## Geochemistry of Mafic Enclaves and Host Granitoids from the Chilliwack Batholith, Washington: Chemical Exchange Processes between Coexisting Mafic and Felsic Magmas and Implications for the Interpretation of Enclave Chemical Traits

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#### ABSTRACT

Mafic enclaves from three plutons in the Chilliwack batholith have been compared with contemporaneous mafic stocks in order to determine (1) the processes by which mafic and felsic magmas hybridize in the plutonic environment and (2) whether analysis of early-formed enclave minerals, particularly apatite, can provide a means of seeing through hybridization effects and deciphering the original trace element characteristics of enclave magmas. Whole rock and mineral chemistry data reveal a two-stage history of enclave hybridization. Stage 1, a diffusive exchange of trace elements between coexisting liquids, produced enclaves with distinctive concave-upward rare earth element patterns that parallel those of the host granitoids but had minimal impact on the major elements, whose transfer is rate limited by the slow diffusion of Si. This stage probably occurred at a mafic-felsic interface in a stratified magmatic system. Stage 2, a partial reequilibration of enclave minerals with a differentiated and hybridized interstitial melt, occurred after the enclaves were entrained in the host and partially crystallized. This process caused enclave and host minerals (amphibole, biotite, apatite) from each pluton to have similar major oxide chemistries but did not reequilibrate the trace elements. As a result of these hybridization processes, even early-formed apatite crystals do not preserve information about the original trace element characteristics of enclave magmas in this case. However, the results of this study illustrate the potential of using enclave chemistry to constrain the nature and timing of mafic magma inputs into felsic magma bodies.

### Introduction

Mafic enclaves are a widespread feature of granitic rocks, particularly in continental arc settings, and have been the subject of numerous studies over the past century (Didier and Barbarin 1991 and references therein). Although some aspects of enclave petrology remain contentious, it is generally accepted that the majority of fine-grained dioritic enclaves in arc batholiths represent globules of mafic magma that were incorporated into and undercooled against a molten granitoid host. Compelling evidence for such an origin is provided by mineral textures indicative of rapid cooling, magmatic flow fabrics, chilled and/or crenulate enclave margins indicative of liquid-liquid contacts, and field ex-

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posures that document the formation of enclaves by disruption of mafic dikes or sheets (Reid et al. 1983; Frost and Mahood 1987; Vernon 1991; Blundy and Sparks 1992; Wiebe et al. 1997).

Inputs of mafic magma are integral to the generation of continental arc granitoids (Tepper et al. 1993 and references therein). Enclaves provide direct evidence of these inputs, but their chemical traits are difficult to interpret because most enclaves have undergone chemical modification by hybridization with felsic magmas and/or by fractional crystallization. Hybridization is a multistage, progressive process (Bateman 1995) that can begin before enclave formation with interactions at the mafic-felsic interface of a stratified magma system (Stimac et al. 1990; Wiebe et al. 1997). Following enclave dispersal, additional chemical exchange may occur between the enclave and its enclosing

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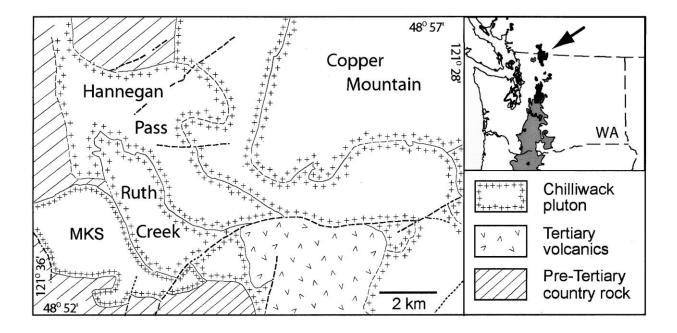
host (Dorais et al. 1990; Blundy and Sparks 1992). The extent of hybridization at any stage depends on an array of factors that are difficult if not impossible to constrain, including the thermal, rheological, and chemical contrasts between enclave and host; the time available for interaction; and the volatile contents of both magmas. These uncertainties led Flinders and Clemens (1996, p. 222) to conclude that "for many granitic intrusions, enclave studies will prove to be an interesting, but time consuming, petrological cul de sac." However, hybridization processes can be constrained if samples representative of the original, unhybridized mafic magma(s) are available (Blundy and Sparks 1992; Wiebe et al. 1997). This study focuses on the Chilliwack batholith, where unhybridized mafic rocks are present in gabbroic and dioritic stocks that are contemporaneous with the rest of the batholith (Tepper 1996). The first objective of this study is to compare samples of mafic stocks with enclaves from nearby granitoids in order to (1) determine the extent to which the enclaves differ chemically from the less modified mafic pluton rocks and (2) identify the hybridization and/or fractionation processes by which the enclaves were chemically modified.

Despite the widespread evidence for hybridization, there are indications that at least some enclaves do preserve information about their original chemistry. Most enclaves in arc batholiths retain a basaltic to andesitic bulk composition, and in rare cases, they also preserve isotopic traits of a mantlederived parent magma (Holden et al. 1987; Metcalf et al. 1995). In addition, some enclave mineral phases can preserve their original chemistry even when other mineral phases and the whole rock composition display evidence of extensive reequilibration (Dorais et al. 1990; Allen 1991). The minerals most likely to preserve information about the original composition of an enclave magma are those that form early and have slow intracrystalline diffusion rates for the elements of interest. These requirements are met by apatite and some plagioclase. Acicular apatite crystals are a common feature of fine-grained mafic enclaves, including those in the Chilliwack, and are thought to form by rapid crystallization from an undercooled melt that existed immediately following emplacement of the enclave magma into the granitic host (Wyllie et al. 1962). Because thermal diffusion rates are several orders of magnitude faster than chemical diffusion rates (Frost and Mahood 1987), it is likely that acicular apatite crystals grew before there was an opportunity for extensive contamination of the mafic enclave liquid by the felsic host. Combined with the slow diffusion rates for rare earth elements (REE) in apatite (Cherniak 2000), this makes apatite a prime candidate for the second objective of this study: to determine whether enclave apatite crystals preserve a record of the original trace element characteristics, including REE, of enclave magmas.

