amphibole compositions, particularly for commonly occurring rocks, there are usually too many thermodynamic degrees of freedom to constrain amphibole-bearing systems enough to use any compositional parameter to quantitatively determine pressure or temperature. We argue here, however, that in calc-alkaline magma systems there may be sufficient thermodynamic constraints to warrant the correlation of Al in hornblende to pressure of solidification.

According to the thermodynamic phase rule, the degrees of freedom of a system at a pressure and a temper-

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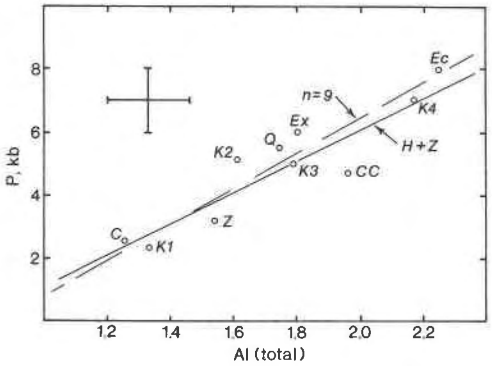

Fig. 1. Plot of pressure based on metamorphic mineral assemblages vs. average Al_T in hornblende from nearby calc-alkaline plutons, as discussed in text (C, Chicken; K1, Kenney; Z, Zbura; K2, Kasiks; Q, Quottoon; Ex, Exchamsiks; K3, Kateen; CC, Carlson Creek; K4, Khyex; Ec, Ecstall). Error bar for Al_T based on multiple analyses of Carlson Creek pluton. Error bar in pressure based on conventional ±1 kbar error due to statistics of microprobe analyses of metamorphic minerals. Solid line is from Hammarstrom and Zen (1986). Dashed line is best fit to our data, excluding CC.

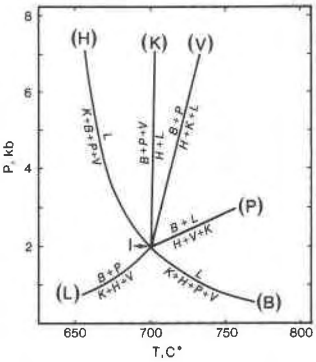

Fig. 2. Schematic phase relations for calc-alkaline magmas, from Clemens and Wall (1981) and Kenah and Hollister (1983). Each reaction curve is labeled for the phase not involved in the reaction: H (hornblende), K (orthoclase), V (vapor), P (plagioclase), B (biotite), L (melt). Point I is the pseudo-invariant point discussed in the text.

ature are determined by the number of phases subtracted from the minimum number of chemical species needed to define the system. For a calc-alkaline rock, the 10 major oxides are Na_2O, CaO, FeO, MgO, K_2O, Al_2O_3, Fe_2O_3, H_2O, TiO_2, SiO_2. The seven solid phases of the hornblende-bearing calc-alkaline plutons that we are considering are plagioclase, quartz, hornblende, biotite, orthoclase, magnetite, and titanite. Assuming that melt and an H_2O-bearing vapor phase are present at the end of crystallization, with $P_{vapor} = P_{total}$, there are a total of nine phases, with any CO_2 acting as a dilutant for H_2O in the vapor phase. With these phases present at the *end* of crystallization, the system has a variance of 3: pressure, temperature, and one compositional degree of freedom. Fugacity of oxygen is buffered by the above assemblage.

In order for the composition of a phase to be a function of pressure only, the variance needs to be reduced to one. The variance is effectively lowered to two because in most calc-alkaline plutons, the rim composition of plagioclase is nearly uniform (between An_{25} and An_{35} for the samples we studied), thus providing an additional compositional constraint.

Based on published phase diagrams, amphibole can crystallize between ~950 and 650°C in calc-alkaline compositions (e.g., Helz, 1982). This temperature range is fairly narrow compared to the total temperature range over which amphibole is stable for all possible compositions in the crust and upper mantle. A tighter constraint on the temperature range of solidification of hornblende in calc-alkaline rocks is that the solidus curves for hornblende-bearing melts of calc-alkaline compositions are relatively insensitive to pressure and vary ~100 deg at most for pressures above about 2 kbar. This point is illustrated in Figure 2. Point I is a pseudo-invariant point in that there is, according to our assumptions, only one degree of freedom at specified temperature, fugacity of oxygen, and plagioclase composition. The pseudo-invariant point changes position along each of the phase-absent curves (including metastable extensions) with variation in composition of the absent phase until the position of the pseudo-invariant point is fixed at the pressure of solidification.

Below about 2 kbar, the temperature of final crystallization increases rapidly with drop in pressure (Fig. 2). Thus, temperature-sensitive Al-bearing components in hornblende would be expected to be important relative to pressure-sensitive components. The discussion of the geobarometer in the present paper is therefore restricted to pressures above ~2 kbar.

