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Evolution of magmatic AFM mineral assemblages in granitoid rocks: The hornblende + melt = biotite reaction in the Liberty Hill pluton, South Carolina

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ABSTRACT

The Liberty Hill pluton comprises a central, coarse-grained edenite + biotite granitoid facies grading to a biotite, pargasite + biotite, or muscovite + biotite granitoid marginal facies. The replacement of amphibole by biotite, mineral compositions, and "liquid" variation diagrams for the Liberty Hill help determine the AFM mineral-crystallization reactions in the Liberty Hill pluton. These reactions evolved from liquid = amphibole to liquid = biotite with an intervening liquid + amphibole = biotite reaction resulting from either (1) movement along the amphibole-biotite liquidus boundary from the even, liquid = amphibole + biotite, to the odd, liquid + amphibole = biotite, crystallization reaction with decreasing temperatures or (2) movement of the liquid composition from the amphibole field into the biotite field. The liquid + amphibole = biotite reaction involved additional phases; the full reaction may have taken the form liquid 1 + amphibole + ilmenite = biotite + quartz + anorthite + K-feldspar + titanite + magnetite + liquid 2, where the liquid is the interstitial melt. The extended crystallization history to lower temperatures and higher water activities at the margins of the pluton allowed the reaction to exhaust the amphibole before the liquid; the subsequent liquid = biotite crystallization reaction produced the biotite granitoid facies. Locally, muscovite crystallized according to the reaction liquid = muscovite + biotite, producing the muscovite + biotite facies. The pluton is intruded by a finer-grained biotite granitoid believed to be derived from interstitial melt of the coarser-grained granitoids. This derivation explains why biotite is the only AFM mineral in the finer-grained granitoids and why biotites from all Liberty Hill granitoids are generally similar in composition.

The average K_D value $[(X^{Bt}_{Mg}/X^{Bt}_{Fe})/(X^{Hbl}_{Mg}/X^{Hbl}_{Fe})]$ is 1.04 for coexisting Hbl and Bt. This K_D is higher than the 0.69–0.93 normally observed in igneous rocks, but equal to values for specific instances of biotite replacing amphibole in the Peruvian Coastal batholith. Combined with the results obtained from the contact aureole, the central granitoids preserve conditions of 725°C, $P_{total} \approx 4.5$ kbar, $P_{fluid} \approx 0.5\ P_{total}$, and $f_{O_2} \approx 10^{-15}$, slightly more oxidizing than the NNO solid buffer. Marginal granitoids yield conditions of 647°C, $P_{fluid} \approx P_{total}$, and $f_{O_2} \approx 10^{-16}$, suggesting a more prolonged reaction history.

INTRODUCTION

Many of the late Paleozoic granitoid plutons of the southern Appalachians are composite bodies with coarse-grained amphibole + biotite and biotite varietal facies (Speer et al., 1980). From field relations, these facies appear closely related, and multiple intrusion or differentiation comes to mind as an explanation for the relationship. In the Liberty Hill pluton, the coarse-grained central amphibole + biotite granitoids grade imperceptibly into marginal biotite granitoids, seemingly ruling out multiple intrusions. The compositions of the marginal biotite facies overlap those of the central granitoids, arguing against significant differentiation (Speer et al., unpub. ms.). The marginal facies do show minor wall rock–magma interaction that affected some trace-element and oxygen-isotope compositions (Wenner and Speer, 1986). An alternative explanation for the mineralogical relation between the central and marginal facies is suggested by the widespread texture of biotite replacing amphibole.

Understanding the mineral assemblages and compositions in igneous rocks requires linking them to the evolving conditions and compositions of the interstitial melt during crystallization. This is a well-developed area of investigation for gabbroic rocks, but much less so for granitoid rocks. Recently, Abbott and Clarke (1979) and Abbott (1981, 1985) have given the sequence of AFM

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crystallization reactions in granitoids in more detail than Bowen's (1928) reaction series. These have been used in interpreting the crystallization reactions in strongly peraluminous granitoids, such as the cordierite-bearing Clouds Creek pluton, South Carolina (Speer, 1981b). Their use is extended here to the metaluminous Liberty Hill pluton, South Carolina, in order to understand the evolution of amphibole + biotite, biotite, and muscovite + biotite granitoids.

GEOLOGIC SETTING

The Liberty Hill pluton is roughly elliptical, covering 360 km^2 in Kershaw, Lancaster, and Fairfield Counties, north-central South Carolina. The Liberty Hill pluton comprises several texturally and mineralogically distinct facies (Fig. 1). The predominant facies is a coarse-grained ferro-edenite + biotite granitoid occupying the center of the pluton. Coarse-grained biotite, ferroan pargasite + biotite, and muscovite + biotite granitoids occur along the northern and eastern borders of the pluton and have gradational contacts with the central ferro-edenite + biotite granitoids. This reverse zoning of the mineral facies is believed to result from accumulation of magma with a greater percentage of evolved, interstitial melt near the margin as a result of the pluton's emplacement as well as a minor amount of contamination from the wall rocks (Wenner and Speer, 1986). There are several younger facies in the Liberty Hill pluton that intrude the coarse-grained granitoids as dikes or plugs up to 1 km^2 in area. The most prominent are fine- to medium-grained biotite granitoids in the west-central part of the pluton (Fig. 1), which are believed to have differentiated from the coarse-grained facies.

The contact aureole of the pluton was described by Speer (1981a). The pelitic assemblage in the country rock, muscovite + chlorite + albite + epidote + quartz + magnetite + ilmenite, changes in response to prograde metamorphism on approaching the pluton. The following isograds are encountered: porphyroblastic magnetite in, epidote + albite out, biotite + cordierite in, chlorite out, K-feldspar in, and muscovite or magnetite out. Several additional metamorphic minerals appear in the xenoliths: garnet, orthopyroxene, andalusite, sillimanite, and fibrolite. It was concluded that the pluton was emplaced at a depth corresponding to 4.5-kbar pressure. The magma was relatively dry, and the xenoliths yield estimated temperatures of about 725°C for the central granitoids and 650°C for the marginal granitoids.

MINERALOGY

Compositions of the minerals in polished thin sections were determined with a nine-spectrometer, automated ARL-SEMQ electron microprobe using silicates and oxides as standards and the analytical scheme QALL described by Solberg and Speer (1982). These are reported in Appendix 1,[1] and selected analyses are given in Tables 1 to 3. Mineral formulas and components were calculated using the computer program SUPERRECAL of Rucklidge (1971). The program also calculated an assumed stoichiometric amount of water and added it to the oxide weight percentages for the hydrous minerals. Mineral abbreviations in the text, tables, and figures are those recommended by *The American Mineralogist* (Kretz, 1983).

Amphibole

Amphibole occurs as euhedral to subhedral prismatic crystals up to 0.5 cm long. They are pleochroic dark yellow green to moderate blue green and are locally twinned on (100). Microprobe analyses (App. 1, selected analyses in Table 1) show that the amphiboles in the central granitoids are ferro-edenites and ferro-edenitic hornblendes (Fig. 2a), hereafter referred to as ferro-edenites. These ferro-edenites have a narrow compositional range with an Fe/(Fe + Mg) near 0.6 and a Si content in the half-unit-cell formula of 6.56 to 6.85 atoms per 24 anions. The F and Cl contents range between 0.08 and 0.22 mol% F/(OH + F + Cl) and between 0.005 and 0.03 mol% Cl/(OH + F + Cl), respectively. Amphiboles in granitoids of the northeast corner of the pluton have thin, discontinuous aluminous rims of ferroan pargasite (Fig. 2B). These aluminous rims are less than 0.01 mm thick and are only locally visible, where there is a color difference. According to graphical representations of Doolan et al. (1978) and Thompson (1981), the substitution in the aluminous rims is primarily a tschermakite [$Al_2Mg_{-1}Si_{-1}$] + edenite [$NaAlSi_{-1}$] substitution to form pargasite.

Many amphiboles are intergrown with biotite, but generally the order of crystallization is uncertain. Where textures are unambiguous, the amphiboles are partially (Fig. 3a) or completely (Fig. 3b) replaced by biotite. In what is interpreted as a later reaction texture, amphiboles can be replaced by chlorite + epidote + plagioclase. Scattered throughout the pluton are amphiboles with clinopyroxene inclusions (Fig. 3c). The amphibole adjacent to these pyroxenes is pale green actinolite that is discontinuously zoned to ferro-edenite at the rim, comparable in composition to amphiboles elsewhere in the pluton (Fig. 2b).

Biotite

Greenish-black biotite is a ubiquitous mafic phase in the Liberty Hill pluton, forming up to 5 modal percent of the rock. Biotite occurs interstitially to feldspars and quartz, replacing amphibole, and as inclusions in leucocratic minerals. Individual flakes are up to 5 mm across. Biotite is pleochroic grayish orange to greenish black in thin section.