### Geologic Setting and Sample Descriptions

The Cascade plutonic arc is a chain of epizonal calc-alkaline intrusions, extending from Oregon to British Columbia, that were emplaced during the past 36 Ma in response to subduction of the Juan de Fuca plate beneath the western edge of North America. The largest batholith in this arc is the Chilliwack (fig. 1), which is made up of at least 40 individual plutons and contains rock types ranging from gabbro to granite (Tepper et al. 1993). Scattered mafic plutons represent ~2% of the exposed area of the Chilliwack, and their ages (34-22 Ma) overlap with those of the granitoid rocks (35–2 Ma). These gabbroic and dioritic stocks are the plutonic equivalents of calc-alkaline and tholeiitic arc basalts and their differentiates and are divided into a medium-K suite (MKS) and a low-K suite (LKS; Tepper 1996). Granitoid plutons comprise the remaining ~98% of the Chilliwack and range from quartz diorite to granite (57%–78% SiO<sub>2</sub>). The granitoids are assigned on the basis of geochemical and mineralogical traits into three groups: (1) intermediate (quartz diorite, tonalite, and granodiorite), (2) transitional (granodiorite and tonalite), and (3) leucocratic (leucocratic granodiorite and granite). Contrasts between these groups are particularly evident in their REE patterns. Intermediate plutons show modest light rare earth element (LREE) enrichment  $(La/Nd_N = 1.4-2.0, Dy/Lu_N = 1.14-1.29)$ , whereas leucocratic plutons have distinctive concaveupward REE patterns (Dy/Lu<sub>N</sub> < 1) and more fractionated LREE (La/Nd<sub>N</sub> = 2.3-3.1). The transitional plutons have some characteristics of both other groups (Dy/Lu<sub>N</sub> < 1, La/Nd<sub>N</sub> = 1.8-1.9), but it is important to note that each individual pluton belongs to only one group; no examples of zoned plutons that grade from one group to another (e.g., from intermediate to transitional) have been identified. Tepper et al. (1993) attribute the differences among these three pluton groups to variations in water fugacity during melting of amphibolitic lower crust.

Mafic enclaves in the Chilliwack share many of the field and petrographic characteristics of enclaves in other calc-alkaline batholiths (Didier and Barbarin 1991). They occur as oblate spheroids up to ~60 cm in diameter and are commonly found in



**Figure 1.** Simplified geologic map (after Tabor et al. 1994) showing the locations of enclave-bearing plutons sampled for this study. The margins of individual Chilliwack plutons are outlined by plus signs, but only the studied plutons are labeled by name. Also labeled is one medium-K series (MKS) mafic stock. Faults are indicated by bold dashed lines. Regional map shows the location of the Chilliwack (*arrow*) in relation to other plutonic (*black*) and volcanic (*gray*) rocks of the Cascade arc.

clusters, although no enclaves examined in this study were spatially associated with dikes or larger mafic bodies. The enclaves are finer grained than the host, but no chilled margins have been observed. Modal abundances of amphibole and opaque oxides are higher in the enclaves than in the host granitoids (table 1), and enclave apatites are more elongate (average L/W = 10-15 in enclaves vs. 5–6 in hosts), but the enclaves contain no mineral phases that are not found in the host.

The enclaves examined in this study were collected from three plutons, each representing one of the three Chilliwack granitoid groups (fig. 1). This selection makes the effects of enclave-host interactions easier to recognize because each host granitoid has a distinctive REE pattern. Representing the intermediate group is the ~14-km<sup>2</sup> biotitehornblende granodiorite of Hannegan Peak, which contains widely scattered enclaves that record varying degrees of hybridization. Hannegan Peak enclaves range up to 20 cm in length and display a spectrum of textures from those that are sharply bounded and noticeably more mafic than the host to those that are barely discernable in outcrop. Deuteric alteration, manifested in chloritization of biotite and sericitization of feldspar, is pervasive in these enclaves but less so in the host granodiorite.

For the transitional granitoid group, samples were collected from the ~100-km<sup>2</sup> hornblende-biotite tonalite of Copper Mountain. Enclaves are heterogeneously distributed in this pluton, but many appear to be concentrated in clusters. Samples for this study were collected from one such cluster where randomly oriented enclaves up to 60 cm in length account for ~1% of the outcrop over an area of several hundred square meters. These enclaves are texturally diverse, and many contain phenocrysts of amphibole, plagioclase, and/or biotite. Alteration has resulted in extensive chloritization of biotite and some sericitization of feldspar in the enclaves, but again these effects are less pronounced in the host. The third pluton examined is the leucocratic group biotite granodiorite of Ruth Creek. Most enclaves in this ~5-km² stock occur in trains or swarms that are probably disaggregated dikes; away from these zones, enclaves are extremely rare. The Ruth Creek enclaves studied are smaller (<10 cm in diameter) and finer grained than those from the other two plutons. Alteration is also much less pervasive and is limited to sericitization of some plagioclase cores and localized replacement of biotite by chlorite + rutile.

All three plutons are inferred to have crystallized at shallow (<5 km) crustal depths based on amphi-