We presume that the pressure-sensitive substitution is the tschermakite component $[Ca_2(Fe,Mg)_3Al_2Al_2Si_6O_{22}(OH)_2]$ because in most reaction systems, pressure favors minerals with octahedral Al coordination relative to those with tetrahedral Al. A reaction governing the tschermakite substitution for calc-alkaline plutons is

$$2\ \text{Quartz} + 2\ \text{Anorthite} + \text{Biotite} = \text{Tschermakite} + \text{Orthoclase}. \qquad (1)$$

This reaction, which is water conservative, has the relatively shallow slope of about 11 bars/°C based on approximations for ΔS and ΔV. Assuming that this is the most important reaction governing the pressure effect on Al_T in hornblende, the importance of assemblage and the assumption of uniformity of composition of plagioclase are clear: lack of orthoclase (activity of orthoclase in coexisting melt <1) favors more tschermakite in hornblende, and low activity of anorthite component in plagioclase favors less tschermakite.

We conclude that in order to reliably apply an empirical geobarometer based on hornblende composition, the following conditions must be met: (1) The phases quartz, plagioclase, hornblende, biotite, orthoclase, titanite, and

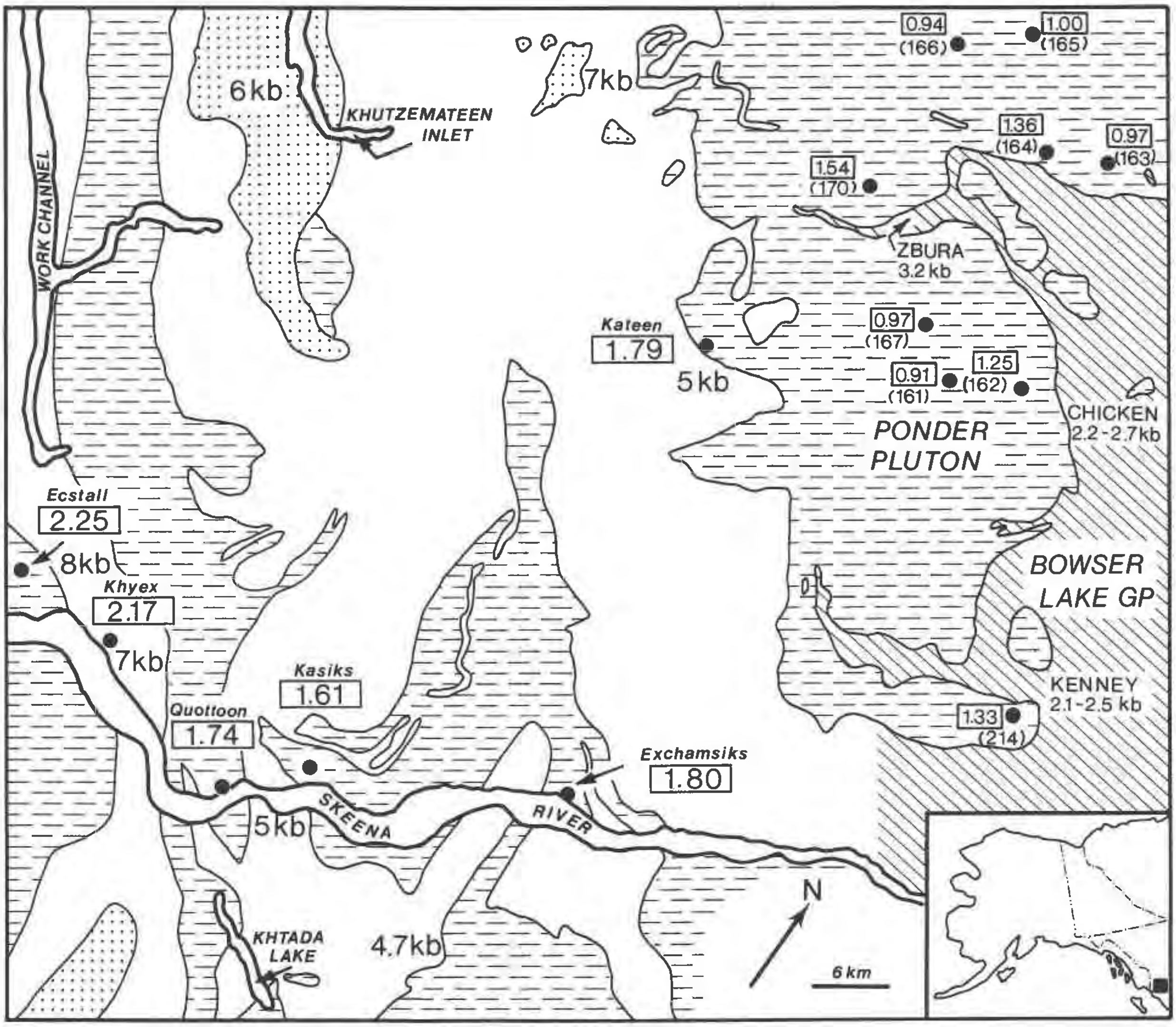

Fig. 3. Location of calc-alkaline plutons (horizontal striping), migmatite and gneiss (blank), amphibolite-facies metamorphic rock (stippled), and only contact-metamorphosed sedimentary rocks (diagonal lines) in the Coast Plutonic Complex of British Columbia, showing locations of pressure estimates and average rim values of hornblende (numbers in rectangles; names are referred to in text). For east side of Ponder pluton, sample numbers are shown in parentheses. Map from Sisson (1985), based on Hutchison (1982), Duffel and Souther (1964), and unpublished maps of Hollister.