Microprobe analyses (App. 1, selected analyses in Table 2) show that biotite compositions from the granitoids fall approximately midway between phlogopite and annite with an intermediate Al content. The range of molar Fe/(Fe + Mg) is small with an average of approximately 0.59. The amount of tetrahedral Al is systematically related to the coexisting minerals (Fig. 4). Biotites coexisting with ferro-edenite have tetrahedral Al contents between 2.27 and 2.35 atoms per 24 anions. The tetrahedral Al contents of biotites coexisting with the pargasite-rimmed hornblendes are decidedly more aluminous, in the range 2.29 to 2.75 atoms per 24 anions. Biotites in the fine-grained and coarse-grained biotite granitoids and enclaves have tetrahedral Al contents that overlap the biotites coexisting with ferro-edenite. The biotites of the finer-grained rocks can be more iron rich, with an average Fe/(Fe + Mg) = 0.64; in biotites from the aplites, Fe/(Fe + Mg) is as high as 0.75. The biotites in coarse-grained muscovite + biotite granitoids are aluminous and comparable in composition to biotites coexisting with the pargasite-rimmed

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[1] To obtain a copy of Appendix 1, order Document AM-87-355 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

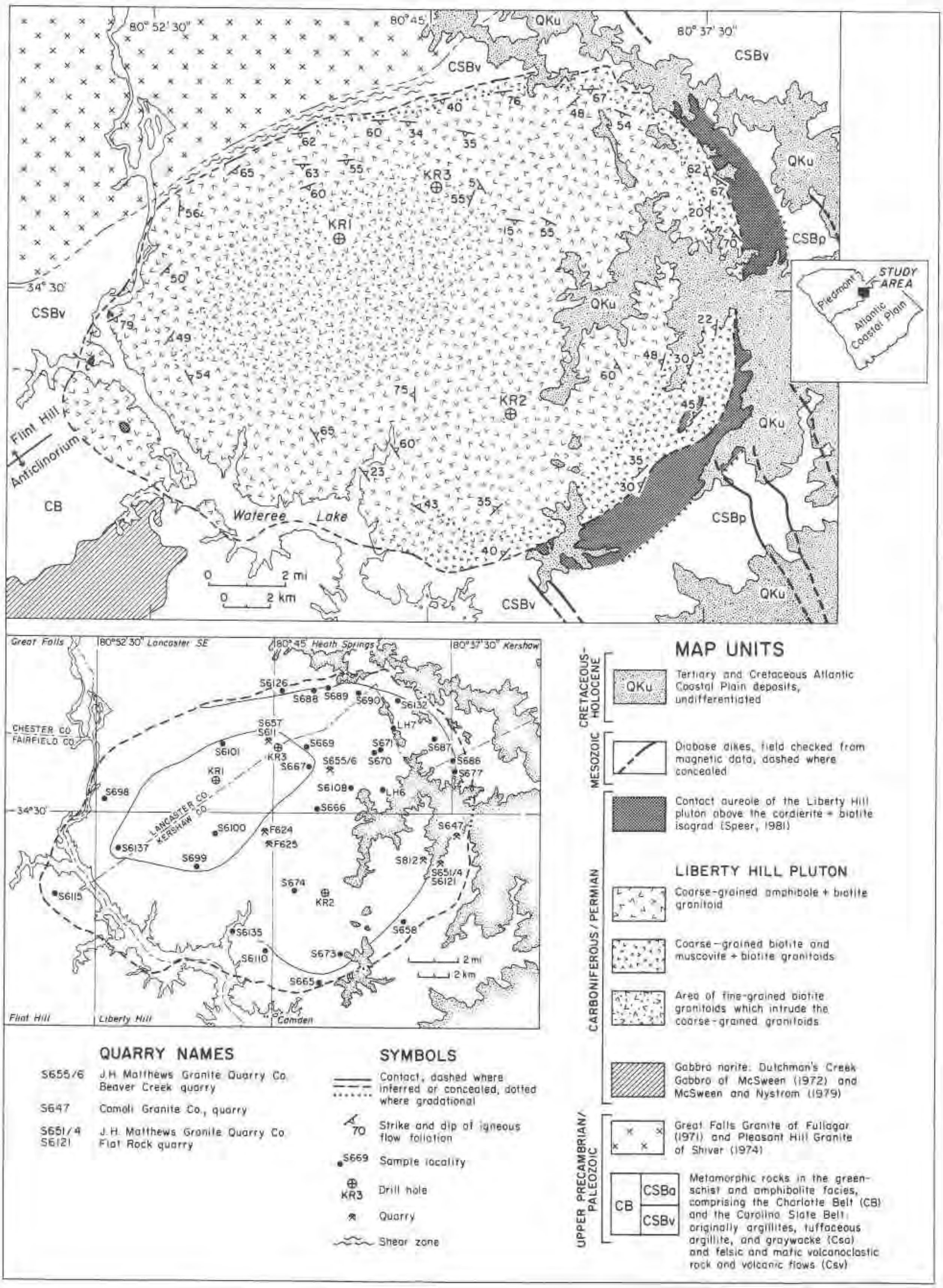

Fig. 1. Geologic and sample maps of the Liberty Hill pluton, South Carolina.

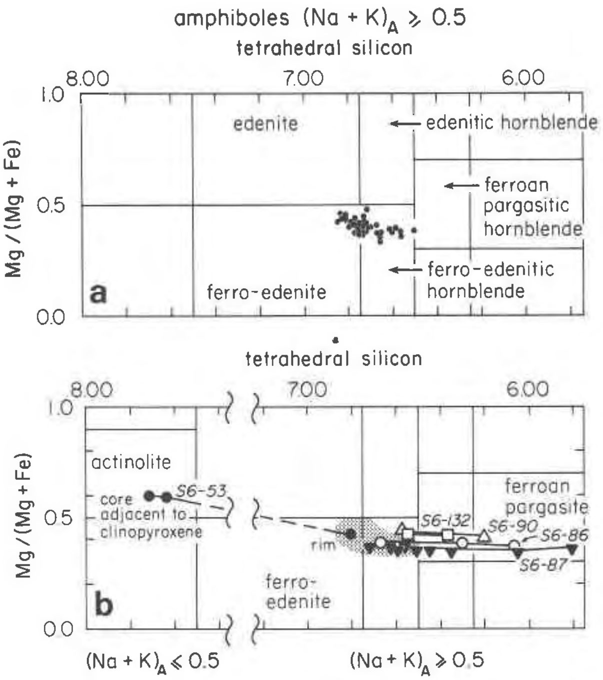

Fig. 2. Compositions of the Liberty Hill amphiboles according to the IMA nomenclature (Leake, 1978). The majority of the amphiboles in the granitoids are ferro-edenite and ferro-edenitic hornblendes (a), whereas the amphiboles adjacent to the clinopyroxene cores are actinolite (b), and the zoned rims on the amphiboles of granitoids along the northeastern margin of the pluton (S6-8, -87, -90, -132) are ferroan pargasite (b).

amphiboles. The biotite octahedral Al and total Al contents vary, like the tetrahedral Al content, with the coexisting AFM mineral assemblage.

Except for F, the remaining elemental compositions for the biotites are similar from different occurrences. The F contents of biotites in the enclaves and edenite-bearing granitoids have an average F/(OH + F) of 0.11. The complete range of F/(OH + F) is 0.06 to 0.20. Biotites in the coarse-grained biotite granitoids are more F rich with an average F/(OH + F) of 0.17. The biotites in muscovite + biotite and fine-grained biotite granitoids are less F rich with average values of F/(OH + F) of 0.05 and 0.09, respectively.

Clinopyroxene

Pyroxene in the Liberty Hill pluton occurs as very pale green, irregular or skeletal cores in amphiboles (Fig. 3c) and in the more calcic plagioclases. Microprobe analyses (App. 1, selected analyses in Table 3) show the pyroxene to be salite with an average composition $Wo_{46.49}En_{31.61}Fs_{20.82}Rdn_{1.08}$.

Coexisting AFM minerals

Figure 5 summarizes rock and mineral compositional relations from the Liberty Hill pluton. Rock compositions are more iron rich than the ferromagnesian silicate assemblage because of the presence of iron oxides.

A notable aspect of Figure 5 is the differing distribution coefficients for coexisting amphiboles + biotite, evident by the slopes of tie lines, and differing Al contents. The distribution coefficient, defined as $K_D = (X^{Bt}_{Mg}/X^{Bt}_{Fe})/(X^{Hbl}_{Mg}/X^{Hbl}_{Fe})$, depends on the overall mineral assemblage and bulk composition. In the enclaves and enclave-bearing rocks, assemblages with clinopyroxene have an average $K_D = 0.92$ with a range of 0.86–0.99 (Fig. 6a). The central edenite + biotite granitoids have $K_D = 1.04$ with a range of 0.96–1.17 (Fig. 6b), whereas the marginal pargasite + biotite granitoids have $K_D = 1.22$ with a range of 1.13–1.30 (Fig. 6c). The finer-grained biotite granitoids and aplites have more iron-rich biotites than the other granitoids, approaching the Fe/(Fe + Mg) values of the granitoids themselves (Fig. 6d). The most aluminous biotites coexist with muscovite or amphiboles having pargasite rims; biotites coexisting with edenite or in a single AFM phase assemblage are less aluminous.

Feldspars

The alkali feldspar in coarse-grained granitoids is macro- and microperthite, exhibiting both primary Carlsbad growth twins and Albite-Pericline inversion twins. Large-area microprobe analyses (App. 1) of alkali feldspars give estimated original bulk alkali feldspar compositions of $Or_{82.46}Ab_{16.97}An_{0.57}$ (S6-56) and

TABLE 1. Selected amphibole compositions for the Liberty Hill pluton, South Carolina

	Zoned amphiboles					Amphiboles from the central granitoids			
	Cpx → Tr → Ed-Hbl		Ed-Hbl → Prg						
	S6-53 core	S6-53 rim	S6-86 core	S6-86 mid.	S6-86 rim	S6-56	F6-24	F6-25	K3-1303
SiO_2	52.75	45.38	43.94	42.41	40.13	43.59	42.30	44.20	43.06
TiO_2	0.16	1.45	1.68	1.09	1.53	1.82	1.37	1.57	1.46
Al_2O_3	2.05	7.69	7.56	9.28	13.02	8.59	9.41	7.93	8.73
FeO	16.63	21.19	22.30	23.05	19.92	20.26	21.68	21.56	21.28
MnO	0.61	0.58	0.80	0.75	0.73	0.71	0.70	0.74	0.85
MgO	13.85	9.39	8.17	7.84	7.18	8.73	7.92	8.35	8.20
CaO	11.85	11.40	10.58	10.79	10.16	10.69	11.33	11.53	10.34
BaO	0.04	0.08	0.01	0.05	—	—	—	—	0.22
Na_2O	0.75	1.86	1.85	1.84	1.35	1.68	1.61	1.49	1.70
K_2O	0.30	1.05	1.02	1.27	1.00	1.02	1.14	1.01	1.13
F	0.89	0.77	0.52	0.69	0.51	0.47	0.59	0.44	0.41
Cl	0.02	0.22	0.12	0.07	—	—	—	—	0.15
H_2O*	1.63	1.58	1.62	1.59	1.67	1.73	1.65	1.75	1.69
−O≡F + Cl	0.38	0.37	0.29	0.31	0.21	0.20	0.25	0.19	0.21
Total	101.15	102.27	99.90	100.41	96.99	99.09	99.45	100.38	99.01

* Calculated on the basis of (OH + F + Cl) = 2/24 anions.

