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Hornblende chemistry in southern Appalachian granitoids: Implications for aluminum hornblende thermobarometry and magmatic epidote stability

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ABSTRACT

Recent studies differ on whether the Al content of hornblende in granitic rocks is pressure dependent or has a temperature dependence which masks any pressure effect. To test these hypotheses, hornblendes in 15 late Paleozoic granitoids from the southern Appalachian Piedmont have been analyzed by electron microprobe. All but one of these plutons contain the assemblage hornblende + biotite + quartz + two feldspars + titanite + magnetite in apparent textural equilibrium. In addition, plagioclase rim compositions are approximately uniform, and hornblende, plagioclase, and biotite exhibit consistent distribution coefficients. Observed chemical variations in the Piedmont granitic hornblendes are attributed to hastingsite, pargasite, and CANT substitutions, summarized by the exchange vectors $^{[A]}(Na,K)^{[6]}(Fe^{3+},Al)^{[4]}Al_2{}^{[A]}\square_{-1}{}^{[6]}Mg_{-1}{}^{[4]}Si_{-2}$, $^{[6]}(Fe^{2+},Mn)^{[6]}Mg_{-1}$, and $^{[M4]}Ca^{[6]}Al^{[M4]}Na_{-1}{}^{[6]}Ti_{-1}$. Calculated pressures of emplacement for Piedmont plutons range from 2.1 to 5.1 kbar; temperatures range from 711 to 788 °C and correlate with pressure. Pressures and temperatures are comparable with those estimated from contact metamorphic assemblages. The temperature range is within the uncertainty of the geothermometer calibration; however, if the temperature differences are real, these hornblendes show both pressure- and temperature-dependent substitutions. Coexisting phases are related through a complex magmatic reaction, whose odd-even nature may restrict the pressure-sensitive hornblende substitution to only a part of the plutonic crystallization history. Epidote exhibiting textural and compositional characteristics suggestive of magmatic origin occurs in plutons emplaced at pressures of 2.8 ± 0.5 kbar or greater. This observation suggests that the occurrence of magmatic epidote in calc-alkaline plutons does not always require high pressures.

INTRODUCTION

Several recent studies have revealed that the Al content of hornblende in calc-alkaline granitoids varies linearly with pressure of crystallization, thereby providing a means of determining depth of pluton emplacement. In a mineralogic study of hornblendes from two shallow and three deep-seated calc-alkaline plutons, Hammarstrom and Zen (1986) observed a linear relationship between total Al (Al_{tot}) and pressure estimated from contact metamorphic assemblages and previous experimental work on the stability of magmatic epidote (Fig. 1):

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

Hollister et al. (1987) discussed the thermodynamic basis for this barometer and refined the empirical calibration of Hammarstrom and Zen with additional hornblende compositional data from intrusives that crystallized at intermediate pressures (Fig. 1):

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

Both groups emphasized that the barometer is restricted to calc-alkaline rocks containing the specific assemblage quartz + plagioclase + potassium feldspar + hornblende + biotite + titanite + an Fe-Ti oxide phase (magnetite or ilmenite). Unreversed, vapor-absent experiments of Rutter et al. (1989) on a partially melted tonalite at 10 kbar with unbuffered f_{O_2} demonstrate that deviations from the above assemblage (e.g., addition of garnet) may introduce significant variation in the total Al content of hornblende.

Johnson and Rutherford (1989) equilibrated the specified assemblage from natural samples of both volcanic and plutonic rocks in reversed, f_{O_2}-buffered, vapor-present experiments over the range from 2 to 8 kbar at 740–780 °C. Their results yielded the following relationship (Fig. 1):

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$$P\ (\pm 0.5\ \text{kbar}) = -3.46 + 4.23\ \text{Al}_{\text{tot}}, \qquad r^2 = 0.99. \quad (3)$$

Both Johnson and Rutherford (1989) and Hollister et al. (1987) suggested that the pressure-sensitive hornblende exchange vector is $^{[4]}\text{Al}^{[6]}\text{Al}^{[4]}\text{Si}_{-1}{}^{[6]}\text{Mg}_{-1}$.

The aluminum hornblende geobarometer has been criticized by Blundy and Holland (1990), who concluded from a review of hornblende synthesis data that the Al content of hornblende is primarily temperature dependent in subassemblages of the specified assemblage. They proposed a geothermometer based on the exchange vector $^{[A]}\text{Na}^{[4]}\text{Al}^{[A]}\square_{-1}{}^{[4]}\text{Si}_{-1}$ for hornblende coexisting with plagioclase in silica-saturated rocks.

These studies illustrate that the factors controlling Al substitutions in natural hornblendes are not yet satisfactorily resolved. In order to assess possible relationships between pressure, temperature, and hornblende compositions in granitic systems, we have undertaken a chemical study of hornblendes from 15 late Paleozoic granitoid plutons in the southern Appalachian Piedmont.

Studies of experimentally synthesized and naturally occurring epidotes indicate that this phase may crystallize directly from calc-alkaline magmas under appropriate conditions. Naney (1983) investigated the stabilities of common ferromagnesian silicates in synthetic granodiorite systems as functions of temperature and H_2O content at pressures of 2 and 8 kbar. Epidote was reported to be in equilibrium with melt in the experiments at 8 kbar, but was absent at 2 kbar. Zen and Hammarstrom (1984) described magmatic epidote in several granodiorite plutons and concluded, on the basis of Naney's experimental work and their own pressure estimates from contact aureoles, that the plutons crystallized at pressures of $\approx$8 kbar. The empirical aluminum hornblende barometers of Hammarstrom and Zen (1986) and Hollister et al. (1987) were calibrated using this pressure, but Zen and Hammarstrom (1988) have since argued that the minimum pressure required to crystallize epidote from a tonalite melt may be 6 rather than 8 kbar. Johnson and Rutherford (1989) noted that use of an emplacement pressure of 6 kbar for plutons containing magmatic epidote reduces the discrepancy between the empirical and experimental calibrations of the aluminum hornblende barometer (Fig. 1). Epidote which exhibits textural relationships and compositions similar to those described as magmatic by Zen and Hammarstrom (1984, 1986) and Tulloch (1986) is present in many of the southern Appalachian plutons. Its occurrence, when coupled with aluminum hornblende barometric data, provides additional information on the significance of this phase with respect to pressure.

GEOLOGIC SETTING AND PROPERTIES OF PIEDMONT GRANITOID PLUTONS

In the southern Appalachian Piedmont, at least 50 texturally and compositionally similar, late Paleozoic granitoid plutons form an arcuate chain that stretches from Virginia into Georgia (Sinha and Zeitz, 1982). We have sampled the 15 granitoids of this suite which contain primary amphibole (Table 1). The plutons analyzed outcrop in every lithostructural belt east of the Inner Piedmont belt (Fig. 2), the eastern boundary of which marks the westernmost limit of documented Alleghanian metamorphism (Horton et al., 1987).

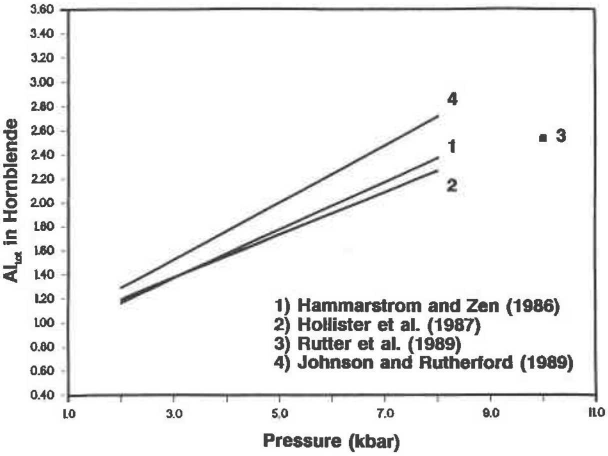

Fig. 1. Aluminum hornblende geobarometer calibrations. Regressions 1 and 2 are empirical calibrations; regression 4 is an experimental calibration. Point 3 represents an unreversed melting experiment which contains the critical assemblage necessary for aluminum hornblende barometry.