magnetite must have crystallized together from a melt. (2) Only the rim compositions of the hornblende should be used because these are the only parts of the hornblende crystals that are candidates to have crystallized with the last melt remaining in the rock; this condition is necessary for the requirement that the final temperature be limited to a small range. (3) The pressure should be above ~2 kbar; this condition is also necessary for there to be a control on temperature at solidification. (4) The rim plagioclase composition should be between ~An$_{25}$ and An$_{35}$; it should be strictly at one composition, but, for determining the empirical calibration, this is the range that we dealt with.

In short, the rationale for using Al in hornblende as a geobarometer is that calc-alkaline plutons have enough thermodynamic restrictions at solidification that the Al content of hornblende is primarily a function of pressure of solidification.

Analytical methods

In all samples, hornblende crystals were analyzed for Si, Al, Fe (total), Mg, Mn, Ti, Na, K, and Ca using an energy-dispersive system (EDS) according to the technique of Hollister et al. (1984). Operating conditions were 15-kV accelerating voltage and 0.2-μA beam current with a spectrum accumulation time set at 50 s. In each thin section, at least two hornblende crystals were examined. For rim analyses, a minimum of six EDS analyses were obtained from within 10 μm of the edge. In the apparent center of each crystal (as seen in the thin section), a minimum of four EDS analyses were obtained. Thus each rim analysis represents an average of 12 or more analyses and each core value represents an average of 8 or more analyses. Step scans at 10-μm intervals using the wavelength-dispersive system (WDS) for Al, Fe, and Mg were done to confirm the EDS results and to ensure that zoning is continuous from core to rim.

The major limitation of the EDS technique relative to WDS is that drift of the total spectrum during analysis precludes using the total as a constraint on the analysis. The percentage change in total specrum is the same as for each element; thus, cation proportions based on cation sums from EDS and WDS analyses are the same for analyses of equal quality. However, because of the variations of oxide totals with spectra drift, cation calculations based on 23 oxygen atoms carry the error of the total oxide analysis; we therefore report our results based on cation sums. For hornblende, we normalized the cations to a total of fifteen excluding Na and K. Na and K were excluded because the A site is typically not fully occupied in calcic amphiboles, and because all of the K and most of the Na occur at this site. The WDS analyses of Hammarstrom (1984) show very little Na at M(4); assuming this to be true for all our hornblende analyses, our cation normalization technique for hornblende in calc-alkaline plutons gives very nearly the same formula as that used by Hammarstrom (1984), who calculated the formulae based on 23 oxygen atoms.

Our analysis and normalization procedures do not allow an independent determination of Fe^{3+} in the amphibole. Although all Fe is reported as Fe^{2+}, it is reasonable to presume, on the basis of Fe^{3+} determinations in calc-alkaline plutons (Dodge et al., 1968), that about 25% of the Fe is Fe^{3+}.

DATA FROM 4–6-KBAR PLUTONS

Several large, synmetamorphic hornblende-bearing tonalite and granodiorite plutons that are associated with sillimanite-garnet-cordierite gneiss and migmatite occur within the Central Gneiss Complex of British Columbia (Fig. 3). The pressure determinations are primarily based on equilibria between garnet, plagioclase, sillimanite, and quartz (Ghent, 1976), which are consistent with those calculated from equilibria between garnet, cordierite, quartz, and sillimanite (Holdaway and Lee, 1977). Temperatures were determined from the assemblages and by garnet-biotite exchange equilibria (Ferry and Spear, 1978). The metamorphic assemblages yield pressures between 4 and 7 kbar. The data supporting these pressure estimates are in articles (Lappin and Hollister, 1980; Kenah and Hollister, 1983; Selverstone and Hollister, 1980; Hollister, 1982) and in Ph.D. theses (Kenah, 1979; Douglas, 1983; Hill, 1985; Sisson, 1985); the approximate locations of the most thoroughly documented pressure determinations are indicated on Figure 3.

The average rim Al contents of hornblende of the several localities are illustrated on Figures 1 and 3, and the data are given in Table 1. Each sample contains the requisite assemblage quartz, biotite, plagioclase, hornblende, orthoclase, magnetite, and titanite.

Average Al_T of hornblende in two samples of Quottoon pluton is 1.74. Relevant pressure estimates from metamorphic assemblages associated with these samples are ~6 kbar, calculated from data obtained east of the pluton at Khutzemateen Inlet (Douglas, 1983), and ~5 kbar, calculated from data obtained east of the pluton (Kenah, 1979); 5.5 kbar is used for the plot of Figure 1.