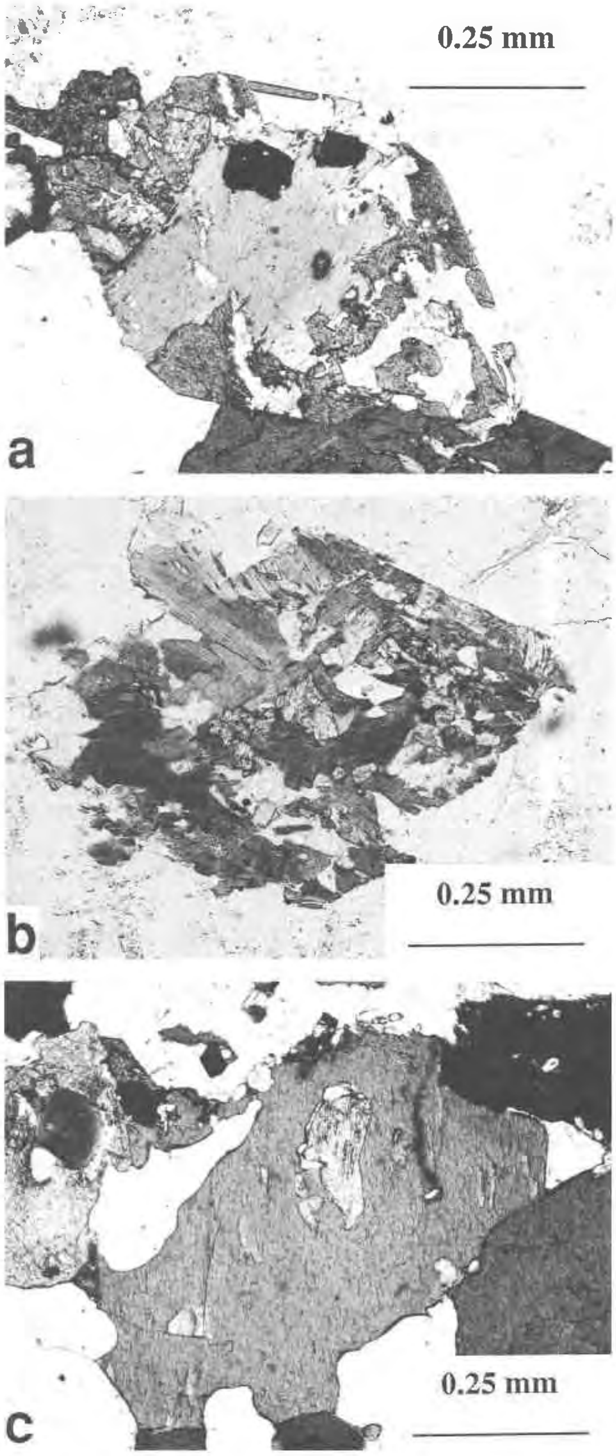

Fig. 3. (a) Photomicrograph of an amphibole grain intergrown with biotite in a coarse-grained granitoid (K3-348.8). The biotite is interpreted as replacing the amphibole in a liquidus reaction. (b) Photomicrograph of a biotite pseudomorph after what is interpreted as an orgiainlly euhedral amphibole in a coarse-grained granitoid (F6-24). (c) Photomicrograph of an inclusion of clinopyroxene in amphibole of a coarse-grained granitoid (K3-289). The granitoid melt is interpreted as having reacted with the pyroxene to form the amphibole that has subsequently armored the pyroxene.

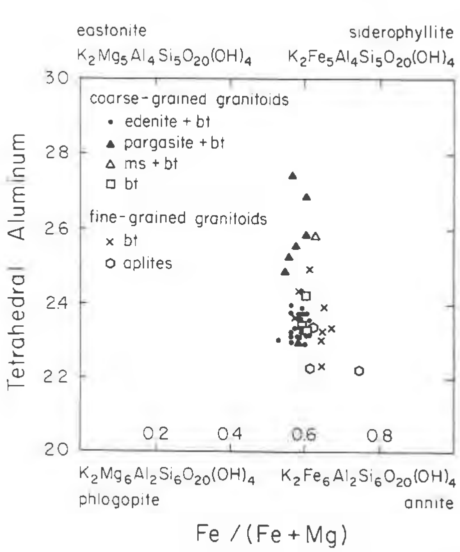

Fig. 4. Compositions of biotites from the Liberty Hill pluton projected onto the phlogopite-annite-eastonite-siderophyllite field and differentiated by occurrence.

$Or_{74.27}Ab_{24.87}An_{0.86}$ (S6-58). Point microprobe analyses show that the exsolved phases are albite, $Ab_{97.15-95.68}An_{0.51-2.92}Or_{2.34-0.33}$, and sodic orthoclase, $Or_{87.09-97.38}Ab_{2.42-10.58}An_{0-1.33}$. The Ba content of the exsolved albite corresponds to less than 0.33 mol% celsian (Cn); the exsolved sodic orthoclase contains less than 1.01 mol% Cn. Alkali feldspar in the fine-grained biotite granitoids is microcline, rarely perthitic, with an estimated bulk composition more potassic than the coarse-grained granitoids: $Or_{81.4-97.1}Ab_{18.33-2.9}An_{0-0.43}$. Single-crystal X-ray studies of Liberty Hill perthites showed that monoclinic orthoclase is the dominant X-ray average phase, but weak, diffuse reflections parallel to a^* and b^* caused by fine-scale Albite and Pericline twins indicate the presence of twinned, triclinic microcline. This is consistent with the commonly observed microcline grid twinning. The sodic phase is an Albite-twinned low albite.

Plagioclase forms white to very light gray, anhedral to subhedral grains twinned according to the Albite and Pericline laws.

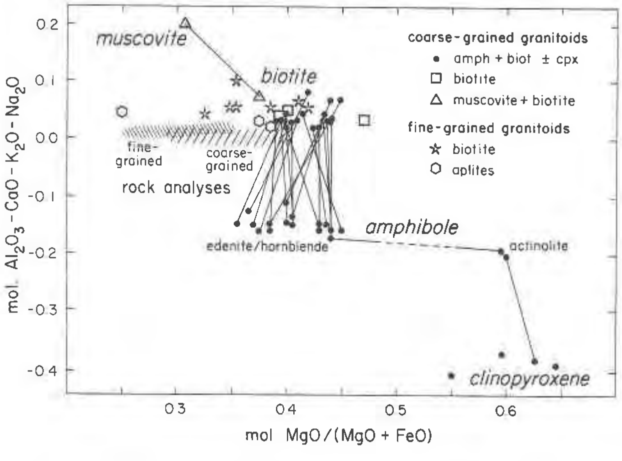

Fig. 5. Summary AFM (A = Al_2O_3-K_2O-Na_2O-CaO, F = FeO, M = MgO) diagram projected from quartz, alkali feldspar, plagioclase, and water for the rocks and minerals of the Liberty Hill pluton, South Carolina.

TABLE 2. Selected biotite compositions for the Liberty Hill pluton, South Carolina

	Coarse-grained Hbl + Bt granitoids						Coarse-grained Bt granitoids			Coarse-grained Ms + Bt granitoid
	S6-53	S6-56	S6-86	F6-24	F6-25	K3-1303	S6-47	S6-54	S6-58	S6-126
SiO_2	36.31	35.02	36.58	36.17	36.71	36.40	36.65	36.59	36.03	35.36
TiO_2	3.82	3.39	3.25	4.05	2.79	2.89	3.73	3.63	3.41	3.33
Al_2O_3	13.29	16.13	13.30	13.63	14.06	13.96	13.47	13.39	14.55	17.71
FeO	22.95	23.33	23.23	22.75	22.55	23.41	23.82	24.13	23.69	22.65
MnO	0.36	0.48	0.46	0.43	0.43	0.59	0.51	0.48	0.56	0.40
MgO	10.07	8.63	9.32	8.93	9.70	9.13	9.05	8.91	8.76	7.59
CaO	0.04	0.10	0.05	0.48	0.06	0.16	0.02	0.07	0.09	0.02
BaO	0.80	0.07	—	—	—	0.34	—	—	—	—
Na_2O	0.16	0.09	0.05	0.05	0.06	0.16	0.07	0.08	0.09	0.05
K_2O	9.53	8.64	8.91	8.77	9.12	9.53	9.17	8.97	8.71	9.41
F	1.07	0.72	1.14	0.92	0.98	0.73	1.01	1.43	1.59	0.44
Cl	0.09	0.05	—	—	—	0.09	—	—	—	—
H_2O*	3.37	3.53	3.31	3.41	3.41	3.53	3.40	3.20	3.13	3.70
$-O{\equiv}F + Cl$	0.47	0.31	0.48	0.39	0.41	0.33	0.43	0.60	0.67	0.19
Total	101.39	99.87	99.12	99.20	99.46	100.59	100.47	100.28	99.94	100.47

* Calculated on the basis of (OH + F + Cl) = 2/24 anions.

Compositional determinations by the *a* normal and microprobe techniques (App. 1) show that plagioclases in the coarse-grained granitoids have normal-oscillatory zoning with cores of An_{45-30} and rims of An_{17-10}. Plagioclases located in the groundmass and included in microcline have an abrupt compositional change to a discontinuous albite rim. Or and Cn contents of the plagioclase are less than 4.4% and 0.44%, respectively. Plagioclases in the fine-grained biotite granitoids are more sodic, with cores less than An_{30}; the Or content is less than 1.8 mol%.