 Table 1. Geochemical and Modal Data for Representative Enclave and Host Samples

_	I	Hannegar	n enclav	re	Hannegan host		Copper	enclave		Copper host	Ruth	Creek ei	nclave	Ruth Creek host
	83-15	92-06	92-08	92-09	92-07b	92-02	92-03a	92-04	92-10	92-03b	92-15	92-16	92-18	RC-92
SiO <sub>2</sub>	55.04	54.56	55.66	55.91	63.92	54.97	53.55	59.96	53.71	65.23	51.02	53.17	51.53	75.10
$TiO_2$	.85	.89	.98	.92	.75	.60	.63	.54	.65	.48	1.11	1.12	.90	.23
$Al_2O_3$	17.46	16.69	17.63	16.60	15.72	17.93	17.82	17.46	18.27	16.34	18.40	18.90	17.66	13.02
$Fe_2O_3^t$	8.04	7.73	7.92	7.29	5.56	8.08	8.92	6.01	8.38	5.25	9.19	9.03	8.09	1.74
MgO	4.12	4.82	4.04	4.52	2.85	3.70	4.82	3.10	3.95	2.26	5.34	4.00	5.64	.48
MnO	.15	.20	.15	.18	.10	.20	.18	.13	.18	.10	.18	.24	.17	.05
CaO	6.42	8.04	7.63	6.80	5.10	7.46	8.22	6.51	7.78	5.49	9.14	5.25	9.17	1.35
$Na_2O$	4.36	4.01	3.81	4.10	3.58	4.39	4.08	3.94	4.15	3.63	3.88	5.12	3.96	3.89
$K_2O$	2.04	1.06	1.62	1.73	2.26	1.05	1.05	1.40	1.15	1.56	1.18	2.25	1.14	3.70
$P_2O_5$	.24	.13	.16	.20	.15	.13	.13	.12	.17	.11	.24	.37	.17	.04
LOI	1.93	1.03	.95	.67	.60	.55	.50	1.00	.62	.51	.61	.54	.68	.24
Total	100.06	99.16	100.55	98.92	100.59	99.06	99.90	100.17	99.01	100.94	100.29	99.99	99.11	99.84
Ni	30	22	24	57	24	6	16	11	9	7	24	17	41	4
Cr	2	33	50	46	40	12	26	10	12	14	31	14	76	8
V	169	204	210	184	122	198	217	141	205	98	262	233	224	14
Sr	399	502	467	419	384	434	460	432	480	417	547	274	519	156
Ba	454	420	418	456	774	373	366	540	380	553	408	748	380	1092
Rb		26	45	43	50	21	20	33	24	35	26	96	22	92
Cs		.94	1.47	.82	1.27	1.42	.70	1.38	1.06	1.30	.32	1.94	.63	1.10
U		.9	1.7	1.4	.9	1.7	.5	.8	2.5	.7	.7	.9	.5	2.2
Th		2.6	3.6	3.7	4.1	3.8	.9	1.4	6.5	2.0	.7	1.0	1.1	9.4
Co	53	56	36	49	57	84	45	59	63	78	51	41	54	47
Nb	13.7	9.8	11.4	12.8	9.3	7.2	7.3	5.2	6.3	7.4	8.7	13.0	8.6	8.8
Ta	•••	.53	.85	.60	.61	.98	.23	.55	.59	.52	.52	.62	.41	.74
Y	34.7	13.5	18.5	29.0	15.5	18.5	24.5	13.5	16.0	11.5	25.5	38.5	23.5	4.0

Zr	66	58	50	86	200	62	61	88	58	117	68	132	60	89
Hf			1.8		5.0		1.6						1.7	.4
La	35.0	12.9	17.2	20.8	16.3	28.0	10.9	13.4	26.0	10.2	13.8	17.4	13.0	19.7
Ce	73.0	30.8	34.3	49.0	33.5	46.7	26.0	24.9	45.1	22.5	33.3	42.8	30.5	37.0
Pr		3.9	4.0	6.3	4.1	6.6	3.8	3.0	4.9	2.9	4.6	6.0	4.2	4.1
Nd	28.9	14.9	15.6	24.4	16.0	28.0	16.8	12.1	16.4	11.5	19.7	26.9	18.7	13.9
Sm	6.20	3.30	3.30	5.33	3.43	6.29	4.04	2.60	2.87	2.52	4.64	6.35	4.36	2.69
Eu	1.34	1.06	1.10	1.19	1.00	2.10	1.26	.76	.66	.67	1.38	1.09	1.19	.46
Gd	5.16	3.18	3.15	5.52	3.28	6.20	3.94	2.55	2.70	2.43	4.60	6.57	4.45	2.32
Tb		.54	.50	.86	.52	1.00	.65	.39	.36	.37	.74	1.06	.70	.35
Dy	5.38	3.28	3.07	5.58	3.17	6.97	4.14	2.44	2.17	2.41	4.67	6.55	4.44	2.12
Ho	1.09	.68	.66	1.18	.67	1.44	.91	.53	.45	.51	1.01	1.38	.93	.43
Er		2.19	1.97	3.45	1.98	4.17	2.61	1.48	1.42	1.55	2.80	3.66	2.65	1.26
Tm		.30	.30	.55	.31	.71	.42	.26	.21	.26	.42	.52	.40	.20
Yb	3.68	2.18	2.18	3.59	2.07	4.78	2.81	1.69	1.55	1.62	2.69	3.23	2.56	1.31
Lu	.59	.36	.35	.55	.33	.75	.46	.25	.25	.27	.40	.48	.40	.20
Modal %:														
Plagioclase		54.2	54.6	49.4	44.6	48.6	43.0	51.8	50.0	48.6	46.8	56.2		
Quartz		9.8	12.2	16.2	23.4	20.4	18.2	18.0	14.8	29.8	8.2	1.4		
Amphibole		32.2	26.6	25.0	12.0	19.8	29.4	17.6	23.2	8.2	26.2	16.0		
Biotite		.8	5.4	5.2		9.0	5.4	4.8	5.2	10.0	9.4	21.2		
K-feldspar					5.6		•••			1.0	1.2	.2		
Apatite		.4	1.0	1.4	Trace	.2	1.0	.8	3.0	•••	1.8	Trace		
Opaque		2.6	2.6	2.8	Trace	1.8	2.6	1.0	3.6	1.2	3.0	4.2		
Chlorite					9.4			3.2		1.0	.6	.2		
Epidote			.2		5.0	.2	.2	.6	•••	.2	2.4	.4		
Accessories		Zir					Zir	Sph, zir				Sph, zir		

Note. Major oxides are in weight percent; trace elements are in parts per million. Total iron is reported as  $Fe_2O_3^t$ . Loss on ignition (LOI) was determined by firing sample for 1 h at  $1000^{\circ}$ C. Modal data are based on point counting a minimum of 500 points per thin section. Zir = zircon, sph = sphene.

bole barometry. Samples from Copper Mountain and Ruth Creek yield pressures <1 kb (Tepper 1991). Rapid cooling of the Ruth Creek pluton, revealed by identical Rb/Sr isochron and zircon fission track ages of 8.7 Ma, is also indicative of shallow emplacement. Additional petrographic and chemical data on all three plutons are given by Tepper (1991).

Interpreting these field relationships, we find that the finer-grained and sharply bounded texture of enclaves at Ruth Creek probably reflects a greater thermal and rheological contrast with the most felsic host. In addition, the occurrence of Ruth Creek enclaves in trains suggests the basaltic magma(s) in this case were introduced late in the cooling history of the host, probably after the host magma was emplaced in the shallow crust. Conversely, the scattered distribution and less distinct appearance of enclaves in the other two plutons suggest they represent mafic magmas that were introduced earlier in the history of the host pluton and/or before the host magma had ascended to its final emplacement level.