For Kasiks pluton, data are averaged for 5 samples; Al_T of the hornblende is 1.61. A U-Pb age from this locality indicates the pluton is 4 m.y. younger than Quottoon pluton (Woodsworth, pers. comm., 1985). The closest pressure determinations are 5 kbar (Kenah, 1979) and 4.7 kbar (Selverstone and Hollister, 1980); the rounded intermediate value of 4.9 kbar is used for the plot of Figure 1.

At the Kateen locality, Sisson (1985) determined a 5-kbar pressure for metamorphic rocks adjacent to an intrusive contact of granodiorite. The hornblende in a sample from across the contact has 1.79 Al_T.

Well-foliated tonalite occurs at Exchamsiks River. By structure arguments (Woodsworth et al., 1983), this melt crystallized before the nearby Kasiks locality and therefore may have crystallized at greater depth, according the the model of synchronicity of pluton intrusion with uplift (Hollister, 1982). The 6-kbar estimate (Fig. 1) is based on solidification of the tonalite at a higher *P* than the prevalent 5-kbar values, but at a lower *P* than the maximum (7 kbar) estimated *P* within the Central Gneiss Complex (Hill, 1985; Sisson, 1985).

Given a ±1-kbar error for metamorphic pressure determinations and a standard deviation of ±0.13 atoms Al (discussed under Carlson Creek pluton, below), the four data points (Fig. 1) support the choice by Hammarstrom and Zen (1986) for the linear fit to their data.

HIGH-PRESSURE DATA (7–8 KBAR)

We analyzed hornblende from Ecstall pluton (Fig. 3), which crystallized at 8 ± 1 kbar according to synmetamorphic assemblages in the vicinity of the pluton (Crawford and Hollister, 1982) and at greater than 6 kbar based on the presence of magmatic epidote (Crawford and Hollister, 1982; Woodsworth et al., 1983; Zen and Hammarstrom, 1984). Epidote is partly rimmed by biotite and may not be part of the final equilibrium assemblage; on the basis of texture, hornblende and the other requisite phases were in equilibrium with melt at solidification. Samples from this pluton were used by Hammarstrom and Zen (1986) for determining the calibration curve, and therefore our data may not constitute an independent evaluation of the calibration curve. Nevertheless, our data (Table 1) are similar to those of Hammarstrom and Zen, showing that there are no real differences in analysis based on the differences in analytical techniques and in assumptions used for the amphibole-formula calculations.

Lappin and Hollister (1980) described hornblende-bearing migmatites at the Khyex locality (Fig. 3) for which a 7 ± 1 kbar pressure was determined from a nearby pelitic unit. The cores of hornblende in rocks from which partial melt had been removed are probably relics from the protolith prior to anatexis. A representative Al_T value, 2.17 (Table 1), falls very close to the calibration curve

TABLE 1. Cation proportions of hornblende from several plutons and a migmatite and pressure estimates from metamorphic assemblages

	σ	Kasiks (5)	Quottoon (2)	Kateen (1)	Exchamsiks (1)	Khyex*	Ecstall†	Ecstall‡
Si	0.17	6.74	6.60	6.53	6.56	6.42	6.41	6.31
Al	0.14	1.61	1.74	1.79	1.80	2.17	2.25	2.23
Fe	0.09	2.03	2.12	2.51	2.31	2.51	2.23	2.30
Mg	0.21	2.54	2.41	2.10	2.18	1.83	2.06	2.17
Ca	0.05	1.83	1.91	1.87	1.91	1.87	1.85	1.85
Na	0.05	0.40	0.31	0.44	0.33	0.42	0.57	0.55
K	0.04	0.18	0.25	0.24	0.27	0.19	0.33	0.32
Ti	0.01	0.20	0.16	0.14	0.18	0.17	0.12	0.10
Mn	0.01	0.05	0.04	0.06	0.07	0.06	0.08	0.07
P (kbar)		4.7–5	5–6	5	5–7	7	8	8

Note: Numbers in parentheses are number of samples at locality; analyses by EDS.

* Representative WDS analysis of hornblende from migmatite (analysis 5, Table 5, Lappin and Hollister, 1980).

† Average of 12 EDS analyses; cations calculated assuming the sum = 15, exclusive of Na + K.

‡ Average of 21 WDS analyses by Hammarstrom (1984); cations calculated for 23 oxygens.