Muscovite

White mica is most abundant in the finer-grained biotite granitoids, but it is present in all rocks. It occurs as discrete poikilitic or skeletal grains intergrown with biotite or as fine-grained masses in the cores of plagioclase. White mica in the coarse-grained muscovite + biotite granitoid at locality S6-126 is relatively abundant and occurs primarily as independent, subhedral grains comparable in size to the biotite. Microprobe analyses (App. 1) show that white micas in the Liberty Hill pluton are muscovites. Except for the Ti contents, the composition of its muscovite is more or less the same regardless of occurrence. Si content averages 6.354 atoms per 24 anions and ranges between 6.191 and 6.548. The muscovites contain 0.178–0.745 Fe, 0.048–0.370 Mg, and 0.034–0.317 Na atoms per 24 anions. The average F content is 0.061 atoms per 24 anions. Average Ti content of the Liberty Hill muscovites is 0.037 atoms per 24 anions with a range of 0.015 to 0.060, whereas muscovite in S6-126 has an average Ti content of 0.110. On the basis of its textural features and higher Ti content, the muscovite in S6-126 is interpreted as an igneous phase, whereas muscovites in the other Liberty Hill samples are interpreted as subsolidus phases on the basis of criteria discussed by Speer (1984).

Accessory minerals

The oxide mineral assemblage of the Liberty Hill granitoids is magnetite + ilmenite. Magnetite in the ferro-edenite + biotite granitoids contains fine, {111}-oriented ilmenite lamellae as well as larger rims and inclusions of granular ilmenite. These ilmenite intergrowths are thought to represent "oxyexsolution" of primary titanomagnetite (Usp-Mt) and are present in the magnetite grains in amounts less than 10 vol%. Microprobe analyses of the magnetites show them to be nearly end-member compositions.

TABLE 3. Selected clinopyroxene and other mineral compositions for the Liberty Hill pluton, South Carolina

	Clinopyroxene				K3-1303.8			
	S6-53	S6-55	S6-98	K2-5	Chlorite	Epidote	Ilmenite	Titanite
SiO_2	51.82	52.46	51.98	51.25	26.13	37.47	0.08	29.78
TiO_2	0.22	0.17	0.27	0.30	0.14	0.16	47.10	35.18
Al_2O_3	0.93	0.48	1.20	1.30	18.66	22.42	0.08	1.75
FeO	12.36	14.14	11.33	13.13	30.90	(11.68)	(45.64)	(1.91)
MnO	0.77	0.96	0.59	0.30	0.90	0.49	5.20	0.30
MgO	11.49	9.69	11.51	10.74	12.31	0.21	0.31	0.22
CaO	21.88	23.11	22.58	21.21	0.16	21.55	0.23	26.15
BaO	0.09	0.10	—	—	0.20	0.21	—	0.36
Na_2O	0.51	0.40	0.49	0.61	0.10	0.09	0.12	0.13
K_2O	0.08	0.03	0.03	0.11	0.09	0.09	0.10	0.09
F	—	—	—	—	0.18	0.08	—	0.53
Cl	—	—	—	—	0.05	0.03	—	0.04
H_2O*	—	—	—	—	11.10	1.79	—	—
$-O{\equiv}F + Cl$	—	—	—	—	0.09	0.04	—	0.24
Total	100.06	101.51	99.98	99.01	100.83	97.53	98.56	94.29

* Calculated on the basis of (OH + F + Cl) = 8 atoms per 18 anions for chlorite and = 1 atom per 13 anions for epidote.

TABLE 2—*Continued*

Fine-grained Bt granitoids					Aplite	
S6-67	S6-99	S6-101	K3-72	K3-130	S666	S677
36.45	35.46	36.78	37.49	36.53	37.19	36.34
2.19	3.55	2.54	2.47	2.63	3.72	3.14
16.12	14.96	16.11	16.29	15.27	14.77	13.31
24.39	23.78	21.47	24.04	25.09	25.97	24.82
0.37	0.45	0.57	0.22	0.36	0.50	0.71
7.31	8.34	8.76	7.32	6.82	4.94	8.52
0.05	0.16	0.04	0.09	0.06	0.06	0.06
0.25	0.93	—	—	0.23	0.07	0.07
0.09	0.09	0.02	0.03	0.10	0.07	0.13
10.02	8.88	9.45	9.37	9.58	9.24	9.31
0.91	0.68	0.72	—	0.65	0.76	0.82
0.05	0.12	—	—	0.07	0.02	0.08
3.45	3.51	3.57	3.94	3.54	3.49	3.43
0.39	0.31	0.30	—	0.29	0.32	0.36
101.26	100.60	99.73	101.26	100.64	100.48	100.38

The reddish-gray ilmenite grains contain networks and blebs of white-gray hematite and indicate exsolution of an original ilmenite-hematite solid solution. The ilmenites contain on average 12 mol% pyrophanite, in the range of 6.4 to 18.4 mol% (App. 1). Calculation of the temperature and oxygen fugacity from microprobe point analyses of exsolved oxides in a ferro-edenite + biotite granitoid (S6-56) by the method of Stormer (1983) shows subsolidus re-equilibration, below the range of the calibrations, consistent with the observed textures.

In the coarse-grained biotite and muscovite + biotite granitoids and in the fine-brained biotite granitoids, the magnetites do not contain exsolved phases and only rarely does the ilmenite have exsolved hematite. This indicates that the composition of the original igneous oxides in these granitoids must have been closer to the end-member compositions than were the oxides in the ferro-edenite + biotite granitoids.

Two sulfide assemblages have been observed in the granitoids; an inclusion assemblage in the magmatic minerals and a matrix assemblage. Pyrrhotite + chalcopyrite + pyrite is the inclusion

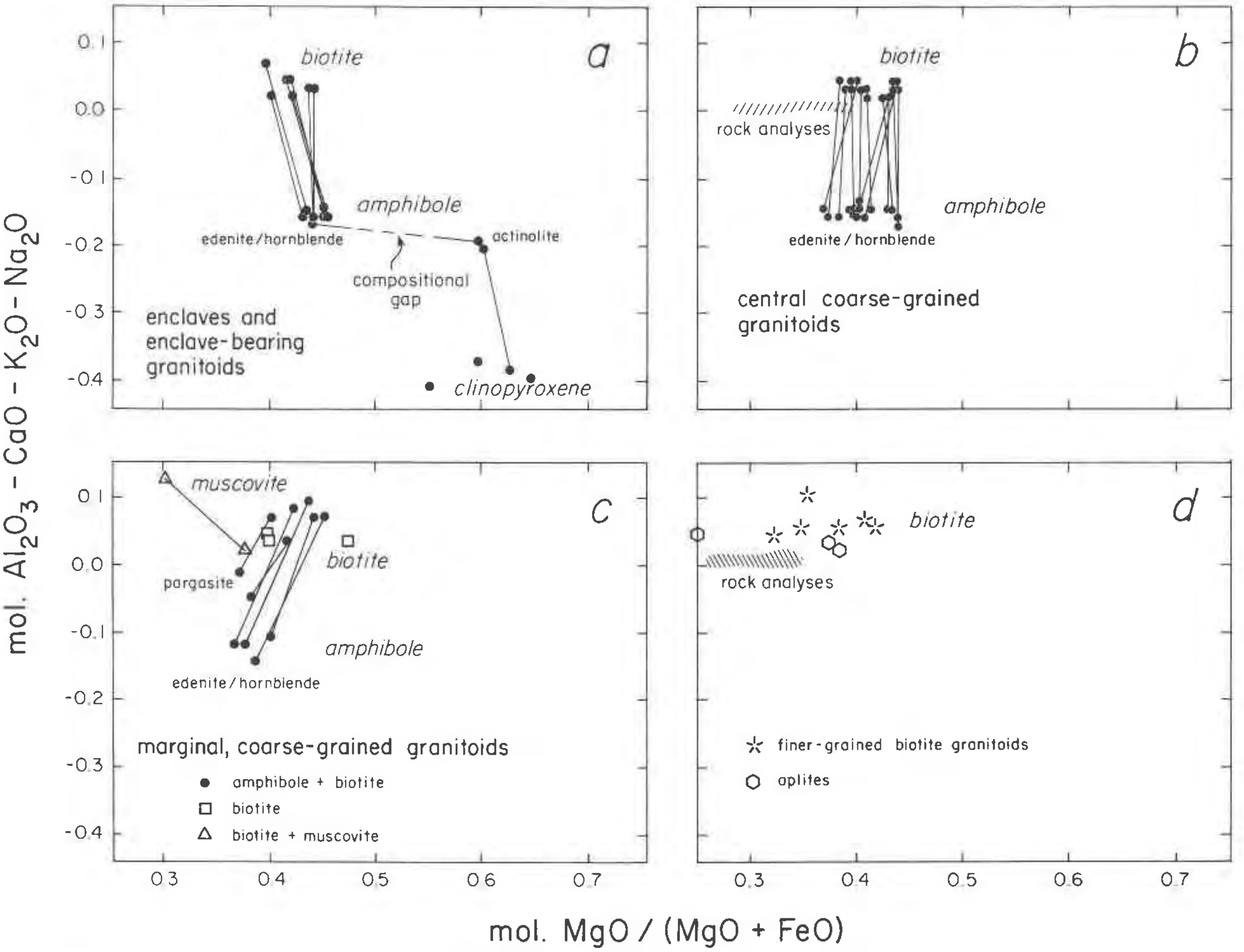

Fig. 6. Summary AFM (A = Al_2O_3-K_2O-Na_2O-CaO, F = FeO, M = MgO) diagrams projected from quartz, alkali feldspar, plagioclase, and water for the rocks and minerals of the Liberty Hill pluton, South Carolina, differentiated by occurrence: (a) enclaves and enclave-bearing granitoid, (b) central, coarse-grained ferro-edenite + biotite granitoid, (c) marginal, coarse-grained biotite, ferroan pargasite + biotite, and muscovite + biotite granitoid, and (d) finer-grained biotite granitoid and aplite facies.

assemblage in magnetite and less commonly in silicates such as titanite and zircon. No sulfide inclusions have been observed in ilmenite. The matrix assemblage is pyrite + chalcopyrite and coexists with magnetite and ilmenite. From the contrasting occurrence of these two sulfide assemblages, it appears the pyrrhotite + chalcopyrite + pyrite is the initial sulfide assemblage that crystallized with magnetite and the early silicates. Pyrite + chalcopyrite is the latter sulfide assemblage that crystallized in equilibrium with both magnetite and ilmenite.