### **Analytical Methods**

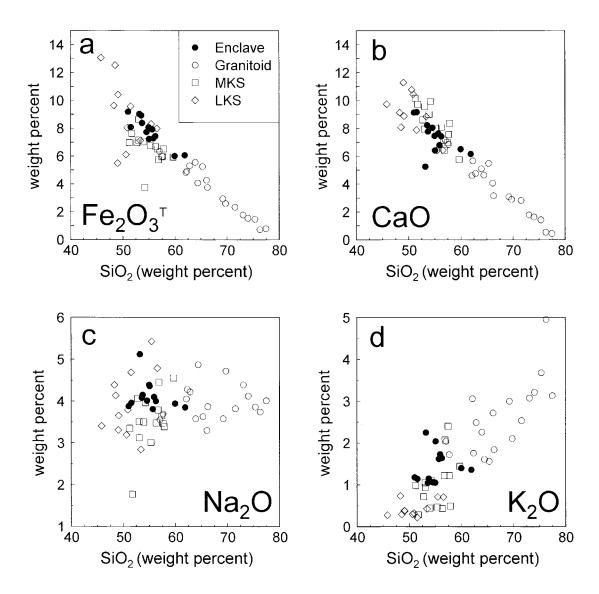
Samples selected for whole rock analysis were cut into thin (~5-mm) slices, trimmed and sanded to remove any recognizable foreign material (e.g., vestiges of host granitoid), and pulverized in a tungsten carbide shatterbox. Major elements and higher abundance trace elements (Ni, Cr, V, Sr, Ba, Rb, Zr, Nb, Y) were analyzed by x-ray fluorescence at the University of Puget Sound using a Philips PW1400 calibrated with 33 natural standards. All analyses were performed in duplicate on 3.5-g samples fused 1:2 with lithium tetraborate. Relative precision, on the basis of analysis of duplicates, is <0.5% for Si, Ca, Mg, Mn, and K; <1% for all other major oxides; ~1% for P, Sr, and Ba; and <5% for all other trace elements except Ni (~10%). Whole rock analyses of other trace elements were performed by inductively coupled plasma mass spectrometry (ICP-MS) at Union College on a VG PQ2+. All samples were run in duplicate against a range of natural standards. Data reduction, including corrections for drift in internal standards and calibration curves, was performed with VGFIX (K. Hollocher, pers. comm., 1994). On the basis of replicate analyses of standards, relative analytical precision of the ICP-MS analyses is estimated at 1%-4% for REE,  $\leq 5\%$ for Hf, ≤10% for Pb and U, and ~20% for Cs and

Mineral separates were prepared by sieving and magnetic separation, and they were then handpicked. Apatite separates were dissolved in highpurity HNO<sub>3</sub>, spiked with an internal standard, and analyzed by ICP-MS using a Union College natural apatite standard. Because these samples were too small to weigh precisely, the results were normalized to 55 wt% Ca instead of attempting a massbased dilution correction. Silicate mineral separates were immersed for 3 h in 50% high-purity HNO<sub>3</sub> to remove any apatite or monazite inclusions, rinsed repeatedly with deionized water, and allowed to dry before digestion overnight at 130°C in an HF-HNO<sub>3</sub> mixture. After evaporation, the residue was redissolved in dilute HNO<sub>3</sub>, spiked with an internal standard, and run against natural rock standards prepared in the same way. All microprobe analyses were obtained with a JEOL 733 Superprobe at the University of Washington. Analytical conditions were 15 kV accelerating voltage with beam currents of 10 nA for apatite and mica analyses and 15 nA for amphibole and feldspar analyses. A defocused beam, 10  $\mu$ m for apatite and 3  $\mu$ m for the other minerals, was always used to minimize potential element mobility caused by beam heating of the sample. Natural apatite, biotite, feldspar, and amphibole standards were used for calibration of the major elements.

# **Enclaves versus Mafic Plutons and Host Granitoids: Whole Rock Chemistry**

Major element analyses (table 1; fig. 2) reveal close agreement between the SiO, range for 12 mafic enclaves (51–62 wt%) and the range for samples from MKS plutons (51–60 wt%). There is less SiO<sub>2</sub> overlap between enclaves and LKS samples (46-57 wt%). In general, samples from mafic plutons display greater variability than do the enclaves in major element composition (fig. 2). This is probably due in large part to crystal accumulation because many of the mafic pluton samples, particularly those with <55 wt% SiO<sub>2</sub>, contain accumulated plagioclase or pyroxene, whereas the enclaves are generally fine grained and display little evidence of mineral accumulation. The only major oxides for which enclave analyses appear to differ from the MKS samples are Na<sub>2</sub>O and K<sub>2</sub>O, both of which are slightly higher on average in the enclaves (fig. 2).

The enclaves in general have lower SiO<sub>2</sub> and K<sub>2</sub>O and higher TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sup>t</sup><sub>3</sub>, MgO, MnO, and CaO than do the host granitoids (fig. 2). However, when major element data from individual plutons are compared, there is no systematic relationship between enclave and host compositions. The enclaves with the lowest SiO<sub>2</sub> and highest TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sup>t</sup><sub>3</sub> are from Ruth Creek, which is the host pluton with the highest SiO<sub>2</sub> and lowest

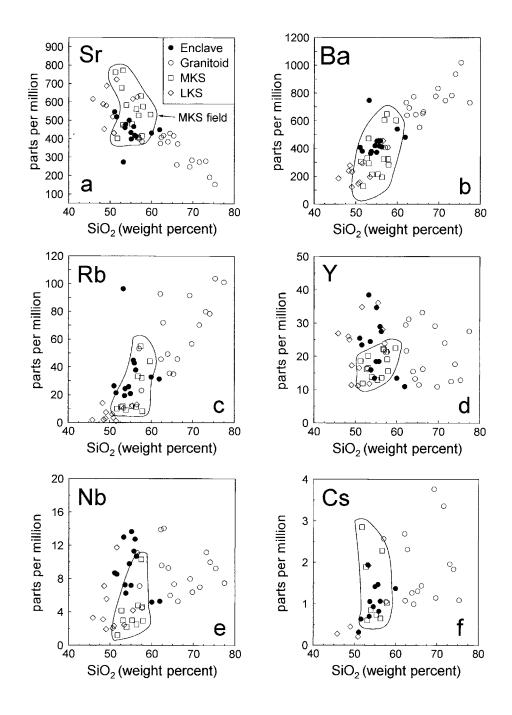


**Figure 2.** Major element variation diagrams. *a, b,* Two elements for which enclaves and medium-K series (MKS) samples show close compositional agreement. *c, d,* Two elements for which enclave compositions have been shifted toward host granitoid compositions. Enclave data are from table 1; granitoid data from Tepper et al. (1993); MKS and low-K suite (LKS) data are from Tepper (1996).

levels of the other three major oxides. Concentrations of MnO, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O overlap among enclaves from all three plutons.