The granitoids consist of up to three distinctive facies that have been recognized on the basis of texture and mineralogy (Speer et al., 1980): (1) coarse-grained granitoids with assemblages of biotite, biotite + amphibole, biotite + cordierite, or biotite + muscovite ± garnet, (2) fine-grained biotite-bearing granitoids, and (3) medium-grained biotite + muscovite ± garnet-bearing granitoids. This classification is supported by slight but systematic variations in mineral chemistry, accessory phases, and modal, chemical, and isotopic compositions (McSween et al., 1991). All three groups have average modes that are monzogranitic (Speer et al., 1980; McSween et al., 1991) and a limited range that clusters around the boundary between metaluminous and peraluminous compositions (Gates et al., 1988). Some Piedmont granitoids are uniform bodies consisting predominantly of one textural and mineralogic facies, but most are composite bodies containing more than one facies (Speer et al., 1980). In composite plutons, contacts between facies that differ only in mineralogy are generally gradational and are believed to result from physical and chemical gradients that existed during or after crystallization. In contrast, contacts between facies that differ primarily in texture are sharp and are interpreted to reflect multiple intrusive episodes (Speer et al., 1980; McSween et al., 1991). The 15 coarse-grained, amphibole-bearing granitoids investigated in this study usually occur in composite plutons with coarse-grained, biotite-bearing granitoids.

Although these plutons are calc-alkaline, their compositions (granite to quartz monzonite) differ from those

Table 1. Late Paleozoic amphibole-bearing plutons

Pluton and state	Map code	Age (Ma)	Method	Best descriptions
Bald Rock, South Carolina	BR	290 ± ?	Rb-Sr Bt (3)	(7)
Butterwood Creek, North Carolina	BC	293 ± 15	Rb-Sr WR (6)	(8), (9)
Castalia, North Carolina	CS	314 ± 11	Rb-Sr WR (6)	(9)
Clover, North Carolina	CL	306 ± 4	Rb-Sr RB (2)	(1), (6), (15)
Dort, Virginia	DO	N.A.		(10)
Graniteville, South Carolina	GV	>305*		(11)
Harbison, South Carolina	HB	309 ± 3	Rb-Sr RB (2)	(1), (6), (15)
Landis, North Carolina	LD	285 ± 55	Rb-Sr WR (6)	(1), (6), (15)
Liberty Hill, South Carolina	LH	295 ± 16	Rb-Sr WR (6)	(12), (13)
		302 ± 1	Ar-Ar Hb (5)	
Lowrys, South Carolina	LO	330 ± 3**	Rb-Sr RB (2)	(1), (6), (15)
Mooresville, North Carolina	MV	N.A.		(1), (6), (15)
Pageland, South Carolina	PG	297 ± 9	Rb-Sr Bt (6)	(1), (6), (15)
		302 ± 1	Ar-Ar Hb (5)	
Rocky Mount, North Carolina	RM	345 ± 1	Rb-Sr WR (4)	(9)
Siloam, Georgia	SM	264 ± 3	Rb-Sr WR (1)	(14)
Winnsboro, South Carolina	WN	295 ± 2	Rb-Sr WR (6)	(1), (6), (15)
		285 ± 6	Ar-Ar Hb (3)	

Note: N.A. indicates that no isotopic age is available. Isotopic dating methods are (Rb-Sr) rubidium-strontium or (Ar-Ar) argon 40–argon 39 on (WR) whole rock, (Bt) biotite, (RB) whole rock and biotite, (Hb) hornblende. Numbers in parentheses refer to the following references: (1) Fullagar and Butler (1979), (2) Fullagar and Kish (1981), (3) Dallmeyer et al. (1986), (4) Fullagar and Spruill (1989), (5) Atekwana et al. (1989), (6) McSween et al. (1991), (7) Speer et al. (1986), (8) Russell et al. (1985), (9) Farrar (1985), (10) Becker (1981), (11) Speer (1982), (12) Speer (1987), (13) Speer et al. (1989), (14) Vincent (1984), (15) Speer et al. (1980).

* A pegmatite dike which crosscuts the Graniteville pluton has been dated at 305 Ma (no uncertainty reported) by Rb-Sr whole rock methods (P.D. Fullagar, personal communication).

** The 330 Ma age for the Lowrys pluton is disputed. Fullagar (1971) reported an age of 399 ± 4 Ma for the granitoid. However, the sample dated may have a closer affinity with rocks of the ≈400 Ma Salisbury plutonic complex. Based on the petrographic similarity between the Lowrys pluton and the other Alleghanian granitoids, the 330 Ma age is preferred.

(granodiorite to tonalite) used for the empirical calibrations of the aluminum hornblende barometer (Hammarstrom and Zen, 1986; Hollister et al., 1987) and for which the high-pressure origin of magmatic epidote has been argued (Zen and Hammarstrom, 1984). However, the experimental calibration of the barometer (Johnson and Rutherford, 1989) included a rhyolite sample with 75.5 wt% silica.

The crystallization ages of the plutons analyzed range from 345 to 264 Ma, with most between 330 and 290 Ma (Table 1), which is broadly coincident with the Alleghanian orogeny (Glover et al., 1983). Intrusion of most of the granitoids postdates regional peak Alleghanian metamorphism (Fullagar and Butler, 1979; Speer et al., 1980; McSween et al., 1991), but may be pre-, syn-, or postdeformational with respect to movement on numerous dextral, strike-slip shear zones that span the length of the Appalachians (Gates et al., 1988).

ANALYTICAL METHODS

All mineral analyses were performed at the University of Tennessee using a fully automated Cameca SX-50 electron microprobe equipped with a four-spectrometer, wavelength-dispersive system. Operating conditions were maintained at an accelerating voltage of 15 kV and a beam current of 20 nA. A beam size of 5 μm was used on amphibole and biotite grains, whereas a defocused beam of 10 μm was used on plagioclase grains to limit Na loss. Analyses of amphibole rims were obtained within 15 μm of grain boundaries, and at least two amphibole grains were analyzed from each polished section. In general, analytical methods for amphibole followed those of Hollister et al. (1987) and Pe-Piper (1988). Analyses with oxide totals outside the range 96.5–98.5 wt%, or those with fewer than 15 cations were rejected. Biotite and plagioclase analyses represent single points, but several analyses were collected for each amphibole grain with the results averaged to provide representative core and rim compositions. Although only amphibole from the Lowrys pluton exhibited systematic core-to-rim zoning, rim compositions were used in temperature and pressure calculations for all the plutons.

Chemical formulas were calculated from the amphibole analyses according to Robinson et al. (1982). The contents of Fe^{3+} and Fe^{2+} were partitioned in the following manner. First, formulas were calculated assuming that cations sum to 13, excluding Ca, Na, and K (13eCNK), and that all Fe is ferrous. Second, charge deficiencies in the amphibole formulas were removed by converting Fe^{2+} to Fe^{3+}; the resulting chemical formulas contain the maximum amount of Fe^{3+} consistent with the crystal structure of calcic amphibole. Amphibole formulas calculated in this manner have Fe^{3+}/Fe_{tot} ratios comparable to those determined by wet chemical methods in other calc-alkaline plutons with similar mineral assemblages (Table 2). Johnson and Rutherford (1989) have shown that the relationship between Al_{tot} and pressure is identical regardless of whether amphibole analyses are reformulated to 23 O atoms or 15 cations exclusive of Na and K; the 13eCNK reformulation also yields the same relationship, to within 0.1 kbar.