Other accessory minerals in the Liberty Hill pluton are allanite, apatite, bastnäsite (?), coffinite, fluorite, galena, molybdenite, monazite, pyrophanite, sphalerite, thorite, titanite, uraninite, and zircon. The molybdenite occurrence in the Liberty Hill pluton has been discussed by Speer (1978). The U- and Th-bearing minerals have been discussed by Speer et al. (1981). The apatites are fluor-apatites, with only minor OH substitution and less than 0.06 wt% Cl. Fluorite is a rare accessory mineral in the finer-grained granitoids, occurring as disseminated anhedral grains. Allanite is the ubiquitous REE primary phase in all granitoids except for the coarse-grained muscovite + biotite granitoid where its role is assumed by monazite. Titanite is the most abundant accessory mineral in the coarse-grained granitoids. It forms subhedral to euhedral, wedge-shaped grains up to 3 mm in length. Titanite has a small variation in composition with substitutions of generally less than 15% Al and 7% Fe^{3+} for Ti. F substitution in the O_1 site is less than 10% (App. 1).

Late minerals

The late minerals in the Liberty Hill granitoids include albite, chlorite, titanite, epidote, muscovite, marcasite, hematite, calcite, laumontite, prehnite, alkali feldspar, rutile, hematite, and hyalite.

Many of the biotites and amphiboles are intergrown with chlorite + rutile, which are believed to be subsolidus replacement products. The chlorites have Fe/(Fe + Mg) ≈ 0.6 (App. 1), similar to the original biotites and amphiboles, and are ripidolites and brunsvigites according to the terminology of Hey (1954). Mn contents are less than 0.10 atoms per 18 anions. Fluorite occurs in lenticular masses in altered biotites, an occurrence that is believed to be secondary with the F derived from the alteration of the F-bearing biotite. Lenticules of prehnite or alkali feldspar also occur in biotite.

Secondary titanite forms anhedral, poikilitic grains rimming magnetite, ilmenite, and biotite. Its major-element composition overlaps that of primary titanite, but can differ in trace-element composition (Speer et al., 1981).

Epidote occurs as skeletal intergrowths with biotite and amphibole, as epitaxial rims on allanite, and as a saussuritization product in plagioclase cores. Microprobe analyses (App. 1), show that the epidotes composing the saussurite are more aluminous, with less than 16 mol% pistacite, than matrix epidotes, which contain between 25 and 34 mol% pistacite. Mn content is less than 0.10 mol% piemontite in the saussurite epidotes and between 0.22 and 1.13 mol% in the matrix epidotes.

Secondary white mica has two occurrences. The first is as discrete poikilitic or skeletal grains of white mica intergrown with biotite. The second is as fine-grained masses in the cores of plagioclases resulting from saussuritization. As noted above, these muscovites are interpreted as being secondary and generally have the same composition as the primary muscovites except for their lower Ti contents.

In weathered granite samples, supergene alteration of the sulfides is common. Pyrite and chalcopyrite have rims of hematite and hydrous iron oxides. Some pyrite is altered to marcasite.

Discussion

Conditions of crystallization

The probable conditions during crystallization of the Liberty Hill granitoids can be deduced from contact metamorphic assemblages of the aureole and xenoliths and, to a lesser extent, from compositions of the igneous minerals. Speer (1981a) found that the depth of emplacement corresponds to a pressure of 4.5 kbar on the basis of Fe-Mg partitioning in the assemblage cordierite + garnet + orthopyroxene + quartz. This is comparable to the estimated pressures of 3.1 to 4.7 kbar calculated from the Al content of the ferro-edenites using the geobarometer of Hammarstrom and Zen (1986). Water pressure was suggested to be half the total pressure in the central granitoids on the basis of the occurrence of dehydration metamorphic reactions in xenoliths at temperatures much lower than they would occur under conditions of water pressure equal to total pressure. Xenoliths in the central granitoids were concluded to have equilibrated at 725 ± 102°C and the border granitoids at 647 ± 20°C on the basis of Fe-Mg partitioning between garnet, biotite, and cordierite. Although not quantified, f_{O_2} was concluded to differ between the central and marginal granitoids.

For the assemblage biotite + magnetite + alkali feldspar, the equilibrium annite + $\frac{1}{2}O_2$ = alkali feldspar + magnetite + H_2O can be written. For this equilibrium Wones (1972) determined that $\log f_{H_2O} = 7409/T + 4.25 + \frac{1}{2}\log f_{O_2} + 3\log X_{Fe^{+2}} + 2\log X_{OH} - \log a_{KAlSi_3O_8} - \log a_{Fe_3O_4}$, where T is absolute temperature, $X_{Fe^{+2}}$ is the fraction of Fe^{+2} in all the octahedral sites of biotite and thus not Fe/(Fe + Mg), X_{OH} is the fraction of OH in biotite, and a is the activity of the $KAlSi_3O_8$ component in alkali feldspar and Fe_3O_4 component in magnetite. This relationship provides a means to relate several physical and compositional variables. Because many of the physical parameters for the Liberty Hill are unknown, the calculations for the compositions of the Liberty Hill minerals were performed at a variety of temperatures, f_{H_2O}, and f_{O_2} (Fig. 7). Stability curves for the Liberty Hill biotites were calculated for both absolute values of f_{O_2} and conditions of appropriate solid f_{O_2} buffers. The stability curves are based on the following assumptions: (1) the activity of $KAlSi_3O_8$ is 0.8. This is obtained from the activity–compositional relations model of Ghiorso (1984) using the estimated original magmatic feldspar compositions in the Liberty Hill pluton. (2) The activity of Fe_3O_4 in magnetite is 1.0. (3) The average biotite $X_{Fe^{+2}}$ is 0.5 and the X_{OH} is 0.9. (4) The oxygen-fugacity values for the solid buffers are from Chou (1978) for MH, from Huebner and Sato (1980) for NNO, from Hewitt (1978) for QFM, and from Wones (1981) for TMQHIL. TMQHIL is the titanite + magnetite + quartz + hedenbergite + ilmenite buffer given by $\log f_{O_2} = -30\,939/T + 14.98 + 0.142\,(P - 1)/T$, where T is in kelvins and P is in bars. Additional limits on the probable conditions were $P_{fluid} = P_{total}$ from Burnham et al. (1969), the stability of muscovite + quartz from Chatterjee and Johannes (1974), and the minimummelting reaction in the granite system from Johannes (1984).

The stability calculations for the igneous biotites of the Liberty Hill pluton and conditions derived from the contact aureole show that water and oxygen fugacities increased from the central granitoids to the marginal granitoids whereas temperature decreased. In Figure 7, the conditions of the marginal granitoids are constrained to lie in the region below the curve $P_{\text{fluid}} = P_{\text{total}}$, above the granite solidus, and in the stability field of muscovite + quartz. This small area, perhaps fortuitously, also includes the temperature estimated for the border granitoids. Estimated water fugacity would be 2.75 kbar, corresponding nearly to conditions of $P_{\text{fluid}} = P_{\text{total}}$ (Burnham et al., 1969), and f_{O_2} would be approximately $10^{-15.8}$. The conditions for the central granitoids are less constrained and lie below $P_{\text{fluid}} = P_{\text{total}}$, above the granite solidus, and to the low-temperature side of the QFM solid buffer. If the estimated temperature of 725°C and water pressure of $P_{\text{fluid}} = 0.5P_{\text{total}}$ corresponding to $f_{H_2O} = 1.7$ kbar are correct for the xenoliths, the f_{O_2} was about 10^{-15}, slightly more oxidizing than the conditions of the TMQHIL and NNO solid buffers (Fig. 7).

The $X_{Fe^{+2}}$ and X_{OH} values of biotites from the amphibole + biotite granitoid core facies and the biotite granitoid rim facies are nearly identical. Originally, this suggested the possibility of subsolidus re-equilibration at uniform conditions throughout the pluton. However, these calculations of Liberty Hill biotite stability from the estimated conditions of the different facies derived from the xenoliths predict uniform magmatic biotite compositions. It is a field demonstration of the results of Wintsch (1980) who found that the biotite composition in a biotite + K feldspar + magnetite assemblage is more or less indifferent to the fluid composition at unspecified P, T, f_{H_2O}, and f_{O_2}. However, the interpretation that conditions in the Liberty Hill pluton's central and marginal granitoids differed is plausible because the intensive parameters have been determined from independent sources.

The differences in oxygen fugacity and temperature between the central and marginal facies ought to be reflected in the oxide mineral compositions. The particular oxygen fugacities and temperatures obtained for the central and marginal facies lie along the same ilmenite compositional isopleth; however, the ulvöspinel component in the magnetites of the central facies should be about 20 mol% higher than the amount of ulvöspinel in the magnetites from the marginal facies (Spencer and Lindsley, 1981). The compositions of the ilmenites throughout the pluton are comparable in the amount of exsolved hematite; however, the magnetites of the border granites contain only traces of exsolved Ti oxides whereas the magnetites of the central granitoids contain up to 25 vol% exsolved ilmenite.