It is convenient to divide the trace elements into three groups when comparing enclaves, host granitoids, and mafic plutons. Group 1 (Sr, V, Ni, Cr, Sc) consists of elements that tend to be present at higher concentrations in mafic magmas than in felsic ones. Abundance ranges for these elements show overlap between enclaves and MKS samples (fig. 3a). Group 2 elements (Co, Rb, Ba, Ta, Th, Zr) are those for which enclave compositions appear to have been shifted toward those of the granitoid

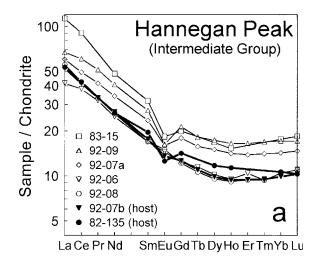
hosts. Concentrations of these elements in the enclaves are higher than the MKS average but lower than or comparable to concentrations measured in the host granitoids (fig. 3b, 3c). Group 3 (Nb, REE, Y, U) includes high field strength elements (HFSE) that generally occur at higher levels in the enclaves than in either the MKS samples or the granitoid host samples (fig. 3d, 3e). Cs does not fit into these groupings; it occurs in the enclaves at levels comparable to or below those measured in MKS samples and, in contrast to the other alkali elements, shows no shift toward the higher levels found in the host granitoids (fig. 3f).

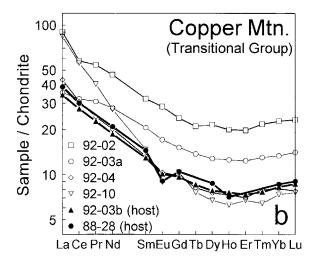


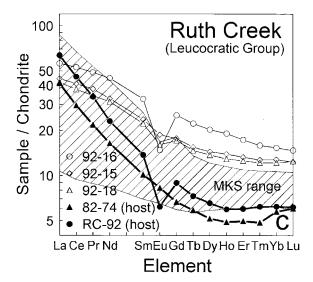
**Figure 3.** Trace element variation diagrams comparing enclaves with samples from mafic plutons (medium-K series [MKS] field is outlined) and granitoids. *a*, Overlap between enclaves and MKS samples that is characteristic of group 1 trace elements. *b*, *c*, Two group 2 trace elements for which enclave concentrations have been shifted toward host granitoid concentrations. *d*, *e*, Two group 3 trace elements for which enclave concentrations exceed those of both mafic plutons and granitoid samples. Enclave Cs data (*f*) show no evidence of a shift toward higher abundances as seen for other alkali elements (e.g., Rb). Enclave data are from table 1; granitoid data are from Tepper et al. (1993); MKS and low-K suite (LKS) data are from Tepper (1996).

The REE patterns of enclaves from Copper Mountain and Hannegan Peak (fig. 4a, 4b) closely resemble those of their granitoid hosts and differ markedly from those of MKS samples. These en-

claves have concave-upward REE patterns (Dy/Lu<sub>N</sub> < 1) with small negative Eu anomalies (Eu/Eu\* = 0.7–1.0) that parallel those of the host rocks but with generally higher absolute REE abun-







**Figure 4.** Whole rock REE data for enclaves (open symbols) and their host granitoids (filled symbols) normal-

dances (Yb<sub>N</sub> = 8–23 in enclaves vs. 8–11 in the host rocks). In contrast, MKS samples do not have concave-upward patterns (average MKS Dy/Lu<sub>N</sub> = 1.18) and have lower HREE (Yb<sub>N</sub> = 6–11). The REE patterns of enclaves from Ruth Creek (fig. 4c) show slight LREE enrichment (La/Yb<sub>N</sub> = 3.4–3.6) and modest negative Eu anomalies (Eu/Eu\* = 0.5–0.9). These patterns do not parallel those of the host granodiorite and are more similar to the MKS samples but with higher HREE (Yb<sub>N</sub> = 12–15).

# **Enclaves versus Host Granitoids: Mineral Chemistry**

Major and trace element concentrations were determined on apatite from one enclave and one host rock sample from each pluton. In addition, amphibole, plagioclase, and biotite from the same samples were analyzed where it was possible to separate a sufficient quantity of fresh material. The following paragraphs summarize these data, emphasizing in particular the contrast between major element and trace element behavior.

Apatites from all three plutons, including both enclave and host crystals, are very similar in major element composition (table 2). Apatite crystals from Ruth Creek have higher Cl/F than do those from the other plutons, and apatites from the Ruth Creek host (RC92) have higher FeO and MnO, but otherwise there is no significant variation in apatite major element chemistry from one sample to the next. By contrast, apatite trace element chemistry differs between plutons, most notably in REE patterns and U/Th ratios, and these differences are present in both enclave and host apatites (fig. 5; tables 3, 4). For example, enclave and host apatites from Hannegan Peak (fig. 5a) have more strongly fractionated LREE and lower U/Th than do apatites from the other two plutons, while apatite from Ruth Creek (fig. 5c) is distinguished by a lack of LREE enrichment, high Y contents, and low Sr

Although enclave and host apatites from each pluton share a number of trace element similarities, it is important to note that there are consistent differences as well. Specifically, the host apatite in

ized to the recommended chondrite values of Boynton (1984). Data are from table 1 except 82–74 (Tepper et al. 1993) and medium-K series (MKS) field, which are from Tepper (1996). Note that enclave and host patterns are parallel in a and b but not in c.

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	RC-92 (RC host)	92-16 (RC enclave)	92-7b (HP host)	92-08 (HP enclave)	92-03b (CM host)	92-04 (CM enclave)
CaO	53.21 (.76)	56.38 (.55)	56.21 (.97)	56.53 (.85)	56.44 (.57)	56.22 (.68)
$P_2O_5$	40.14 (.57)	40.35 (.46)	39.82 (.55)	40.81 (.53)	40.73 (.33)	40.43 (.50)
SiO <sub>2</sub>	.48 (.21)	.34 (.08)	.18 (.06)	.24 (.09)	.42 (.72)	.21 (.14)
FeO	.49 (.12)	.27 (.11)	.16 (.09)	.18 (.12)	.13 (.08)	.23 (.41)
MnO	1.22(.23)	.12 (.04)	.09 (.03)	.09 (.03)	.17 (.05)	.07 (.03)
MgO	.03 (.01)	.01 (.01)	.02 (.02)	.04 (.02)	.01 (.01)	.01 (.02)
SrO	.02 (.01)	.02 (.01)	.02 (.02)	.02 (.01)	.03 (.02)	.03 (.02)
$Ce_2O_3$	.33 (.12)	.27 (.06)	.28 (.14)	.28 (.15)	.29 (.11)	.19 (.09)
F	3.28 (.16)	3.05 (.20)	2.38 (.35)	2.46 (.45)	2.22(.40)	2.55(.50)
Cl	.22 (.07)	.17 (.03)	.60 (.22)	.46 (.21)	.98 (.15)	.65 (.42)
$SO_3$	.04 (.03)	.28 (.28)	.09 (.07)	.04 (.02)	.08 (.06)	.03 (.02)
Total	98.03 (.99)	101.25 (.63)	99.86 (1.4)	101.16 (1.2)	101.49 (.54)	100.63 (.92)