Epidote grains were analyzed using the same conditions as those for amphibole, except that a beam current of 30 nA was used to allow for detection of Ce, La, Y,

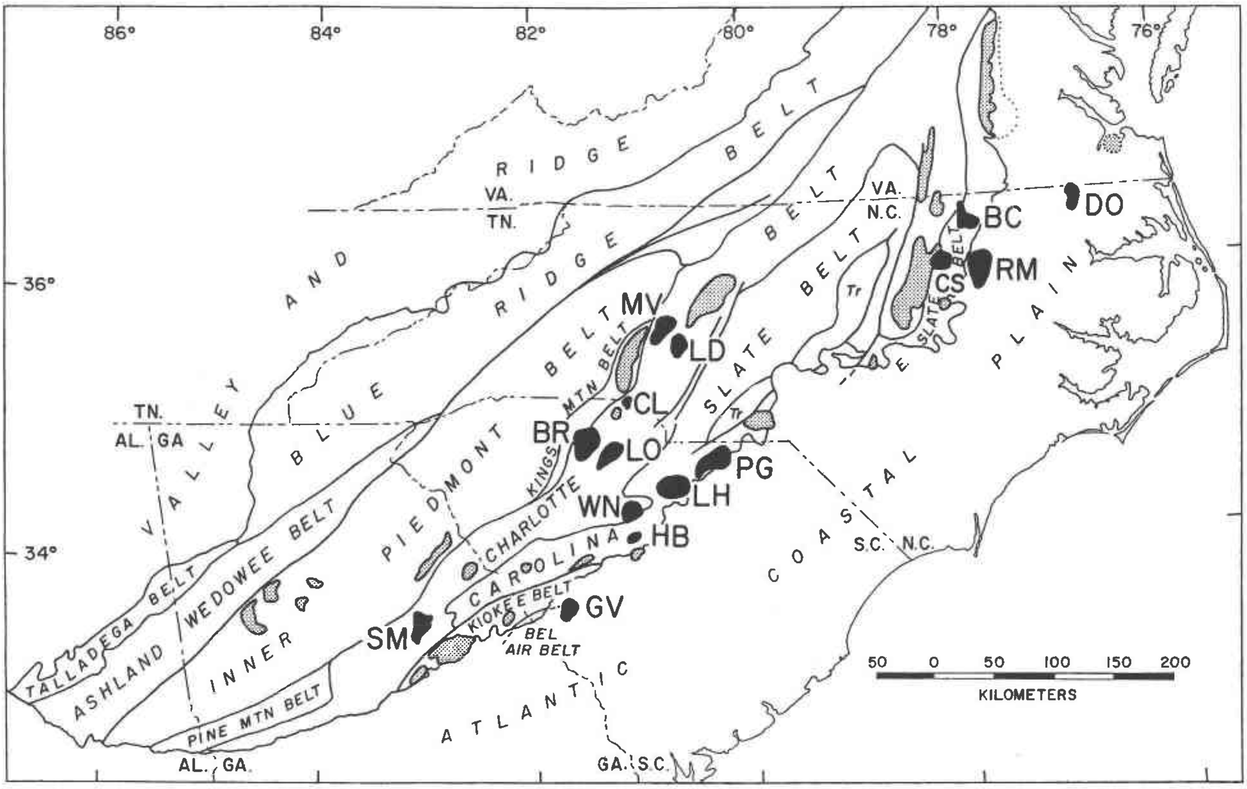

Fig. 2. Geologic setting for Alleghanian granitoids in the southern Appalachians. Black patterns indicate hornblende-bearing plutons investigated in this study, and stippled patterns represent other plutons of equivalent age that do not contain hornblende. Pluton abbreviations are given in Table 1.

and Th. Epidotes exhibiting apparent primary and secondary textural relationships were analyzed in samples from six plutons.

To test for disequilibrium between phases and to identify the principal hornblende substitution mechanisms, various cations and cation ratios were compared and linear regressions were calculated using the reduced major axis (RMA) regression (Davis, 1986), which makes no assumptions regarding the independence of variables and is therefore more appropriate for compositional data than the least-squares regression. Only RMA regression equations with correlation coefficients greater than 0.5 have been reported in this study.

The data include analyses of 64 biotite samples, 82 plagioclase samples, 19 epidote samples, and 109 averages of 573 individual amphibole analyses. A compilation of all data (except for epidote) can be found in Vyhnal (1989).

AMPHIBOLE CRYSTAL CHEMISTRY AND THERMOBAROMETRY

Amphibole classification

Representative hornblende analyses and an assessment of analytical precision are presented in Table 3. In the IMA-approved nomenclature (Leake, 1978), these amphiboles are classified as ferro-actinolite, edenite, ferro-edenite, ferro-edenitic hornblende, and hastingsitic hornblende. Figure 3 shows a simplified classification in which most of the amphibole analyses cluster within the hastingsite, edenite, and hornblende fields (for simplicity,

TABLE 2. Fe^{3+}/Fe_{tot} ratios in hornblendes

Rock type	Fe^{3+}/Fe_{tot} hornblende	Reference
Quartz diorite	0.16*	Yamazaki (1967)
Granite	0.12–0.29*	Dodge et al. (1968)
Granodiorite	0.16*	Czamanske & Wones (1973)
Quartz diorite, tonalite	0.32*	Chivas (1981)
Quartz monzonite	0.22–0.25*	Hammarstrom & Zen (1986)
Quartz diorite, tonalite, granodiorite, granite	0.27*	Hammarstrom & Zen (1986)
Piedmont monzogranites	0.12–0.29**	This study

* Determined by wet-chemical analysis.

** Calculated from 13eCNK reformulation of microprobe analyses (see text).

TABLE 3. Representative hornblende analyses

Pluton average of (n) points		PG 20	BR 6	BC 6	LD 6	SM 6	DO 6
Wt% oxides	SiO_2	41.07 (12)	42.17	45.80	43.36	43.06	40.91
	TiO_2	1.84 (3)	0.87	1.09	1.11	1.15	0.61
	Al_2O_3	8.49 (8)	10.43	7.31	9.32	8.09	11.38
	MgO	4.09 (4)	8.46	11.73	9.12	6.36	7.37
	CaO	10.37 (13)	11.58	11.43	11.39	10.99	11.37
	MnO	1.14 (5)	0.48	0.94	0.72	1.07	0.46
	FeO	26.49 (26)	20.23	16.03	19.56	23.97	22.26
	Na_2O	2.10 (4)	1.43	1.67	1.55	1.57	1.62
	K_2O	1.17 (3)	1.41	1.02	1.30	1.16	1.60
	Total	96.76	97.06	97.02	97.43	97.42	97.58
Cations 13eCNK	Si	6.537	6.445	6.850	6.574	6.672	6.273
M1-, M2-, M3-sites	$^{[4]}Al$	1.463	1.555	1.150	1.426	1.328	1.727
	$^{[6]}Al$	0.130	0.325	0.139	0.240	0.150	0.331
	Fe^{3+}	0.470	0.538	0.424	0.525	0.559	0.724
	Ti	0.220	0.100	0.123	0.127	0.134	0.070
	Mg	0.970	1.927	2.615	2.061	1.469	1.684
	Fe^{2+}	3.056	2.048	1.581	1.955	2.548	2.131
	Mn	0.154	0.062	0.119	0.092	0.140	0.060
M4-site	Ca	1.769	1.896	1.832	1.850	1.825	1.868
	Na	0.231	0.104	0.168	0.150	0.175	0.132
A-site	Na	0.417	0.320	0.316	0.306	0.296	0.350
	K	0.238	0.275	0.195	0.251	0.229	0.313
	Total	15.654	15.595	15.511	15.558	15.526	15.663
	F/FM	0.76	0.52	0.38	0.49	0.63	0.56
	Fe/Mg	3.15	1.06	0.60	0.95	1.73	1.27
	$^{[M4]}Na/^{[4]}Ca$	0.13	0.05	0.09	0.08	0.10	0.07
	Al_{tot}	1.593	1.879	1.289	1.666	1.478	2.057
	A-site	0.654	0.595	0.511	0.558	0.526	0.663

Note: Pluton codes are given in Table 1. Numbers in parentheses are 1σ standard deviations, reported to the least significant figure, for 20 replicate analyses of one grain.

these will hereafter be referred to as hornblende). The remainder are actinolite which forms patchy intergrowths within, or thin discontinuous rims around hornblende. Following Leake (1971) and Chivas (1981), we interpret the actinolite to be a product of subsolidus crystallization because it contains >7.25 Si atoms per 13eCNK.