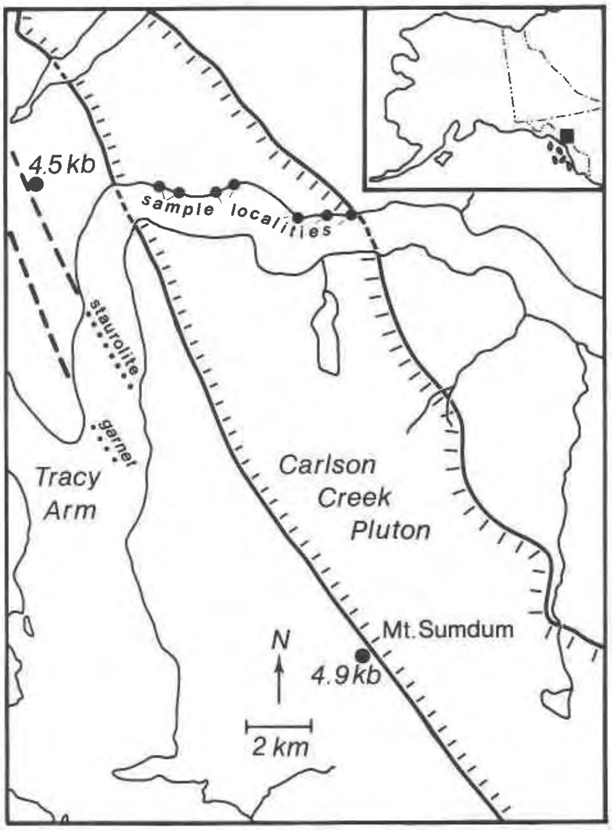

Fig. 4. Sample localities within the Carlson Creek pluton, contacts of Carlson Creek pluton, locations of pressure estimates, and isograds labeled by index mineral (from Stowell, 1981, 1985, 1986; Brew and Ford, 1981).

(Fig. 1) at 7 kbar. Nevertheless, it should be cautioned that the equilibrium assemblage can only be inferred because one or more phases were consumed by the melt-forming reaction and were thereby removed when the melt was extracted.

CARLSON CREEK PLUTON (4.7 ± 1 KBAR)

The Carlson Creek pluton crosses Tracy Arm, in the Coast Ranges of southeast Alaska, approximately 50 km southeast of Juneau (Fig. 4). This tabular, well-foliated, predominantly tonalite pluton is part of the Coast Plutonic Complex sill (Brew and Ford, 1981), which is a Late Cretaceous–early Tertiary belt of plutons averaging 10 km in width and extending 700 km from Lynn Canal near Berners Bay in Alaska to south of Douglas Channel in British Columbia (Brew and Ford, 1981; Crawford and Hollister, 1982; Grissom, 1984); the Quottoon pluton discussed above is included in this belt. The metamorphic history of the terrane west of the pluton has been studied by Stowell (1981, 1985, 1986).

The seven samples used in the present study were collected across the pluton along Tracy Arm, at sea level (Fig. 4) and were described by Grissom (1984). The samples were chosen with the purpose of establishing the range of variation of hornblende composition (within grains, between grains in a sample, and between samples) that could occur in a single pluton assumed to have solidified over a narrow pressure range. The western contact is steep and sharp, and foliations in the pluton and country rock are parallel to the contact. Sphalerite geobarometry from near the contact at the Mount Sumdum prospect (Fig. 4) gives a pressure of 4.9 kbar, and geobarometry based on garnet + muscovite + plagioclase + biotite assemblages west of the pluton contact, near Tracy Arm (Fig. 4), give 4.5 kbar, at a temperature of 570°C that is based on biotite-garnet geothermometry (Stowell, 1985). At the contact 40 km southeast of the Mount Sumdum prospect, a 4.6 ± 1 kbar pressure was obtained from a garnet + sillimanite + plagioclase + quartz assemblage (Stowell, 1986). The pressure at the western contact when the pluton solidified is taken as 4.7 kbar.

Modes of the seven samples indicate that the Carlson Creek pluton is a tonalite (Table 2). The samples have virtually identical mineral content; notable is that most lack orthoclase. Detailed descriptions of the samples, bulk chemical analyses, compositions of individual hornblende crystals, and compositions of coexisting biotite and plagioclase are given in Grissom (1984).

The average core and rim cation contents of the seven samples are given in Table 3. The most pronounced chemical variations, for core to rim of single samples or for rim to rim (or core to core) between samples, are in Mg/(Mg + Fe) and in Al_T.

The two parameters are plotted as a function of distance across the pluton in Figure 5. Clearly, the rim and core compositions are systematically different, and hornblende from the center of the pluton is enriched in Mg/(Mg + Fe) and depleted in Al_T relative to the borders. The inverse relation of Mg/(Mg + Fe) to Al_T is illustrated

TABLE 2. Modes

	Carlson Creek pluton sample nos.							Ponder pluton sample nos.								
	A6	27	25	21	22	18	17	161	162	163	164	165	166	167	170	214
Plagioclase	49.0	46	56	48	47	45	43	66	55	47	49	61	50	48	55	55
Quartz	17	16	18	24	26	17	13	20	15	22	15	21	22	20	28	15
Orthoclase	0.1	0	0	0	0	5	0.5	8	9	20	17	11	18	24	8	2
Biotite	18	5	13	13	11	19	14	4	11	5	7	4	4	4	3	13
Hornblende	15	24	12	13	13	13	28	2	10	6	11	2	5	2	5	13
Others	0.9	9	1.1	2.3	3.3	1.1	1.2	0.3	0.9	1	0.5	1	0.9	2	1.1	1.7

for all analyses in Figure 6. A crystal-chemical basis for this relationship was summarized by Hawthorne (1983): an increase of tetrahedral Al results in an expansion of the double tetrahedral chain of amphibole which, in turn, favors substitution of the large Fe cation for Mg in the adjacent octahedral sheets.