**Table 2.** Apatite Major Element Chemistry

Note. Oxides and halogens are in weight percent; data are averages of a minimum of seven different grains ( $1\sigma$  SD in parentheses). RC = Ruth Creek, HP = Hannegan Peak, CM = Copper Mountain.

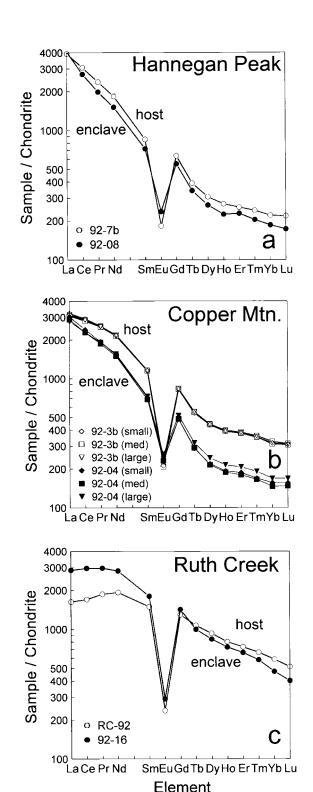
all three plutons has higher Y, higher HREE, and lower Sr than does the enclave apatite (table 3).

The amphibole in all samples is a magnesiohornblende (nomenclature of Leake 1978), but there are differences, most notably in K, Mn, Na, and Ti, that render the hornblende from each pluton distinctive (table 5; fig. 6a). In each pluton, there is a strong similarity in major element chemistry between enclave amphibole and host granitoid amphibole, both of which differ from MKS amphiboles (table 5; fig. 6a). These data suggest that enclave and host amphiboles in each pluton have undergone significant equilibration with regard to the major elements. For the trace elements, however, no such enclave-host equilibration is evident; at Hannegan Peak, the host amphibole contains Rb, Ba, Cs, Y, U, and REE at levels two to three times those of the enclave amphibole (table 5; fig. 7).

Biotite data reveal a similar discordance between the behavior of major elements ("equilibrated") and trace elements ("not equilibrated"). Biotites from the Ruth Creek and Copper Mountain plutons differ from one another in Mn and Ti contents, but within both plutons, the enclave and host analyses cluster tightly (table 5; fig. 6b). Conversely, the trace element data reveal pronounced intrapluton contrasts between enclave and host biotites, particularly in Ruth Creek samples, where concentrations of Ba, Rb, Cs, U, Th, Y, Nb, and REE are four to 140 times higher in the host biotite than in the enclave biotite (table 5).

Plagioclase is the only mineral for which enclavehost pairs from the same pluton show differences in both major element and trace element composition. All plagioclases show normal zoning, but the compositional range is greater in enclave feldspars because they have more calcic cores (up to  $An_{85}$ ). Plagioclase rim compositions average 5 mol% more calcic in the enclaves  $(An_{25}-An_{29})$  than in the granitoid hosts  $(An_{18}-An_{28})$ , and there is a correlation between enclave-host pairs (i.e., Copper Mountain has the most calcic rims on both enclave and host plagioclase, while Ruth Mountain has the most sodic rims for both). Trace element contrasts between enclave and host plagioclase are most pronounced for V, Sr, Rb, Y, Nb, and U (table 5).

Combining these mineral chemistry data with the whole rock and modal data leads to the following conclusions: (1) contrasts in major element chemistry are evident for plagioclase, amphibole, biotite, and to a lesser extent apatite when comparisons are made between samples from different plutons. However, with the exception of plagioclase, none of these mineral phases differs significantly in major element composition between enclave and host granitoid from the same pluton. This suggests there has been significant equilibration of major elements between enclave and host minerals (other than plagioclase). (2) Trace element data for apatite, amphibole, biotite, and plagioclase reveal pronounced chemical differences not only between samples of the same mineral from different plutons but also between enclave-host mineral pairs from the same pluton. There is thus a decoupling of major element chemistry (enclave and host minerals have equilibrated) and trace element chemistry (enclave and host minerals have not equilibrated). (3) Neither the trace element contrasts between enclave-host mineral pairs from the same pluton nor the contrasts between mineral pairs from different plutons can be attributed to differences in whole rock chemistry. For example, at Hannegan Peak and Copper Mountain, the enclaves have whole rock REE and Y contents equal to or greater than those of the host granites, yet in both cases, the enclave apatite has significantly lower REE and



**Figure 5.** REE data for apatite separates, normalized to the recommended chondrite values of Boynton (1984). Data are from table 3. Note the similarity of enclave and host patterns in each pluton.

Y contents. Similarly, the Ruth Creek host (RC92) has the highest LREE content and highest La/Yb<sub>N</sub>, yet apatite from this sample has the lowest La<sub>N</sub> and La/Yb<sub>N</sub>. (4) Differences in trace element composition between enclave-host mineral pairs are strongly correlated with differences in the modal abundances of other minerals in the rock. In general, a mineral is enriched in those elements for which alternative repository minerals are scarce and impoverished in those elements for which other repository minerals are abundant. For example, at Ruth Creek, elements that normally partition into biotite (Rb, Cs, Ba) are strongly enriched in host rock biotite compared with the enclave biotite because the modal abundance of biotite is much lower in the granodiorite (<5%) than in the enclave (21%). Similarly, at Hannegan Peak and Copper Mountain, enclave apatites have lower REE and Y contents than do host granitoid apatites because there is a greater abundance of amphibole in the enclaves. The fact that apatite trace element chemistry is influenced by the modal abundance of amphibole and other minerals in the rock indicates either that significant apatite growth occurred after these other minerals had formed or that the original apatite REE patterns have been modified by late magmatic or subsolidus processes. (5) Similarities between the REE patterns of enclave apatites and granitoid host apatites from all three plutons indicate that the enclave apatites crystallized from (or reequilibrated with) a melt that had already acquired REE characteristics of the host granitoid.