Coupled substitutions in amphibole

There are a number of substitution mechanisms in amphibole which involve coupling of cations with different valence states to maintain charge balance. Assuming a compositionally simple end-member such as tremolite as the starting material, some common coupled substitutions include

Site/charge balance equation	**Substitution**
${}^{[A]}\square + {}^{[4]}\mathrm{Si} = {}^{[A]}\mathrm{Na} + {}^{[4]}\mathrm{Al}$	edenite
$2{}^{[4]}\mathrm{Si} + 2{}^{[6]}\mathrm{Mg} = 2{}^{[4]}\mathrm{Al} + 2{}^{[6]}\mathrm{Fe}^{3+}$	iron tschermakite
$2{}^{[4]}\mathrm{Si} + 2{}^{[6]}\mathrm{Mg} = 2{}^{[4]}\mathrm{Al} + 2{}^{[6]}\mathrm{Al}$	aluminum tschermakite
$2{}^{[4]}\mathrm{Si} + {}^{[6]}\mathrm{Mg} = 2{}^{[4]}\mathrm{Al} + {}^{[6]}\mathrm{Ti}$	titanium tschermakite
${}^{[A]}\square + {}^{[6]}\mathrm{Mg} + 2{}^{[4]}\mathrm{Si} = {}^{[A]}\mathrm{Na} + {}^{[6]}\mathrm{Fe}^{3+} + 2{}^{[4]}\mathrm{Al}$	hastingsite
${}^{[A]}\square + {}^{[6]}\mathrm{Mg} + 2{}^{[4]}\mathrm{Si} = {}^{[A]}\mathrm{Na} + {}^{[6]}\mathrm{Al} + 2{}^{[4]}\mathrm{Al}$	pargasite
${}^{[A]}\square + {}^{[M4]}\mathrm{Ca} = {}^{[A]}\mathrm{Na} + {}^{[M4]}\mathrm{Na}$	richterite
$2{}^{[M4]}\mathrm{Ca} + 2{}^{[6]}\mathrm{Mg} = 2{}^{[M4]}\mathrm{Na} + 2{}^{[6]}\mathrm{Fe}^{3+}$	riebeckite
$2{}^{[M4]}\mathrm{Ca} + 2{}^{[6]}\mathrm{Mg} = 2{}^{[M4]}\mathrm{Na} + 2{}^{[6]}\mathrm{Al}$	glaucophane

where ${}^{[A]}\square$ indicates vacancy in the A-site. Only the edenite and aluminum tschermakite substitutions are linearly independent.

A plot of ${}^{[A]}(\mathrm{Na} + \mathrm{K})$ vs. ${}^{[4]}\mathrm{Al}$ is shown in Figure 4a, with end-members indicated for various substitutions. The linear regression equation has a slope of 0.77, implying dominance of the hastingsite-pargasite substitution, a linear combination of edenite and tschermakite. The intercept of the regression line at ${}^{[4]}\mathrm{Al} \approx 0.2$ indicates that not all ${}^{[4]}\mathrm{Al}$ is coupled with alkalies in the A-site. Couplings of ${}^{[4]}\mathrm{Al}$ with octahedral cations (Figs. 4b and 4c) support this inference. Because Fe^{3+} is the dominant R^{3+} cation, the hastingsite component dominates over the pargasite component in these amphibole samples. The importance of the hastingsite component in hornblende from granitic rocks was previously recognized by Czamanske and Wones (1973).

Various cations are plotted against ${}^{[M4]}\mathrm{Na}$ in Figure 5. No correlation is observed between ${}^{[M4]}\mathrm{Na}$ and either A-site occupancy (Fig. 5a) or Fe^{3+} (Fig. 5b), as would be expected for simple richterite and riebeckite substitutions, respectively. The negative correlation between ${}^{[6]}\mathrm{Al}$ and ${}^{[M4]}\mathrm{Na}$ (Fig. 5c) is in the opposite sense from that expected for the glaucophane substitution. Instead, this

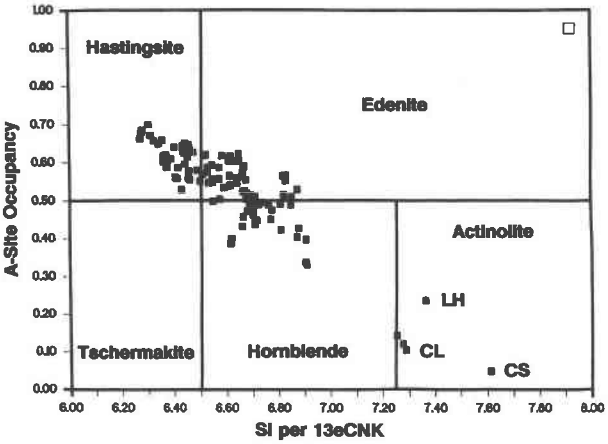

Fig. 3. Classification of calcic amphibole, modified from Leake (1978). The hastingsitic and tschermakitic hornblende fields of Leake have been combined with the hastingsite and tschermakite fields. Hastingsite and actinolite are used in preference to pargasite and tremolite, respectively, because $Fe^{3+} > {}^{[6]}Al$ and $Fe^{2+} > Mg$ in most analyses. Actinolite samples are from the Castalia (CS), Clover (CL), and Liberty Hill (LH) plutons. The term 13eCNK indicates the amphibole reformulation scheme used (see text). Open box in the upper right corner indicates 1σ uncertainty for 20 replicate analyses of a representative hornblende.

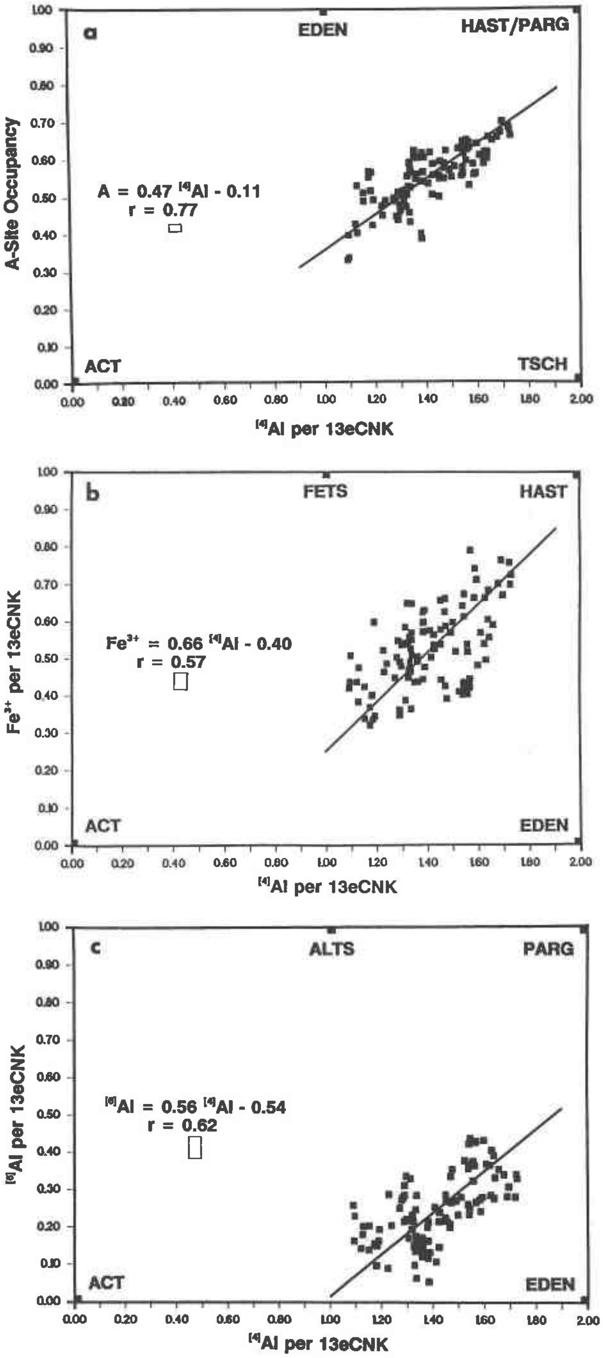

Fig. 4. Plots illustrating $^{[4]}Al$ substitition mechanisms in hornblendes: **(a)** A-site occupancy vs. $^{[4]}Al$, **(b)** Fe^{3+} vs. $^{[4]}Al$, and **(c)** $^{[6]}Al$ vs. $^{[4]}Al$. End-member amphibole compositions are: actinolite (ACT), edenite (EDEN), hastingsite (HAST), pargasite (PARG), aluminum tschermakite (ALTS), and ferric-tschermakite (FETS); TSCH refers to all tschermakite-type substitutions. Open boxes indicate 1σ uncertainties for 20 replicate analyses of a representative hornblende.

correlation and one between Ti and $^{[M4]}Na$ (Fig. 5d) imply a substitution of the form $^{[M4]}Ca + {}^{[6]}Al = {}^{[M4]}Na + {}^{[6]}Ti$, hereafter referred to as CANT. Although Czamanske and Wones (1973) first suggested that this substitution is plausible, to our knowledge this is its first reported occurrence in natural amphibole. This is a relatively minor substitution, however, accounting for <8% of the octahedral site occupancy in these hornblende samples.