Evolution of the mineral assemblages

There are five AFM varietal mineral assemblages in the Liberty Hill pluton: clinopyroxene → actinolite → ferro-edenite, ferro-edenite + biotite, biotite, muscovite + biotite, and ferro-edenite → ferroan pargasite + biotite. The clinopyroxene-bearing assemblage is restricted to enclaves or their immediate vicinity. Most of the pluton is dominated by the central, coarse-grained ferro-edenite + biotite granitoids that show abundant evidence for replacement of ferro-edenite by biotite. The central granitoids grade imperceptibly into coarse-grained biotite, muscovite + biotite, or ferro-edenite → ferroan pargasite + biotite granitoids at the pluton margins. These coarse-grained facies are intruded by the later and finer-grained biotite granitoids. The mineralogical evolution among these varietal assemblages is discussed in this section.

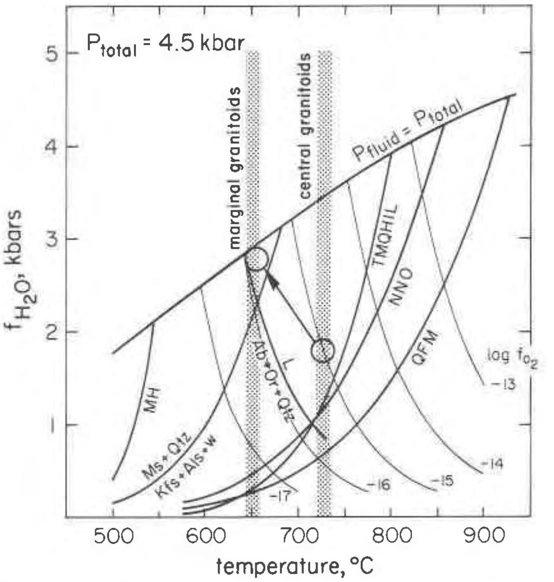

Fig. 7. The biotite + magnetite + alkali feldspar assemblage stability in the Liberty Hill pluton corresponding to the equilibrium annite + ½ O_2 = alkali feldspar + magnetite + H_2O over a range of temperatures and f_{H_2O} for both absolute values of f_{O_2} and conditions of the MH (= magnetite + hematite), TMQHIL (= titanite + magnetite + quartz + hedenbergite + ilmenite), NNO (= nickel + nickel oxide), and QFM (= quartz + fayalite + magnetite) solid buffers. Other calculated curves in the diagram are $P_{\text{fluid}} = P_{\text{total}}$ (Burnham et al., 1969), stability of muscovite + quartz (Chatterjee and Johannes, 1974), and beginning of melting in the granite system (Johannes, 1984). The temperature and pressure estimates for the Liberty Hill granitoids are from Speer (1981a).

Clinopyroxene → actinolite → ferro-edenite. The occurrence of clinopryoxene in the Liberty Hill pluton could represent either crystallization from the melt, xenocrysts, or restite minerals in equilibrium with the melt. Once present, it reacted with the melt, first producing actinolite, then ferro-edenite. The sharp, discontinuous nature of the zoning in the amphiboles may indicate either incomplete reaction because of slow diffusion, a miscibility gap, or a discontinuity in crystallization conditions. The compositional gap is similar to though wider than, that

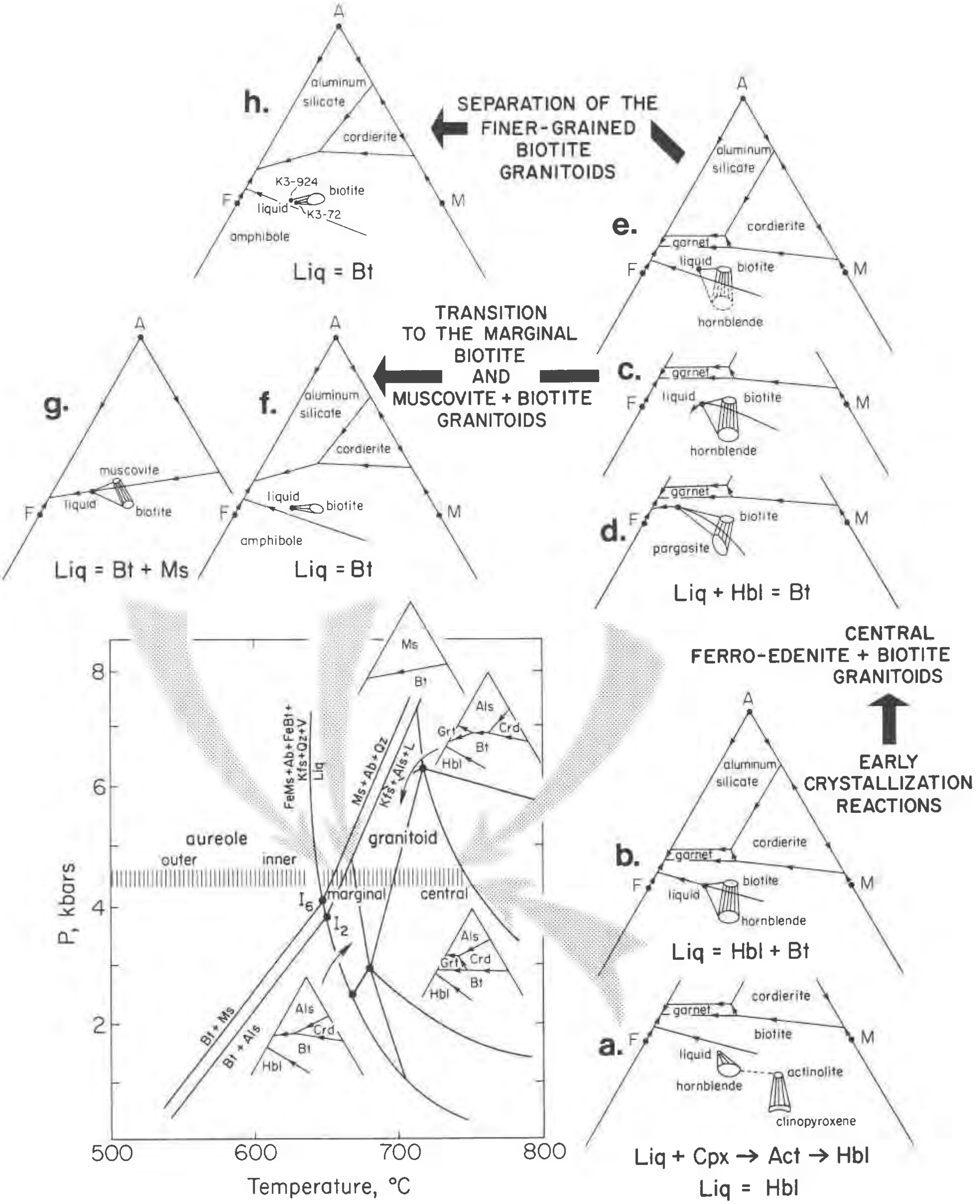

Fig. 8. Regions of distinct AFM liquidus topologies in *P-T* space and pertinent schematic phase relationships among hornblende, biotite, cordierite, garnet, aluminum silicate, and muscovite in AFM (A = Al_2O_3-K_2O-Na_2O-CaO, F = FeO, M = MgO) liquidus projections from quartz, alkali feldspar, plagioclase, and water for granitoid magmas (Abbott and Clark, 1979; Abbott, 1981, 1985). The surrounding AFM diagrams illustrate the evolution of crystallization reactions in the Liberty Hill pluton: (a) The Liq + Cpx = Act = Hbl reaction observed in the enclaves and enclave-bearing granitoids. (b) The probable Liq = Hbl + Bt reaction in the

found by Czamanske and Wones (1973), Mason (1978), and Chivas (1981) for other igneous occurrences. At the elevated pressures, temperatures, and Fe contents of the amphiboles in the Liberty Hill, the compositional gap should be small or nonexistent. Oba (1980) found no miscibility gap between tremolite and pargasite at magmatic temperatures above 1 kbar and found the gap decreased with increasing Fe content at lower pressures (Oba, 1986). Based on thermochemical data, Graham and Navrotsky (1986) have suggested that disequilibrium rather than a miscibility gap is the more likely interpretation for such compositional gaps. The Si content of the actinolite being >7.6 atoms per 24 anions also is evidence that it is not a magmatic phase; Chivas (1981) concluded that $Si = 7.3$ is the limit of hypersolidus crystallization on the basis of Leake's (1971) suggestions about the compositional limits of igneous amphiboles.

In the absence of a miscibility gap, the actinolite rims on clinopyroxene must be incomplete reaction products of xenocryst + melt or restite + melt, and the actinolite did not crystallize from the Liberty Hill magma. If the actinolite is not magmatic, it is unlikely that the clinopyroxene is either. However, clinopyroxene was present in the melt; forming inclusions in plagioclase and reacting with the melt to produce a more magesian ferro-edenite and giving amphibole-biotite K_D values between 0.86 and 0.99 (Fig. 6a). The reaction sequence clinopyroxene → actinolite → ferro-edenite could have occurred either before or after biotite began to crystallize. Because the biotite compositions appear unaffected by the presence of the clinopyroxene, the Liq + Cpx (xenocryst, restite) → actinolite → ferro-edenite sequence must have occurred before the appearance of biotite, suggesting that the early crystallization reaction in the Liberty Hill magma was Liq = Hbl (Fig. 8b).

Ferro-edenite + biotite. The ferro-edenite + biotite granitoids are the dominant crystallization products of the Liberty Hill magma. The widespread texture of biotite replacing ferro-edenite is evidence that crystallization conditions and compositions at the level of emplacement were those of the reaction Liq + Hbl = Bt described by Abbott (1981).