### **Enclave-Felsic Liquid Interactions**

The similarities between enclaves and samples from the MKS mafic plutons in major element composition (other than Na<sub>2</sub>O and K<sub>2</sub>O) and in group 1 trace element contents are consistent with the hypothesis that the enclaves originated from MKS-like magmas. Chemical differences between enclaves and MKS samples are therefore assumed to reflect hybridization and/or fractionation processes. We use whole rock and mineral chemistry to assess the contributions of magma mixing, fractionation, and diffusion to enclave chemistry and to constrain the timing of enclave hybidization relative to crystal growth.

Magma Mixing. Several lines of evidence argue against a significant role for mixing of an MKS-like magma and a liquid having the composition of the host granitoid. (1) The presence of group 3 trace elements (Nb, REE, Y, U) at higher levels in the enclaves than in the host granitoids cannot be explained by physical mixing between mafic magma

Table 3. Apatite Trace Element Chemistry

	RC-92	92-16	92-7b	92-08	92-03b (small)	92-03b (medium)	92-03b (large)	92-04 (small)	92-04 (medium)	92-04 (large)
La	506	889	1219	1260	998	954	971	938	893	865
Ce	1378	2397	2477	2201	2354	2268	2314	1946	1847	1850
Pr	228	363	290	242	313	308	311	236	228	233
Nd	1160	1699	1103	908	1293	1286	1305	917	896	932
Sm	292	352	166	141	224	225	226	139	134	142
Eu	17.4	21.4	13.5	17.3	15.6	15.3	16.8	18.3	17.0	19.1
Gd	336	369	165	143	214	216	217	125	126	134
Tb	50.7	47.4	18.5	16.2	25.6	25.9	26.2	13.6	13.8	15.1
Dy	300	271	99	85.5	141	142.1	143.1	70.6	69.1	78.3
Ho	57.5	52.4	19.5	16.2	28.0	28.2	28.5	13.8	13.5	15.4
Er	153.9	139.1	53.6	48.1	79.1	79.3	80.6	39.2	37.6	43.4
Tm	21.5	18.9	7.8	6.6	11.4	11.4	11.7	5.5	5.4	6.2
Yb	123	99	46.2	38.8	66.2	65.2	67.9	32.6	30.6	35.2
Lu	16.6	13.0	7.0	5.6	10.0	9.9	10.1	5.0	4.7	5.4
Sr	72	95	127	168	126	126	131	153	149	148
Y	1689	1477	599	497	865	863	862	420	413	470
Pb	5.8	32.4	3.2	20.5	2.7	3.4	2.7	3.9	3.0	2.3
Th	18.3	51.4	25.7	42.0	14.6	18.5	13.9	16.1	15.7	15.4
U	39.8	22.6	13.0	22.1	15.8	17.5	13.2	14.7	15.2	12.4

Note. Trace element data are in parts per million.

and host. (2) Mixing between mafic enclave magma and late stage differentiates of the felsic host granitoid is unlikely because the enclaves would be largely or completely solidified by the time such felsic differentiate liquids formed. (3) There is minimal petrographic evidence for mixing or mingling; the enclaves analyzed for this study are generally fine grained and devoid of veining or pockets of felsic material. In porphyritic enclaves, the plagioclase phenocrysts commonly have calcic cores (up to An<sub>86</sub>) and likely represent early-formed crystals from the enclave magma rather than xenocrysts introduced from the host granitoid.

*Fractionation.* Fractional crystallization is likely to accompany hybridization and has been successfully modeled to explain the trace element characteristics of some enclaves (Wiebe et al. 1997). We assess whether fractional crystallization is capable of producing the most distinctive feature of the Copper Mountain and Hannegan Pass enclaves, which is their concave-upward REE patterns. Amphibole, with its preference for MREE, is the only major mineral capable of producing differentiated melts with Dy/Lu<sub>N</sub> < 1. Exchange of  $H_2O$  across the interface between stratified mafic and felsic magmas can promote amphibole growth in a mafic magma (Wiebe 1993); the question in this case is whether amphibole fractionation can produce a melt with enclave-like REE traits from an MKStype parent. The process is modeled as simple Rayleigh fractionation with a typical MKS sample (CB89-002, Dy/Lu<sub>N</sub> = 1.15; Tepper 1996) as the parent magma. Using partition coefficients for basaltic liquids (Nicholls and Harris 1980; Irving and Frey 1984) and assuming that only amphibole is removed, a minimum of 30% amphibole fractionation is required to achieve  $\mathrm{Dy/Lu_N} < 1$ . Even larger degrees of crystal fractionation are required if plagioclase or pyroxene, which do not efficiently lower  $\mathrm{Dy/Lu}$ , are included in the calculation. Such large degrees of crystallization are difficult to reconcile with the fact that enclaves show only modest incompatible element enrichments relative to MKS samples (~50% for Ba, Th, La). These results suggest that although fractional crystallization may have contributed to some enclave traits (e.g., lower average Cr and Sr than in the MKS samples), it is an unlikely explanation for their REE patterns.

Diffusion. Enrichments in alkali elements and highly charged cations (HFSE, REE) are a common feature of enclaves worldwide and are widely attributed to diffusive exchange with the felsic host liquid (Orsini et al. 1991; Blundy and Sparks 1992). For the rapidly diffusing alkali elements, this exchange can occur before the enclave is solidified (Blundy and Sparks 1992) because experimental studies show that K will diffuse between a basic liquid and a silicic liquid until a transient equilibrium is achieved at a concentration ratio (K in granite/K in basalt) of 2:1 to 3:1 (Watson 1982). This equilibrium is considered transient because as Si diffusion proceeds, compositional differences between enclave and host will gradually diminish. Any biotite growth that consumes alkalis from the interstitial enclave melt will further help to drive diffusion of these elements from the silicic host

Table 4. Trace Element Comparisons of Enclave and Host Apatite

	Hannegan Peak	Copper Mountain	Ruth Creek
La/Yb <sub>N</sub> :			
Énclave	17.8	19.7-16.6	6.1
Host	21.9	10.2-9.6	2.8
$La/Sm_N$ :			
Enclave	5.6	4.3 - 3.8	1.6
Host	4.6	2.8 - 2.7	1.1
U/Th:			
Enclave	.53	.9781	.44
Host	.51	1.0895	2.20

Note. Comparison of chemical characteristics of enclave and host apatites that illustrate similarities between samples from the same pluton and contrasts between apatites from different plutons. Data are from table 3.

melt into the enclave melt (Blundy and Sparks 1992).