Simple substitutions in amphibole

Simple 1:1 substitutions that do not require coupling of cations to maintain charge balance are observed for the divalent, octahedral cations (R^{2+}) in the Piedmont granitic hornblende samples. In Figure 6, Fe^{2+} + Mn is plotted against Mg. The regression equation has a slope of nearly -1, and the excellent correlation observed indicates that a simple substitution of Fe^{2+} or Mn for Mg adequately explains the relative proportions of these cations. This is an important point for the following reason: if dioctahedral substitutions ($3R^{2+}$ cations = $2R^{3+}$ cations) are observed, the 13eCNK reformulation is invalid because charge balance can be maintained despite vacancies in the octahedral sites. However, the relationship observed in Figure 6 indicates that R^{2+} cations are coupled with each other rather than with R^{3+} cations and therefore confirms that the 13eCNK reformulation is valid for these hornblende samples.

Textural equilibrium of the critical assemblage

For aluminum hornblende barometry to be applicable, quartz + plagioclase + potassium feldspar + hornblende

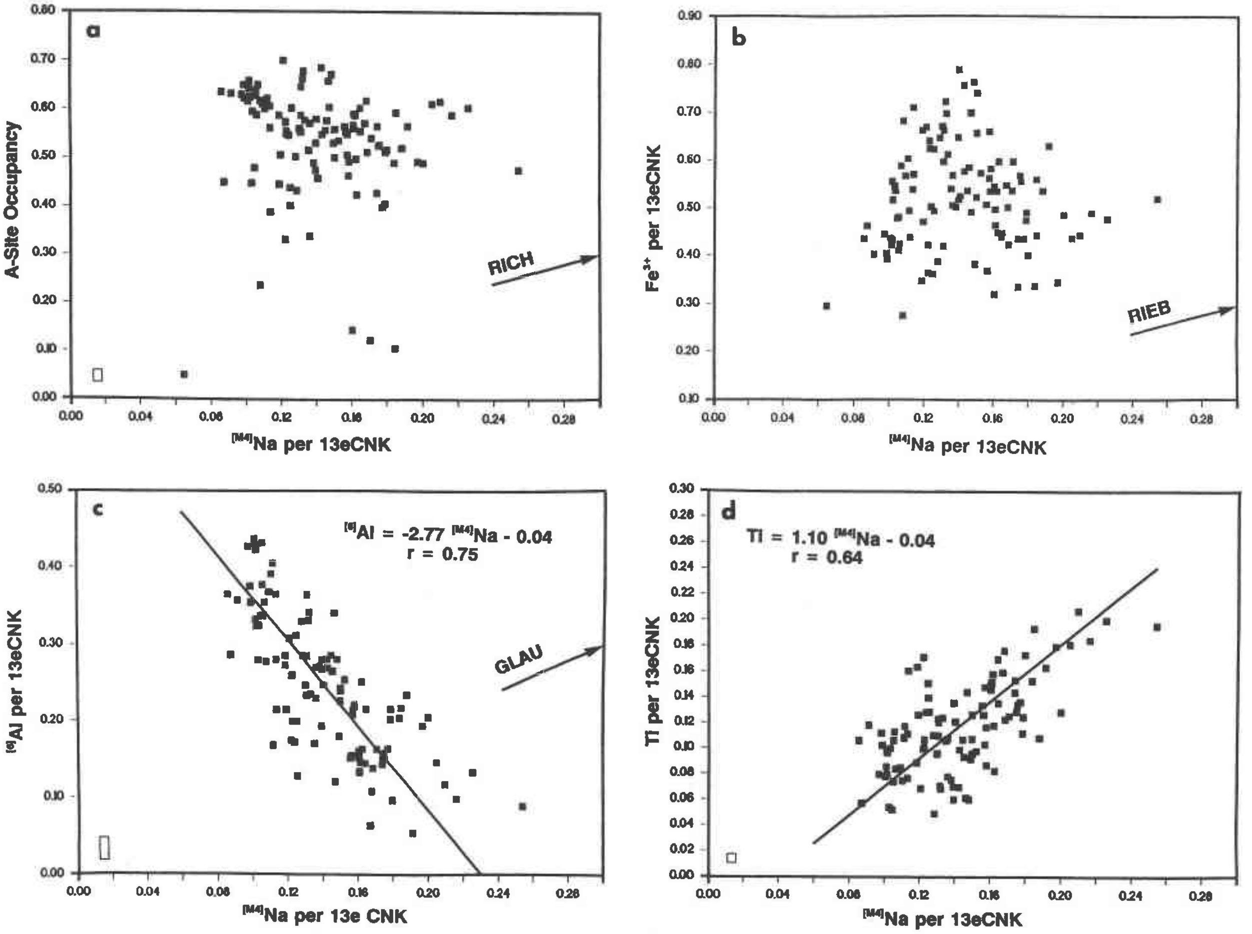

Fig. 5. Plots illustrating $^{[M4]}$Na substitution mechanisms in hornblendes: (**a**) A-site vs. $^{[M4]}$Na, (**b**) Fe^{3+} vs. $^{[M4]}$Na, (**c**) $^{[6]}$Al vs. $^{[M4]}$Na, (**d**) Ti vs. $^{[M4]}$Na. Substitution vectors for richterite (RICH), riebeckite (RIEB), and glaucophane (GLAU) are shown. Open boxes in lower left corners indicate 1σ uncertainties for 20 replicate analyses of a representative hornblende.

+ biotite + titanite + magnetite or ilmenite must represent a magmatic, equilibrium assemblage (Hammarstrom and Zen, 1986; Hollister et al., 1987; Rutter et al., 1989; Johnson and Rutherford, 1989). All of these minerals (± ilmenite) are present in the thin sections we analyzed.

Plagioclase in Piedmont granitoids exhibits normal or oscillatory zoning with cores generally of An_{25-30} and rims of An_{10-20}. Although rim compositions are slightly more sodic than those observed by Hollister et al. (1987), they still have a narrow compositional range and therefore provide the additional restriction necessary for the Al content in hornblende to be solely a function of pressure (Hollister et al., 1987). The larger plagioclase grains commonly contain small inclusions of hornblende and biotite (with compositions indistinguishable from matrix grains), which may be arranged in concentric growth zones. Plagioclase is variably altered to fine-grained epidote, calcite, and quartz. The potassium feldspar is microcline or microcline microperthite and may have a cloudy appearance as a result of sericitic alteration. Potassium feldspar grains may contain small inclusions of biotite and quartz. Quartz grains vary considerably in size, and most grains exhibit polygonal outlines. Quartz occurs in association with feldspars and as inclusions in hornblende and biotite.

Color indices of the granitoids are never >20, and are usually <10. All of the mafic phases tend to occur together as interstitial clots between the felsic minerals. Biotite is the most abundant mafic phase and is generally several millimeters in size. Inclusions in biotite commonly consist of apatite, allanite, hornblende, quartz, feldspar, titanite, epidote, zircon, and opaque oxides. Chlorite and rutile may occur as alteration products.

Hornblende is usually larger and more euhedral than biotite, and some grains are twinned. The phases included in biotite may also be present in hornblende. In addition, hornblende may contain inclusions of biotite, and the two phases are commonly intergrown. Rare clinopyroxene xenocrysts with concentric rims of actinolite and hornblende are present in the Liberty Hill pluton and have been interpreted as resulting from incomplete re-

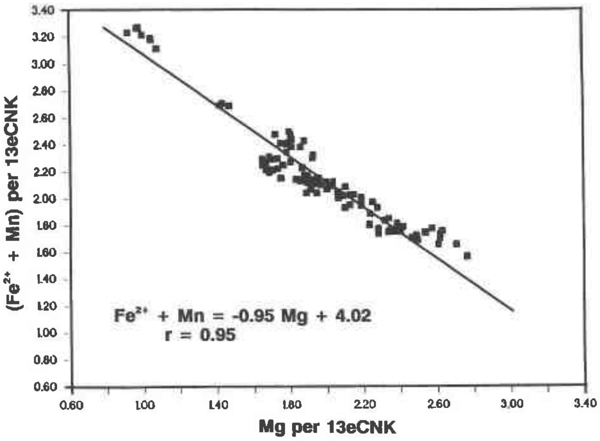

Fig. 6. Simple substitutions of Fe^{2+} and Mn for Mg in hornblende. Error bars of 1σ are smaller than the plotted points.

action of high-pressure clinopyroxene with melt (Speer, 1988). Thin (<10 μm), discontinuous pargasite and actinolite rims are also associated with several hornblende samples from the Liberty Hill pluton. Although the origin of these rims is poorly understood, similar relationships between actinolite and hornblende have been described by a number of authors (Czamanske and Wones, 1973; Chivas, 1981; Hendry et al., 1985; Yamaguchi, 1985; Speer, 1987; Pe-Piper, 1988). Hornblende occurs in the Castalia pluton only as small grains partially rimmed by actinolite and completely included within quartz grains. The hornblende in this pluton is therefore isolated from the rest of the critical assemblage. Hornblende in the Clover pluton forms patchy intergrowths with actinolite.