In its simplest form, the Liq + Hbl = Bt reaction would use the melt as both source and sink of all the necessary components to complete the reaction and thus is better written as Liq 1 + Hbl = Bt + Liq 2. Because the granitoids were emplaced as mixtures of melt + crystals, Liq 1 and Liq 2 would be the interstitial melt. The finer-grained biotite granitoids intruding the pluton are believed to be derived from the interstitial liquids of the crystallizing coarse-grained granitoids and thus can be used as estimates of these Liquid compositions. A constraint on Liq 1 and Liq 2 in the reaction should be the compositional evolution of the Liberty Hill magma as shown by "liquid" variation diagrams. On the basis of the variation diagrams for the Liberty Hill pluton (Speer et al., unpub. ms.), Liq 2 should differ from Liq 1 by decreased Si, Al, Ti, Fe, Mg, and Ca, yet have generally the same K and Na contents. As shown below, this liquid variation could only be accomplished with the participation of other phases in the reaction. Indeed, the reaction may be the reason that K and Na remain relatively constant, an atypical trend in a crystallizing melt.

The least-squares petrologic-mixing-model program GENMIX (Le Maitre, 1981) was used to balance the anhydrous components of the various Hbl + Liq = Bt model reactions. A finer-grained granitoid (K3-72) was used as an estimate of Liq 1, and a more differentiated, finer-grained biotite granitoid (K3-924) was used as an estimate of the product, Liq 2. Mineral compositions from K3-1303.8, in the same drillhole as K3-72, were used as estimates of the phases that may have participated in the reaction (Tables 1, 2, and 3). The feldspars and quartz were assumed to have end-member and ideal compositions, respectively. All Fe was calculated as FeO, and analyses were recalculated to 100% on an anhydrous basis. Magnetite was assumed to be 93.09% FeO.

Model 1 (Table 4) is the essential Liq 1 + Hbl = Liq 2 + Bt reaction. The differences indicate insufficient Si, Ti, Fe, Mg, and Na and excess Al and Ca to balance the reaction. Ilmenite is ideal as a source for Ti. Anorthite or titanite can serve as Ca sinks; Al, K, and Na sinks are albite and K-feldspar. Si and Fe can be balanced by use of magnetite and quartz. Model 2 (Table 4) is the reaction incorporating these remaining minerals. The reaction can be acceptably balanced, as would be expected, by adding relatively simple minerals and more phases than components. Excellence in balancing the reaction does not prove that it occurred but does show that biotite may be produced from amphibole while allowing the melt to con-

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magma. (c–e) There are three possible reasons for the Liq + Hbl = Bt reaction of the central, coarse-grained ferro-edenite + biotite granitoid: (c) the low-temperature end of the Hbl-Bt liquidus boundary is odd, (d) the low-temperature end of the Hbl-Bt liquidus boundary is odd but with different geometry from (c) because the amphibole is pargasite, or (e) Liq has moved from the Hbl into the Bt field. (f–g) With completion of the Liq + Hbl = Bt reaction by the consumption of Hbl in the marginal, coarse-grained granitoids, the crystallization reaction is (f) Liq = Bt or, more rarely, (g) Liq = Bt + Ms. (h) the finer-grained biotite granitoids are concluded to be interstital melt separated from the coarse-grained granitoids in which only Bt crystallizes by the reaction Liq = Bt. The estimated conditions of the central granitoids are 725°C, $P_{total} \approx 4.5$ kbar, $P_{fluid} \approx 0.5P_{total}$, and $f_{O_2} \approx 10^{-15}$ above to the NNO and TMQHIL solid buffers. The marginal granitoids yield conditions of 647°C, $P_{fluid} \approx P_{total}$, and $f_{O_2} \approx 10^{-16}$, relatively more oxidizing.

TABLE 4. Coefficients (*N*, wt%) of least-squares mixing models for progressively more inclusive magmatic Liquid 1 + Hbl = Bt + Liquid 2 and subsolidus Hbl = Bt reactions in the Liberty Hill pluton, South Carolina

	N	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
					Model 1					
Reactants										
Liquid 1†	99.95	72.52	0.35	14.74	1.95	0.04	0.41	1.55	3.08	5.37
Hbl*	0.05	44.51	1.51	9.02	21.99	0.88	8.48	10.69	1.76	1.17
Products										
Liquid 2‡	95.14	74.46	0.15	14.18	1.04	0.04	0.20	1.18	3.58	5.17
Bt*	4.86	37.83	3.00	14.51	24.33	0.61	9.49	0.17	0.17	9.90
Difference		−0.17	0.06	0.54	−0.22	−0.03	−0.24	0.43	−0.34	−0.03
Residual sums of squares: 0.7297										
					Model 2					
Reactants										
Liquid 1†	96.53	72.52	0.35	14.74	1.95	0.04	0.41	1.55	3.08	5.37
Hbl*	3.47	44.51	1.51	9.02	21.99	0.88	8.48	10.69	1.76	1.17
Ilm*	<0.00	0.08	47.64	0.08	46.17	5.26	0.31	0.23	0.12	0.10
Products										
Liquid 2‡	84.30	74.46	0.15	14.18	1.04	0.04	0.20	1.18	3.58	5.17
Bt*	5.43	37.83	3.00	14.51	24.33	0.61	9.49	0.17	0.17	9.90
Qtz	3.69	100.00	—	—	—	—	—	—	—	—
An	3.93	43.19	—	36.55	—	—	—	20.16	—	—
Kfs	1.92	64.76	—	18.83	—	—	—	—	—	16.92
Ttn*	0.25	31.18	36.83	1.83	2.00	0.31	0.23	27.38	0.14	0.09
Mag	0.47	—	—	—	93.09	—	—	—	—	—
Difference		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Residual sums of squares: 0.0001										
					Model 3					
Reactants										
Hbl*	49.52	44.51	1.51	9.02	21.99	0.88	8.48	10.69	1.76	1.17
An	42.62	43.19	—	36.65	—	—	—	20.16	—	—
Mag	5.04	—	—	—	93.09	—	—	—	—	—
Ilm*	2.82	0.08	47.64	0.08	46.17	5.26	0.31	0.23	0.12	0.10
Products										
Bt*	5.05	37.83	3.00	14.51	24.33	0.61	9.49	0.17	0.17	9.90
Chl*	26.13	29.23	0.16	20.87	34.57	1.01	13.77	0.18	0.11	0.10
Ep*	52.64	39.79	0.17	23.81	12.40	0.52	0.22	22.89	0.10	0.10
Ab	6.59	68.74	—	19.44	—	—	—	—	11.82	—
Qtz	3.69	100.00	—	—	—	—	—	—	—	—
Ttn*	0.25	31.18	36.83	1.83	2.00	0.31	0.23	27.38	0.14	0.09
Cal	0.79	—	—	—	—	—	—	56.03	—	—
Difference		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Residual sums of squares: 0.0000										

† Composition of a less-evolved dike of fine-grained biotite granitoid K3-72.
‡ Composition of a more evolved dike of fine-grained biotite granitoid K3-924.
* Mineral analysis from the coarse-grained amphibole + biotite granitoid K3-1303.8 (Tables 1–3).

tinue its magmatic trend by involving other minerals in the reaction in amounts commensurate with their modal abundances. Biotite appears to be replacing a subequal amount of hornblende. Textural evidence for the reaction is the replacement of ferro-edenite by biotite (Figs. 3a, 3b) and rims of secondary titanite on ilmenite. The production of anorthite component could show up in a more calcic zone in plagioclase. However, the calcic zone would be minor because of the small modal abundance of the products. Plagioclases do have oscillatory zoning, but it is not clear how a particular calcic zone can be correlated with the Liq + Hbl = Bt reaction.

Albite has been omitted from these model crystallization reactions. Addition of $NaAlSi_3O_8$ as a phase changes the reaction to the dominant granitoid crystallization reaction Liq = An + Ab + Kfs + Qtz, and the Liq + Hbl = Bt reaction is subordinated to less than 1% of the overall reaction, as would be expected. In order to better examine the Liq + Hbl = Bt reaction, albite was not included.

The average K_D value for the coexisting ferro-edenite + biotite of the Liberty Hill is 1.04, with a range of 0.96–1.17 (Fig. 6b). Although many coexisting metamorphic hornblendes and biotites have K_D values near 1.0, Mason (1985) has noted that in igneous rocks, hornblendes are more magnesian than the coexisting biotites (Kanisawa, 1972). Mason (1985) found that, for the coexisting hornblendes and biotites in the Peruvian Coastal batholith, the K_D is about 0.63. The only exceptions in the Peruvian granitoids are samples in which biotite has formed by replacement of hornblende. In these instances, K_D values are near 1.0, and Mason concluded that the distribution coefficient can be used to distinguish biotites that crystallized directly from a melt from those formed by replacement of hornblende. Such a compositional distinction is consistent with the apparent formation of biotites by the replacement of ferro-edenite in the Liberty Hill pluton. The absence of more "igneous" K_D values may reflect the difficulty of re-equilibrating the amphibole.

The Liq + Hbl = Bt reaction in the Liberty Hill pluton could have taken place as a result of either equilibrium or disequilibrium crystallization. Abbott (1981) has concluded that the low-temperature end of the Bt-Hbl liquidus boundary is odd; thus, the crystallization path could encounter a higher-temperature even reaction, Liq = Hbl + Bt (Fig. 8B), after the supposed initial Liq = Hbl reaction (Fig. 8a). With continued equilibrium crystallization, liquids following the boundary would crystallize by the odd reaction, Liq + Hbl = Bt, observed throughout the pluton. It is possible that the melt encountered the Hbl-Bt liquidus boundary where the equilibrium Liq + Hbl + Bt is odd; this would eliminate a need for the intervening even reaction. Abbott (1981) has drawn a fairly gentle liquidus boundary; however, the compositions of the Liberty Hill amphiboles and biotites require a sharper change in direction in the AFM diagram (Fig. 8c) for an odd reaction. Alternatively, the sharp change in liquidus direction could be in the larger compositional space rather than in the simple AFM projection or could be made less sharp by interpreting the pargasite rims as igneous minerals (Fig. 8d).