The hornblende values plotted in Figure 6 provide an average hornblende-rim composition and standard deviation for a pluton. Two-thirds of the values fall between 1.75 and 1.95 Al, giving a standard deviation of ±0.1 Al. The average rim value, 1.96, is shown relative to the calibration curve of Hammarstrom and Zen (1986) in Figure 1, with a standard deviation for only the rims of ±0.13 Al. A possible reason for the offset of the Carlson Creek point from the calibration curve is discussed following the next section.

PONDER PLUTON (2–3 KBAR)

A large complex granodiorite pluton, the Ponder pluton (Fig. 3), has a low-pressure contact aureole containing cordierite- and andalusite-bearing assemblages (Sisson, 1985) along its eastern contact with the sedimentary rocks of the Bowser Lake Group.

Although the pluton varies in composition from its center to the margins (Hutchison, 1982), the same major mineral phases are found in each sample studied (Table 2), and orthoclase is present in all, in contrast to the Carlson Creek pluton. Detailed modal data, chemical analyses, and analyses of biotite, orthoclase, and plagioclase are in Peters (1984). Sisson (1985) found that the crystallization history of the eastern margin was influenced by metamorphic fluid derived from the Bowser Lake Group.

TABLE 3. Cation proportions of hornblende in samples from Carlson Creek pluton (Fig. 4)

	A6	27	25	21	22	18	17
				Rims			
Si	6.61	6.90	6.44	6.81	6.43	6.45	6.58
Al	2.11	2.23	1.91	1.78	1.89	1.88	1.95
Fe	2.46	2.27	2.41	2.18	2.45	2.38	2.37
Mg	1.85	1.67	2.22	2.25	2.16	2.23	2.09
Ca	1.78	1.71	1.84	1.79	1.87	1.88	1.84
Na	0.29	0.38	0.39	0.28	0.42	0.36	0.28
K	0.26	0.29	0.21	0.20	0.23	0.28	0.26
Ti	0.13	0.14	0.14	0.14	0.14	0.15	0.14
Mn	0.06	0.05	0.06	0.05	0.06	0.04	0.04
				Cores			
Si	6.73	6.84	6.57	6.95	6.55	6.44	6.59
Al	1.88	1.75	1.71	1.62	1.78	1.84	1.74
Fe	2.45	2.23	2.26	2.07	2.34	2.38	2.35
Mg	1.99	2.22	2.42	2.43	2.27	2.25	2.26
Ca	1.78	1.75	1.87	1.78	1.88	1.89	1.84
Na	0.26	0.39	0.29	0.26	0.37	0.34	0.34
K	0.23	0.22	0.19	0.16	0.21	0.25	0.25
Ti	0.13	0.15	0.11	0.11	0.13	0.14	0.16
Mn	0.05	0.06	0.05	0.05	0.05	0.06	0.06

Note: Analyses are arranged from west to east (Fig. 4). Sum of cations = 15, exclusive of Na + K.

Peters (1984) determined core and rim compositions of hornblende for 3–4 crystals in each of 10 specimens from the eastern portion of this pluton. The averaged data are tabulated in Table 4, and the Al_T values are shown on Figure 2 along with the pressure estimates of Sisson (1985).

A complex intrusive history of the Ponder pluton is implied by the range of pressures determined from its margins and by the large spread of Mg/(Mg + Fe) vs. Al_T (Fig. 7). Pressures determined at Kateen (included with the 4–6-kbar plutons), Zbura, Chicken, and Kenney are 5, 3.2, 2.5, and 2.3 kbar, respectively. The average hornblende rims from the four pluton samples closest to these localities have Al_T values of 1.79, 1.54, 1.25, and 1.33, respectively. The additional data for the three low-pressure localities are plotted on Figure 1 and support the Hammarstrom and Zen calibration curve.

On the basis of data from the Ponder pluton, we suggest that for determinations of pressure of intrusion of a calc-alkaline pluton, in the absence of diagnostic mineral assemblages in the aureole, the field relations of the sample be carefully considered. It is likely that the Ponder pluton contains successive injections of melt that came up along a tectonic boundary as the Central Gneiss Complex was being uplifted relative to the Bowser Lake Group. Rapid uplift of the Central Gneiss Complex has been previously proposed (Hollister, 1982). If melt had been continuously injected along the boundary with the Bowser Lake Group during the uplift, then a pressure range of samples from the Ponder Pluton of at least 2 kbar would be expected.