Titanite occurs as euhedral to subhedral crystals up to a few millimeters in size. Titanite almost invariably contains inclusions of magnetite and may also form thin rims around magnetite and biotite, in what has been interpreted as a secondary texture (Speer, 1987). Magnetite is present as subhedral to euhedral grains generally <1 mm in size. Speer (1987) recognized ilmenite exsolution lamellae in magnetite in amounts <10 vol%.

Textural relationships in the coarse-grained granitoids suggest that magnetite, plagioclase, and potassium feldspar crystallized early and were followed shortly thereafter by biotite, hornblende, quartz, and titanite (Speer et al., 1986). This supports the hypothesis that all phases of the critical assemblage (including melt) were present when hornblende formed. An exception is the Castalia pluton in which amphibole occurs only as isolated inclusions.

Chemical equilibrium of the critical assemblage

Additional evidence consistent with equilibrium among the phases of the critical assemblage comes from chemical analyses of the phases with the most variable compositions—plagioclase, biotite, and hornblende.

Spear (1980) demonstrated that, for hornblende in equilibrium with plagioclase, the amount of $^{[M4]}Na$ in hornblende bears a systematic relationship to the albite component in plagioclase. Accordingly, rim compositions of plagioclase and hornblende were averaged by sample, with Na/Ca in plagioclase plotted against Na/Ca in the M4-site in hornblende (Fig. 7). A reasonable correlation is observed (excepting one Castalia sample in which hornblende is isolated from plagioclase), supporting the suggestion that plagioclase and hornblende have attained chemical equilibrium in Piedmont granitoids.

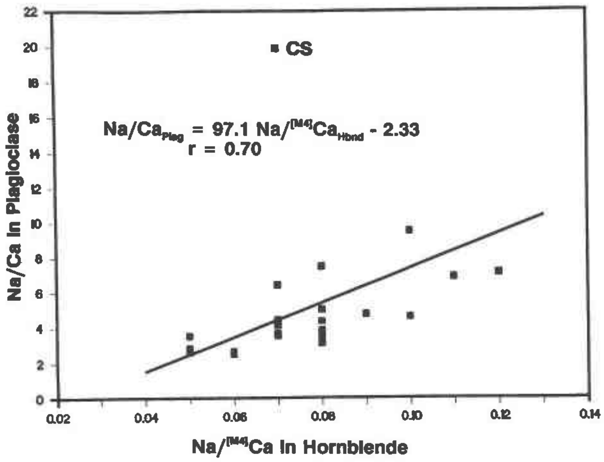

Fig. 7. Distribution of Na and Ca in coexisting hornblende and plagioclase rims averaged and plotted by sample. Point CS represents data from the Castalia pluton, in which hornblende is isolated from plagioclase.

A similar plot of Fe^{2+}/Mg ratios in biotite vs. hornblende rims is shown in Figure 8. The linear regression for the data has a slope of ≈1, and the excellent correlation observed indicates that biotite and hornblende have achieved equilibrium. Fe^{2+}/Mg distribution coefficients near unity between coexisting biotite and hornblende have been observed in other granites and have been interpreted to reflect formation of biotite through replacement of hornblende in the presence of a melt (Mason, 1985).

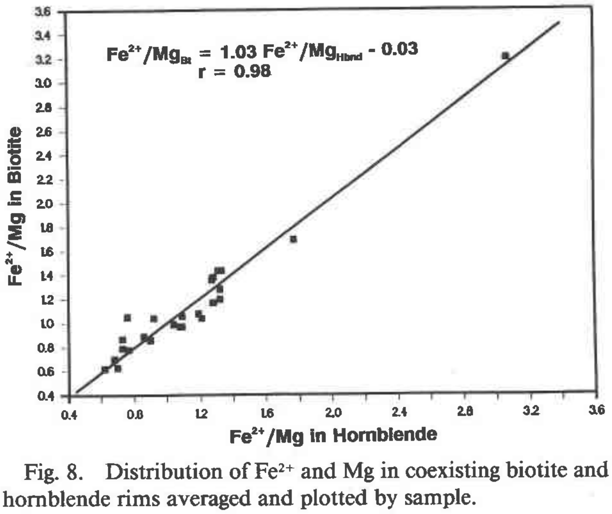

Fig. 8. Distribution of Fe^{2+} and Mg in coexisting biotite and hornblende rims averaged and plotted by sample.

Table 4. Pluton emplacement pressures and equilibration temperatures

Pluton	Number of hornblendes averaged	Average pressure (kbar)	Temperature (°C)
Bald Rock	7	4.8 ± 0.5	773
Butterwood Creek	3	2.1 ± 0.5*	711
Castalia	3	3.0 ± 0.7	666
Clover	1	3.4 ± 0.5**	377
Dort	4	5.1 ± 0.5	774
Graniteville	1	3.2 ± 0.5	738
Harbison	4	2.9 ± 0.5	730
Landis	5	3.7 ± 0.5	744
Liberty Hill	6	2.8 ± 0.5	735
Lowrys	4	2.8 ± 0.6	724
Mooresville	4	5.0 ± 0.5	777
Pageland	5	3.0 ± 0.5	736
Rocky Mount	6	4.3 ± 0.5	760
Siloam	2	4.5 ± 0.5	788
Winnsboro	5	3.0 ± 0.5	715

Note: Pressure estimates are based on the experimental calibration of Johnson and Rutherford (1989). Temperature estimates are based on the hornblende-plagioclase geothermometer of Blundy and Holland (1990), which has a reported uncertainty of ±75 °C.

* The 2.1 kbar estimate for the Butterwood Creek pluton is from the undeformed portion of the granitoid east of the Hollister shear zone. Hornblende from the deformed granitoid west of this fault gives an estimated pressure of 3.1 ± 0.5 kbar at the same temperature.

** The hornblende grain used in the Clover pressure estimate has an oxide total of 95.68 wt%. Although this falls outside the range of accepted oxide totals, it has been included here for completeness.

Systematic zoning of hornblende was not observed in any samples except those from the Lowrys pluton, where rim compositions are enriched in $^{[4]}$Al, $^{[6]}$Al, Fe^{3+}, Ca, $^{[A]}$Na, and Fe/(Mg + Fe). These analyses were from one sample that may have been an enclave and may thus be unrepresentative of hornblende in the pluton.

Calculated pressures and temperatures of emplacement

Crystallization pressures for each pluton (Table 4) have been calculated from hornblende rim compositions using the calibration of Johnson and Rutherford (1989). Although these authors indicate an absolute uncertainty of ±0.5 kbar, the relative analytical uncertainty associated with each pressure estimate is considerably less (Vyhnal, 1989). We suggest that pressure differences of at least 0.5 kbar are probably real and significant, with the following qualifications: hornblende in the Clover pluton contains patchy domains of actinolite that may have contaminated our analyses of this sample, and hornblende in the Castalia pluton occurs only as inclusions that are isolated from the critical assemblage. Zoned hornblende in the Lowrys pluton probably indicates a minimum pressure.

Blundy and Holland (1990) noted a strong temperature dependence of Al$_{tot}$ in hornblende coexisting with plagioclase, and suggested that barometric comparisons would only be valid if all rocks equilibrated at the same temperature. Using Blundy and Holland's geothermometer, we determined the equilibration temperatures for all the plutons included in this study (Table 4). Temperatures for the plutons for which we have reliable pressure estimates (i.e., those in Table 4 excluding the Castalia, Clover, and possibly Lowrys plutons) range from 711 to 788 °C.