With disequilibrium crystallization, the interstitial liquid could move from a position in the Hbl field (Fig. 8a) to one within the Bt field (Fig. 8e). Such an abrupt movement could result from either a change in the positions of the AFM field boundaries or a change in melt composition because of crystallization or contamination. The movement of the AFM field boundaries would be caused by a change in physical conditions, most likely P_{total} or P_{fluid}. Increasing P_{fluid} would increase the size of the liquidus field for biotite (Abbott, 1981).

It is possible that the reaction of biotite replacing hornblende is a subsolidus one. Using what are interpreted as the subsolidus minerals intergrown with hornblende—chlorite, epidote, calcite, and quartz—and their compositions from sample K3-1303.8 (Table 3), a reaction to produce biotite from amphibole without involvement of a melt can be written (Model 3, Table 4). Although feasible, this reaction is considered unlikely to have caused the replacement of amphibole by biotite because the proportions of the replacement products are not consistent with their modal abundances. Biotite or chlorite, rather than epidote, are the most abundant replacement products. Locally, biotite replacement of amphibole occurred in the absence of chlorite, epidote, albite, or calcite, and the replacement of amphibole by chlorite, epidote, albite, or calcite occurred in the absence of biotite. In addition, late-stage subsolidus or deuteric reactions in granitoids produce magnesian actinolite (Mason, 1978; Lanier et al., 1978; Chivas, 1981), not a ferro-edenite. For these reasons, biotite replacement of amphibole in the Liberty Hill pluton is interpreted as a magmatic process.

Marginal facies. The possible origins of the three varietal AFM mineral assemblages in the coarse-grained biotite, muscovite + biotite, and ferroan pargasite + biotite granitoids along the margins of the Liberty Hill pluton have been examined previously by Wenner and Speer (1986). They concluded that the marginal facies compositionally overlap the central granitoids, which argues against significant differentiation. The marginal facies do show minor amounts of wall rock–magma interaction that affected some trace-element and oxygen-isotope compositions.

The varietal biotite assemblage could be produced easily from the central granitoids if Hbl is exhausted before Liq in the reaction Liq + Hbl = Bt. Estimations of conditions for the marginal facies yield lower temperatures and higher water pressures than those for the central granitoids; the interpretation is that the marginal-facies conditions are conditions of final re-equilibration. Because it might be assumed that at some earlier instance the conditions in the Liberty Hill magma were relatively homogeneous, an extended reaction or re-equilibration history for the marginal rocks is implied, allowing the complete reaction of Hbl. Once the amphibole has disappeared, the reaction equation would be Liq = Bt (Fig. 8f). The extended reaction history of the marginal rocks may have been feasible because of a minor influx of water from the wall rocks (Wenner and Speer, 1986). The increased a_{H_2O} could also shift the AFM liquidus boundaries if the Liq + Hbl = Bt reaction resulted from disequilibrium crystallization.

The origin of the biotite + muscovite granitoids in the northern margin of the pluton is probably the extreme consequence of events that formed the marginal biotite granitoids. Decreasing temperature and increasing water pressure would allow the appearance of the muscovite field in the AFM topology (Fig. 8g) and the crystallization reaction Liq = Bt + Ms (Abbott, 1985). The absence of intervening assemblages containing cordierite and aluminum silicate more than likely results from their restricted occurrence in *P-T* space or from subsequent reactions.

The occurrence of amphiboles with aluminous ferroan pargasite rims coexisting with aluminous biotites along the border of the pluton is not readily predicted. The irregular zoning of the amphiboles from ferro-edenite to ferroan pargasite is essentially a manifestation of a rapid increase in Al with only a small increase in Fe/(Fe + Mg) (Fig. 2b). The occurrence as thin rims is evidence of a late feature; however, the more aluminous and magnesian nature of the coexisting biotites (Figs. 4, 6c) indicate that the biotites equilibrated with the Al-rich amphibole rims.

The occurrence of aluminous amphiboles in metamorphic rocks has been attributed to extremely aluminous rock compositions, differing phase assemblages, differing temperatures (Bunch and Okrusch, 1973), increased pressure (Leake, 1965), and increased oxygen fugacity (Morteani, 1978). The granitoids along the margin of the pluton have rock compositions and silicate and oxide mineral assemblages comparable to other granitoids in the pluton. Hammarstrom and Zen (1986) quantified the relation of Al content of amphiboles in granitoid rocks with pressure. Using their geobarometer, the Al contents of the Liberty Hill pargasites correspond to estimated pressures of 3.4 to 6.3 kbar, compared to estimated pressures of 3.1 to 4.7 kbar for the ferro-edenites. This simple explanation is attractive, but there is no evidence that the granitoids in the northeastern section of the pluton are deeper or preserve a late crystallization at deeper levels. The compositional trend of aluminous amphibole rims is opposite to those found by Czamanske and Wones (1973), Mason (1978), and Chivas (1981), whose rocks have also recorded an increase in f_{O_2} and Si activity with crystallization to form tremolite rims. The zoning to aluminous amphiboles with crystallization in the Liberty Hill pluton is also at odds with the expected compositional trend from the tremolite + albite = edenite + quartz reaction qualitatively determined by Graham and Navrotsky (1986). Chivas (1981) has noted that amphiboles crystallizing from magmas that did not evolve a fluid (nonmineralized trends) should have a limited compositional range. In a magma that does evolve a fluid, magmatic amphiboles would re-equilibrate or grow rims in the subsolidus and have variable compositional trends depending on the conditions and coexisting phase assemblage.

The most reasonable conclusion is that the ferroan pargasite rims are late magmatic or subsolidus features. The average K_D value of 1.22, with a range of 1.13–1.30, for the coexisting ferroan pargasite + biotites may be indicative of such nonmagmatic origin and explain K_D values of >1.0 found in other marginal Liberty Hill granitoids not studied in such detail (Fig. 8c). The higher water pressures and oxygen fugacities of the marginal facies may favor such reactions and explain the restriction of such ferroan pargasite + biotite assemblages to the margin of the pluton.

Finer-grained biotite granitoids. The finer-grained biotite granitoids are interpreted as having crystallized from interstitial melts, extracted from the coarse-grained granitoids. The multiple compositions of these rocks (melts) indicates that they separated either at several different times or from different volumes with differing degrees of crystallization. Interstitial melts of the coarse-grained granitoids were producing biotite by the Hbl + Liq 1 = Bt + Liq 2 and Liq = Bt crystallization reactions. If interstitial melts separated to produce the finer-grained rocks, these crystallization reactions would explain the essential similarity in compositions between biotites in the coarse-grained rocks and biotites crystallized from the extracted melts.

Pyrrhotite → pyrite. The inclusion assemblage pyrrhotite + chalcopyrite + pyrite is the initial sulfide assemblage that crystallized with an early magnetite + silicate assemblage. However, this sulfide inclusion assemblage is a re-equilibrated one. At temperatures between 400 and 600°C, pyrrhotite and chalcopyrite react to form pyrite + intermediate Cu-Fe solid solution + vapor (Vaughan and Craig, 1978). The high-temperature inclusion assemblage, therefore, was pyrrhotite + pyrite + intermediate Cu-Fe solid solution + magnetite, which has a thermal stability at higher temperatures than the granite solidus. The pyrite + chalcopyrite matrix assemblage is the later sulfide assemblage that crystallized in equilibrium with the magnetite + ilmenite + silicate assemblage. This sequence of sulfides indicates that the activities of oxygen and sulfur appear to have increased during crystallization of the Liberty Hill magma.

CONCLUSIONS

Enclaves and a traverse from core to rim of the Liberty Hill pluton represent a small portion of the cooling history of the pluton and indicate the nature of the Liq + Hbl = Bt crystallization reaction and reactions before and after it (Fig. 8). The prevalence of replacement textures and the rarity of $K_D = (X^{Bt}_{Mg}/X^{Bt}_{Fe})/(X^{Hbl}_{Mg}/X^{Hbl}_{Fe}) < 1$ indicate that little biotite was present before the Liq + Hbl = Bt reaction. It is envisioned that the Liberty Hill magma initially began crystallizing with the Liq = Hbl reaction, concurrent with a Liq + Cpx → Act → Hbl reaction where the Cpx crystals were xenocrysts or restites (Fig. 8a). If the magma solidified as a result of equilibrium crystallization, the Hbl-Bt liquidus boundary would have been reached where either (1) the Liq = Hbl + Bt even reaction was encountered before the Liq + Hbl = Bt odd reaction (Fig. 8b) or (2) conditions of the Liq + Hbl = Bt odd reaction were directly encountered (Figs. 8c, 8d). If the magma solidified as a result of disequilibrium conditions, the interstitial liquid would move from a position in the Hbl field (Fig. 8a) to one within the Bt field (Fig. 8e). Such an abrupt change in the positions of the AFM field boundaries, melt compositions, or both would result in the Liq + Hbl = Bt reaction. Such changes could be brought about by movement of magma, adding or removing melt, or an influx of water from the country rocks. Perhaps significantly, the finer-grained biotite granitoid magmas are believed to represent the interstitial melt that separated from the coarse-grained rocks at this stage. The interstitial melt of the coarse-grained granitoid was crystallizing Bt by either Hbl + Liq = Bt or Liq = Bt and, upon separation, the Liq = Bt reaction would be expected to be the separated melt's crystallization reaction (Fig. 8h).

The Liq solidification of the central granitoids was completed before the consumption of Hbl, preserving the Hbl + Bt assemblage. Locally, the Hbl may have been sufficiently isolated from the Liq to prevent further reaction. The extended reaction history of the marginal coarse-grained granitoids allowed the Hbl to be exhausted before Liq in the reaction Liq + Hbl = Bt, whereupon the melt completed its solidification by the Liq = Bt reaction (Fig. 8f) and, locally, by the Liq = Bt + Ms reaction where there was sufficient water pressure (Fig. 8g). Thus, differing coarse-grained granitoid mineral facies in the Liberty Hill pluton have not resulted from multiple intrusion or differentiation, but rather from extended reaction histories of the marginal portions of the pluton. The extended reaction history may be caused by the increased availability of water at the margins, possibly from the country rocks.

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