COMPARISON OF DATA FROM CARLSON CREEK AND PONDER PLUTONS

It was pointed out above that orthoclase is absent from most samples of the Carlson Creek pluton, whereas it is present in all from the Ponder pluton. According to Reaction 1, an orthoclase activity of less than 1 in the melt would result in higher Al_T in hornblende. This may explain why the Carlson Creek pluton data point falls off

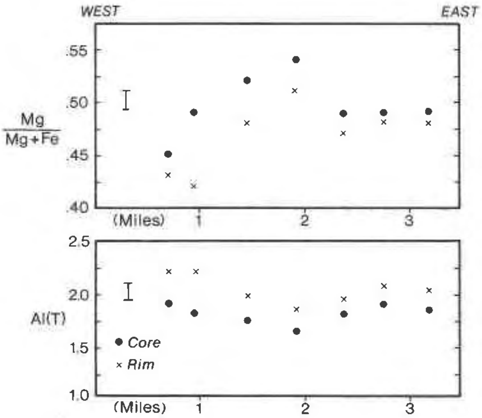

Fig. 5. Plot of Mg/(Mg + Fe) and Al_T, for average hornblende rims (×) and cores (●) vs. miles across the Carlson Creek pluton (Fig. 2). All points taken at sea level, along Tracy Arm (Fig. 4). Error bar based on multiple analyses at each locality.

the calibration curve to the high-Al side. If the Al data were taken at face value, a pressure of emplacement of the pluton would be over 1 kbar higher than obtained from the metamorphic assemblages.

On the other hand, the Carlson Creek pluton may also consist of successive pulses of magma injected along a tectonic boundary during uplift. Occurrences of kyanite west of the pluton (Stowell, 1986) suggest that higher pressures prevailed in the country rock prior to the later, lower-pressure equilibration. Note that the Al_T value of the most interior specimen (sample 21, $Al_T = 1.78$, Table 3) would fall near the calibration curve at the 4.7-kbar pressure.

The average core and rim values of all cations and the average differences for selected parameters for both plutons are given in Table 5. Because of the relatively large standard deviation of some elements, especially due to the errors inherent in the EDS system for minor elements, it is necessary to use the average of all the analyses in order to obtain the highest possible precision for the differences between cores and rims. Although the absolute value of ^{VI}Al is subject to systematic errors of Al_T and Si, the amount of change (increase) in ^{VI}Al between core and rim only carries the statistical errors of analysis.

TABLE 4. Cation proportions of hornblende in samples from Ponder pluton (Fig. 3)

	161	166	167	163	165	162	214	164	170
				Rims					
Si	7.24	7.21	7.17	7.30	7.16	6.98	6.94	6.78	6.81
Al	0.91	0.94	0.97	0.97	1.00	1.24	1.33	1.35	1.54
Fe	1.76	1.79	1.87	1.78	2.03	2.06	2.24	2.25	2.32
Mg	3.02	3.04	2.97	2.96	2.76	2.64	2.48	2.57	2.26
Ca	1.87	1.86	1.86	1.84	1.91	1.86	1.90	1.90	1.88
Na	0.20	0.29	0.31	0.26	0.18	0.37	0.26	0.29	0.36
K	0.11	0.12	0.13	0.13	0.13	0.17	0.14	0.18	0.19
Ti	0.08	0.08	0.09	0.09	0.08	0.15	0.08	0.11	0.09
Mn	0.08	0.08	0.08	0.07	0.08	0.07	0.04	0.05	0.10
				Cores					
Si	7.05	7.02	6.37	6.90	6.85	6.96	6.91	6.75	6.61
Al	1.07	1.11	1.45	1.25	1.31	1.28	1.31	1.37	1.71
Fe	1.87	1.94	1.95	2.05	2.20	2.02	2.07	2.25	2.45
Mg	2.92	2.88	2.49	2.80	2.58	2.68	2.63	2.55	2.09
Ca	1.89	1.87	1.77	1.78	1.84	1.84	1.90	1.85	1.86
Na	0.28	0.32	0.43	0.22	0.21	0.41	0.33	0.39	0.40
K	0.14	0.15	0.15	0.24	0.20	0.16	0.12	0.21	0.24
Ti	0.12	0.12	0.24	0.15	0.14	0.15	0.12	0.17	0.11
Mn	0.08	0.08	0.08	0.08	0.09	0.07	0.06	0.06	0.10

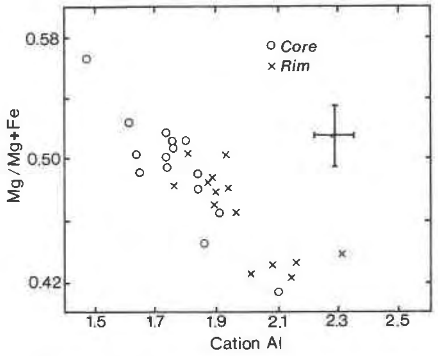

Fig. 6. Plot of Mg/(Mg + Fe) vs. Al_T for average hornblende rims (×) and cores (○) from Carlson Creek pluton.