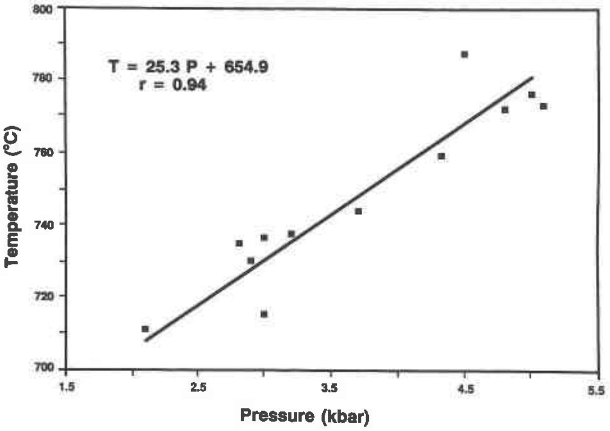

Fig. 9. Relationship between equilibration temperature, calculated from the hornblende-plagioclase geothermometer of Blundy and Holland (1990), and emplacement pressure, calculated from the aluminum-hornblende barometer of Johnson and Rutherford (1989).

There are several ways to interpret the temperature data. Given that the reported uncertainty for this calibration is ±75 °C (Blundy and Holland, 1990), the hornblende equilibration temperatures for all these plutons might be considered to be the same, within analytical error. In this case, there is no temperature effect in these hornblendes, and Al$_{tot}$ is only a function of pressure. However, even though the temperature range is small, there is a strong correlation between calculated temperatures and pressures for these plutons (Fig. 9). Such a correlation could result from some crystallographic control that couples the pressure- and temperature-sensitive exchange vectors, but it is also an expected consequence of variable pressures acting on the granite solidus. Blundy and Holland (1990) estimated that the substitution of Al resulting from a 50 °C variation in temperature would be equivalent to a pressure change of about 1.2 kbar. Figure 9 predicts that a change of about 30 °C would correspond to this pressure increment, implying that the temperature effect alone is not sufficient to explain these data.

Comparison with previous pressure and temperature estimates

Pressure and temperature from the aluminum hornblende barometer and thermometer can be evaluated for these granitoids by comparing values obtained from contact metamorphic aureoles. In the southeastern Piedmont contact metamorphic aureoles are only well developed around the plutons that intrude greenschist-facies rocks in the King's Mountain, Carolina slate, Eastern slate, and Belair belts, and only a few of these aureoles have been studied in detail.

Emplacement pressure of the High Shoals pluton in the King's Mountain belt has been constrained to 4.5–5 kbar

(Horton et al., 1987), which agrees well with the aluminum hornblende pressure of the nearby Bald Rock pluton (4.8 kbar) which straddles the boundary between the King's Mountain belt and the Charlotte belt. The emplacement pressure of the Liberty Hill pluton, based on coexisting cordierite + garnet + orthopyroxene and on aluminum silicate phase relations in the contact aureole, has been estimated at approximately 4.5 kbar (Speer, 1981). Preliminary study of similar metamorphic assemblages in the contact aureoles of the Pageland and Winnsboro plutons yielded comparable emplacement pressures (Speer et al., 1980). Given that uncertainties associated with the contact metamorphic pressure estimates are ±1 kbar at best and may be as much as ±2 kbar, emplacement pressures calculated from aluminum hornblende barometry are consistent with those derived previously from studies of contact aureoles. This comparison suggests that any temperature-sensitive substitutions in these hornblendes do not drastically affect calculated pressures. The implications of the barometric data for Alleghanian tectonism and uplift in the southern Appalachians are discussed elsewhere (Vyhnal and McSween, 1990).

The only temperature estimate made for an amphibole-bearing granitoid is for the Liberty Hill pluton (Speer, 1981, 1987). On the basis of garnet-biotite pairs found in xenoliths, Speer estimated a temperature of 725 °C. The temperature calculated from the Al content of the hornblende in this pluton is 735 °C (Table 4).

DISCUSSION

Pressure- and temperature-sensitive substitutions in amphibole

As already noted, previous workers have proposed that the change in the Al content of hornblende with increasing pressure is governed by the aluminum tschermakite substitution with exchange vector ${}^{[4]}\mathrm{Al}{}^{[6]}\mathrm{Al}{}^{[6]}\mathrm{Mg}_{-1}{}^{[4]}\mathrm{Si}_{-1}$. Hollister et al. (1987) based this conclusion on a study of amphibole samples from a group of otherwise similar plutons emplaced at different pressures. Johnson and Rutherford (1989) observed the same substitution in amphibole from experiments equilibrated at different pressures. Blundy and Holland (1990) found that amphibole from the Ademello massif shows the principal exchange vector ${}^{[A]}\mathrm{Na}{}^{[4]}\mathrm{Al}{}^{[A]}\square_{-1}{}^{[4]}\mathrm{Si}_{-1}$ that is temperature dependent. However, because the Ademello suite crystallized at a constant pressure of 2 kbar but over a temperature range of 1075–675 °C, their finding of only a temperature dependence would be expected. The observed exchange vector ${}^{[A]}(\mathrm{Na,K}){}^{[6]}(\mathrm{Fe}^{3+},\mathrm{Al}){}^{[4]}\mathrm{Al}_2{}^{[A]}\square_{-1}{}^{[6]}\mathrm{Mg}_{-1}{}^{[4]}\mathrm{Si}_{-2}$ in the hornblende samples from Piedmont plutons is an additive combination of both the pressure- and temperature-sensitive substitutions proposed by previous workers, plus the exchange vector ${}^{[6]}\mathrm{Fe}^{3+}{}^{[6]}\mathrm{Al}_{-1}$. This observation lends support to the idea that hornblendes in the granitoids of this study may record both pressure and temperature effects. In fact, for many granitic plutons, it may be difficult to decouple temperature- and pressure-sensitive substitutions in hornblendes because the temperature of the solidus is linked to pressure.

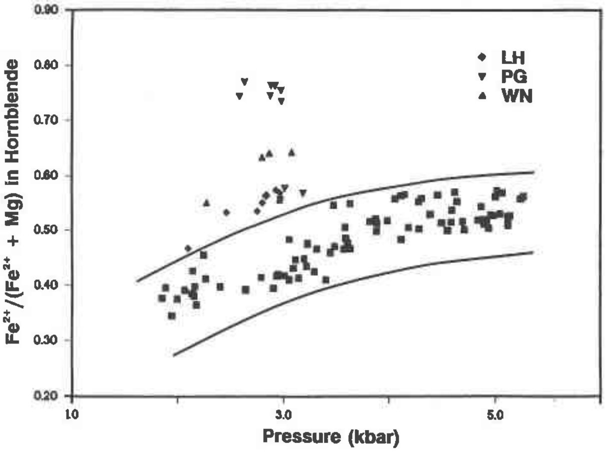

Fig. 10. The apparent pressure dependence of $Fe^{2+}/(Fe^{2+} + Mg)$ ratio in hornblende. Amphibole samples that violate this relationship are from the Liberty Hill (LH), Pageland (PG), and Winnsboro (WN) plutons. Analytical uncertainties of 1σ for $Fe^{2+}/(Fe^{2+} + Mg)$ are approximately the same as dimensions of the plotted points.

It is also noteworthy that most hornblendes in the specified assemblage exhibit a trend of increasing $Fe^{2+}/(Fe^{2+} + Mg)$ with pressure (Fig. 10), similar to that observed for experimental calcic amphibole (Mysen and Boettcher, 1975; Allen et al., 1975; Allen and Boettcher, 1978). This trend may be due to coupling between $Fe^{2+}/(Fe^{2+} + Mg)$ and Al (Robinson et al., 1982) but is not simply explained by such as mechanism, as the Liberty Hill, Pageland, and Winnsboro plutons are clustered geographically (Fig. 2) but are off the trend defined by the other samples.

Reactions governing hornblende substitutions

Simple pressure- and temperature-sensitive reactions relating amphibole components to other phases, as proposed by Hollister et al. (1987) and Blundy and Holland (1990), can be treated thermodynamically, but in reality they must be a part of an overall crystallization reaction involving the granitic magma. One plausible reaction in magmatic systems that might incorporate both equilibria is: liquid_1 + amphibole + ilmenite = biotite + quartz + anorthite + potassium feldspar + titanite + magnetite + liquid_2, where interstitial melt represents both the source of liquid_1 and the sink for liquid_2. This reaction, originally proposed for the Liberty Hill pluton by Speer (1987), includes each of the phases in the critical assemblage (+ melt). The reaction was balanced by Speer using phase compositions as determined by electron microprobe and assuming that late, fine-grained, biotite granitoid dikes approximate the interstitial liquid_1 and liquid_2 compositions.

Following arguments by Abbott (1981), Speer (1987) used this reaction to explain zoning of the Liberty Hill pluton by demonstrating that biotite formed by replace-

TABLE 5. Representative epidote analyses

Pluton		BR	LH	CS	HB	SM	PG
Wt%	SiO_2	36.85	36.14	38.19	36.89	37.30	37.06
	TiO_2	0.11	0.07	0.11	0.11	0.06	0.00
	ThO_2	0.00	0.01	0.00	0.07	0.00	0.00
	Al_2O_3	21.63	20.97	24.00	21.40	22.69	23.98
	Fe_2O_3	15.45	16.43	12.54	15.71	14.32	12.10
	Y_2O_3	0.04	0.00	0.00	0.01	0.08	0.07
	La_2O_3	0.00	0.00	0.00	0.02	0.00	0.00
	Ce_2O_3	0.07	0.00	0.00	0.03	0.00	0.01
	MgO	0.00	0.00	0.02	0.02	0.03	0.01
	CaO	22.61	23.09	23.39	23.16	23.11	23.20
	MnO	0.26	0.05	0.27	0.20	0.17	0.56
	Total	97.02	96.76	98.52	97.62	97.76	96.99
Cations	Si	2.991	2.948	3.015	2.979	2.988	2.970
	Al	2.070	2.017	2.234	2.037	2.143	2.265
	Fe^{3+}	0.944	1.009	0.745	0.955	0.863	0.730
	Mn	0.018	0.003	0.018	0.014	0.012	0.038
	Ti	0.007	0.004	0.007	0.007	0.004	0.000
	Sum	3.038	3.033	3.003	3.012	3.021	3.033
	Ca	1.967	2.018	1.979	2.004	1.984	1.992
	Ce	0.002	0.000	0.000	0.001	0.000	0.000
	La	0.000	0.000	0.000	0.001	0.000	0.000
	Y	0.002	0.000	0.000	0.000	0.003	0.003
	Th	0.000	0.000	0.000	0.001	0.000	0.000
	Mg	0.000	0.000	0.002	0.002	0.004	0.001
	Sum	1.970	2.019	1.981	2.009	1.991	1.997
	xPIST	0.31	0.33	0.25	0.32	0.29	0.24
Pressure	(kbar)	4.8	2.8	3.0	2.9	4.5	3.0

Note: Pluton codes are given in Table 1. Emplacement pressures are based on the calibration of Johnson and Rutherford (1989).

ment of amphibole during the evolution of crystallization reactions from liquid → amphibole, to liquid + amphibole → biotite, to liquid → biotite. What is important for our purposes here is the possible odd-even nature of amphibole-melt equilibria. If Abbott's assessment is correct, the pressure-dependent reaction governing the exchange vector for Al in hornblende may occur only over a limited range of crystallization conditions. The reaction suggested by Hollister et al. (1987) could occur only during the odd, liquid + amphibole → biotite, portion of the crystallization path. At other times during crystallization, the temperature-sensitive reaction governing the Al exchange vector presumably would predominate. Perhaps this observation may explain why the aluminum hornblende barometer works in some cases (including, apparently, the plutons studied here) and why the assumption of a nearly isothermal granitic solidus (Hammarstrom and Zen, 1986) appears to be valid.

Magmatic epidote as a pressure indicator

Previous authors (Naney, 1983; Zen and Hammarstrom, 1984, 1988) recognized that epidote may be in equilibrium with calc-alkaline melts at pressures above 6–8 kbar, but experimental data on epidote stability at pressures between 2 and 8 kbar are lacking. Thus the pressure significance of primary epidotes in granitoids is unclear.

Textural criteria that can be used to distinguish magmatic epidote from epidote that forms by subsolidus (deuteric) reactions are not well established. Tulloch (1979) argued that euhedral, weakly pleochroic epidote enclosed within biotite is magmatic. Zen and Hammarstrom (1984) suggested that some relationships indicative of a magmatic origin for this phase are: euhedral epidote overprinting biotite, epidote overgrowths on euhedral allanite, resorption of hornblende with subsequent precipitation of epidote, wormy intergrowths with plagioclase, involvement of epidote in magmatic flow banding, and occurrence of epidote in rocks that otherwise lack secondary alteration.

Although secondary epidote (replacing plagioclase) and other alteration products occur sporadically in Piedmont granitoids, many epidote crystals in these rocks have magmatic textural characteristics. Large, euhedral epidote overgrowths on allanite grains are widespread; however, epidote encompassing resorbed hornblende or intergrown with plagioclase has not been observed. Other possible magmatic features include zoned and twinned epidote, intergrowth of epidote with other magmatic phases, and similarity in size between epidote and other magmatic phases.

Chemical criteria for recognition of magmatic epidote in granitic rocks have also been proposed. Tulloch (1979, 1986) reported that epidotes formed from alteration of plagioclase ranged from Ps_0 to Ps_{24} [$Ps = Fe^{3+}/(Fe^{3+} + Al)$], those formed by alteration of biotite ranged from Ps_{36} to Ps_{48}, and those exhibiting magmatic textures ranged from Ps_{25} to Ps_{29}. In a study of Piedmont granitoids, Speer et al. (1980) also found that epidotes which formed from plagioclase alteration were less Fe-rich than matrix epidotes of presumed magmatic origin. Epidotes in Piedmont granitoids analyzed for this study range from Ps_{24} to Ps_{33} (Table 5), with one exception (Ps_{41}). This range of values occurs within separate epidote crystals from a single thin section, and within a single zoned epidote (core compositions have lower Ps contents). Tulloch (1986) and Zen (1988) related the composition of magmatic epidote to f_{O_2}: epidote breakdown curves (Liou, 1973) indicate that, within probable f_{O_2} limits for magmas (i.e., between the HM and NiNiO buffers), epidote should range only from Ps_{25} to Ps_{33}.

It remains uncertain whether epidotes in Piedmont granitoids are magmatic, but their textural features and compositions are consistent with the suggested criteria for igneous origin. Such epidote crystals occur in all of the Piedmont plutons that crystallized at pressures greater than 2.8 ± 0.5 kbar but are absent in a portion of the Butterwood Creek pluton which crystallized at 2.1 ± 0.5 kbar (Table 4). This suggests that the minimum pressure required for stability of magmatic epidote in these plutons lies between 2.1 and 2.8 kbar, considerably less than that previously suggested for other bodies (Zen and Hammarstrom, 1984, 1986). Tulloch (1986) also questioned the idea that magmatic epidote stability in calc-alkaline plutons required high pressures, and Moench (1986) described primary epidote from granitic plutons emplaced at pressures of 2–4 kbar. However, given the uncertainties in criteria for identification of magmatic epidote and in the calibration and application of the aluminum-hornblende barometer, we hesitate to suggest a minimum pressure for magmatic epidote stability.

Zen and Hammarstrom (1986) cautioned that magmatic epidote should be used as a pressure indicator only for tonalites or granodiorites with the proper mineral assemblage. They also suggested that evidence of a reaction relation between magmatic epidote and hornblende was desirable. The Piedmont plutons clearly have the critical mineral assemblage, but have bulk compositions that are monzogranitic rather than tonalitic to granodioritic. Textural evidence for a reaction relationship between epidote and hornblende has not been observed in these plutons, nor was it found by Moench (1986). The Piedmont monzogranitic plutons may have solidi lying at lower temperatures than those of tonolites or granodiorites, which could explain the lower-pressure stability limit for epidote. Locations of the intersections of epidote stability curves at magmatic f_{O_2} values with granite melting curves (Fig. 2-1 of Zen, 1988) indicate that primary epidote should be stable at pressures as low as 3.3 kbar under oxidizing conditions in H_2O-saturated granitic magmas.

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