The amount of ^{IV}Al substituting for Si can be charge balanced by combinations of the following coupled substitutions: (1) (Na + K) + ^{IV}Al = A-site vacancy + Si; (2) Ti + $2^{IV}Al$ = 2Si + (Fe + Mg); (3) Fe^{+3} + ^{IV}Al = (Fe + Mg) + Si; (4) ^{VI}Al + ^{IV}Al = Si + (Fe + Mg) (tschermakite). We presume no variation of Fe^{+3}/Fe^{+2} within single crystals and therefore neglect substitution 3. Both total alkalis and Ti for the Carlson Creek pluton increase from core to rim (Table 5). The net change is equivalent to an increase in ^{IV}Al of 0.07 atoms. This is only about one-third of the change in total Al of 0.2 atoms and implies that the major correlation of change of total Al is to ^{VI}Al and/or Mg/(Mg + Fe). Total alkalis and Ti for the Ponder pluton decrease from core to rim as does ^{IV}Al, in contrast to the Carlson Creek pluton; but for both plutons, ^{VI}Al increases. The differences in zoning may reflect

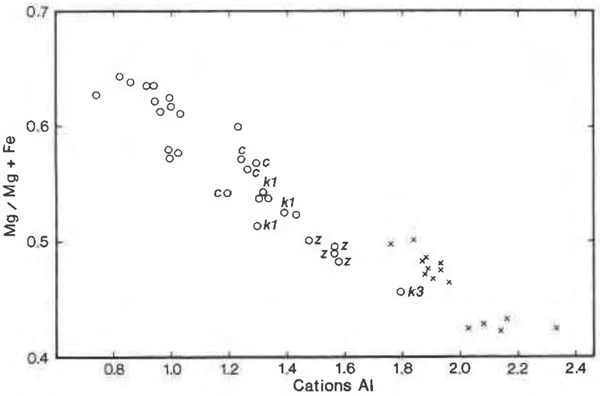

Fig. 7. Plot of Mg/(Mg + Fe) vs. total cations Al for each hornblende rim analyzed from Carlson Creek pluton (×) and from Ponder pluton (○), showing data from Chicken (c), Kenney (k1), Kateen (k3), and Zbura (Z) localities discussed in text.

TABLE 5. Average core, rim, and differences for cation proportions of hornblende, Carlson Creek and Ponder plutons

	Carlson Creek			Ponder*		
	Core	Rim	Δ	Core	Rim	Δ
Si	6.67	6.60	−0.07	6.85	7.10	+0.25
Al	1.76	1.96	+0.20	1.27	1.09	−0.18
Fe	2.29	2.36	+0.07	2.04	1.97	−0.07
Mg	2.26	2.07	−0.19	2.69	2.81	+0.12
Ca	1.83	1.82	−0.01	1.84	1.88	+0.04
Na	0.32	0.34	+0.02	0.32	0.27	−0.05
K	0.22	0.25	+0.03	0.17	0.14	−0.03
Ti	0.13	0.14	+0.01	0.15	0.09	−0.06
Mn	0.05	0.05	—	0.08	0.07	−0.01
^{IV}Al	1.33	1.40	+0.07	1.15	0.90	−0.25
Na + K	0.54	0.59	+0.05	0.49	0.41	−0.08
^{VI}Al	0.43	0.56	+0.13	0.12	0.19	+0.07
Mg/(Mg + Fe)	0.50	0.47		0.57	0.59	

* Sample 170 excluded from averages.

the absence of orthoclase from most of the Carlson Creek samples.

The average difference between core and rim in Al_T in each pluton of about 0.2 atoms is equivalent to about 1 kbar. Thus, if analyses of only the central areas of hornblende crystals are obtained for geobarometry, an additional ±0.5-kbar error may be introduced.

DISCUSSION

Our data confirm the empirical geobarometer of Hammarstrom and Zen (1986). They assumed a linear fit, based on data mainly at ~2 and ~8 kbar. Our new data fill the gap at 4–6 kbar and add points at the low- and high-pressure ends; the r^2 value of a linear fit through nine points (excluding the one for the orthoclase-deficient pluton) is 0.97. The equation of our linear fit is slightly different (Fig. 1) from theirs: P (in kilobars, ±1kbar) = $-4.76 + 5.64Al_T$.

On the basis of data from five representative samples of a pluton that probably crystallized during one intrusive event, we suggest an empirically based standard deviation for correlating Al_T in hornblende to pressure of crystallization: $\pm 0.13Al_T$.

At the end of crystallization of a calc-alkaline pluton, there seem to be sufficient thermodynamic constraints that pressure can be correlated with composition of hornblende. We have argued that temperature at solidification of calc-alkaline plutons varies relatively little, probably over a range of less than 100 deg, at pressures above 2 kbar, thus minimizing the temperature effect on hornblende composition. For pressures below 2 kbar, we suggest that the temperature effect on Al_T in hornblende may be too large to separate from the pressure effect.

Only rim compositions of unaltered hornblende should be used in the application of the geobarometer, because only these could have been in equilibrium with all phases plus the residual melt. However, many analyses of hornblende adjacent to different minerals should be obtained and averaged because this is how the data were obtained to establish the calibration curve.

Presuming our procedures are followed, the geobarometer appears to be good to ±1 kbar between 2 and 8 kbar. The decrease in error of pressure from the ±3 kbar suggested by Hammarstrom and Zen (1986) to ±1 kbar is due mainly to the new data at 4–6 kbar.

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