The REE diffusion rates in silicate melts are several orders of magnitude slower than those for K, although they are still faster than rates for Si and network-forming cations (Watson 1982). Enclave enrichments in the slow-moving REE and HFSE are generally attributed to liquid ⇔ crystal equilibration, presumably over an extended interval, between the granitoid host melt and minerals already formed in the enclave (Allen 1991; Blundy and Sparks 1992). Many REE and HFSE partition preferentially into minerals that are abundant in the enclaves, particularly amphibole and magnetite, and Blundy and Sparks (1992) have shown that enclave REE patterns from the Adamello Massif are consistent with enclave amphibole having equilibrated with the silicic host melt. However, this process cannot explain the REE patterns of enclaves from Hannegan Peak and Copper Mountain. Enclaves from these plutons have concave-upward REE (Dy/Lu<sub>N</sub> = 0.87-1.10) patterns that contrast markedly with the concave-downward patterns  $(Dy/Lu_N = 1.30-1.43)$  calculated for an amphibolerich enclave in equilibrium with the host granitoid melt (fig. 8). These enclave REE patterns are unlike those of the MKS samples, which have higher Dy/  $Lu_N$  (average = 1.18  $\pm$  0.18) and lower HREE abundances (fig. 8), and they cannot be modeled as amphibole-rich cumulates from an MKS-like liquid, which would have Dy/Lu<sub>N</sub> > 1. When normalized to the REE contents of their host granitoids, Hannegan Peak and Copper Mountain enclaves have generally flat REE patterns that are 0.8-2.5 times higher than those of the host. This relationship strongly suggests that the REE patterns of enclaves from these two plutons are the result of liquid ⇔ liquid partitioning between the felsic host melt and the more mafic enclave melt because experimental studies of element partitioning between acid and basic liquids indicate that REE are enriched four- to 10-fold in the basic liquid but are not fractionated (Watson 1976; Ryerson and Hess 1978).

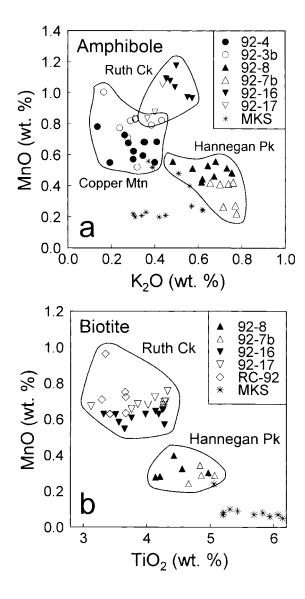
Other whole rock chemical characteristics of these enclaves are also consistent with their having interacted with their granitoid hosts (or a similar felsic liquid) through liquid-liquid diffusion. The extent to which any particular element will migrate from one melt into the other depends on its transient partition factor (concentration in basic liquid/concentration in silicic liquid) as well as its diffusion rate. Little if any exchange between the enclave and host is expected for Mg, Fe, or Ca because these elements prefer the basic liquid and diffuse very slowly (Watson 1982), and indeed, enclaves and MKS samples contain similar levels of these elements (fig. 2). The HFSE will partition into the less polymerized mafic liquid and by analogy with REE (Watson 1982) should diffuse faster than Si. The observed enclave enrichments in Ta, Nb, Ti, Y, Th, and U (fig. 3) are consistent with this scenario. In contrast to the HFSE, the alkali elements favor the more silicic liquid and have estimated transient equilibrium values of 1.5–2 for Na, 2-3 for K, and 3-3.5 for Cs (Watson 1976, 1982). Comparison of these values with the alkali contents of MKS samples and host granitoids suggests that only minor Na and K exchange would have been required to achieve equilibrium between enclave and host. As predicted, there is substantial overlap in Na and K contents of enclaves and MKS samples, although average levels of these elements are slightly higher in the enclaves. Conversely, attainment of Cs equilibrium would require uphill diffusion from the enclave to the host and probably explains why Cs is the only alkali element for which enclave compositions show no evidence of a shift toward higher concentrations (fig. 3f).

Although the chemical characteristics of the enclaves from Hannegan and Copper Mountain are consistent with their having been modified by liquid-liquid diffusion, enclave/host element ratios are generally smaller than experimentally determined transient equilibrium values. At least three factors may contribute to this discrepancy. First, equilibrium may not have been achieved in all cases. Second, SiO<sub>2</sub> contrasts between the felsic liquids and interstitial enclave melts were probably smaller than between the coexisting experimental liquids (18–36 wt% SiO<sub>2</sub>), and this would result in smaller enclave/host enrichment factors. Third, whole rock analyses are unlikely to represent ac-

Table 5. Silicate Mineral Chemistry

	92-08 (Am, HP enclave)	92-7b (Am, HP host)	92-16 (Am, RC enclave)	92-17 (Am, RC host)	92-04 (Am, CM enclave)	92-3b (Am, CM host)	92-16 (Bi, RC enclave)	RC-92 (Bi, RC host)	92-08 (Bi, HP enclave)	92-7b (Bi, HP host)	92-3b (Bi, CM host)	92-16 (Pl, RC enclave)	RC-92 (Pl, RC host)	92-08 (Pl, HP enclave)	92-7b (Pl, HP host)
SiO <sub>2</sub>	46.99	46.99	49.32	51.65	49.84	50.66	36.79	36.14	35.80	36.57					
$Al_2O_3$	(.65) 6.59	(.20) 6.88	(.68) 6.40	(3.39) 4.59	(2.34) 5.64	(1.42) 5.19	(.30) 14.04	(.52) 14.85	(.63) 13.11	(.29) 12.89				•••	
	(.36)	(.19)	(.27)	(2.30)	(1.67)	(1.21)	(.19)	(.10)	(.35)	(.19)					
$TiO_2$	1.44	1.67	1.09	.76	1.02	.81	3.86	3.51	4.46	4.86					
FeO	(.11) 16.06	(.12) 14.56	(.07) 14.20	(.03) 12.75	(.51) 14.48	(.35) 14.08	(.35) 17.63	(.18) 19.04	(.33) 20.74	(.17) 18.84		•••	•••	•••	•••
100	(.53)	(1.01)	(.30)	(.46)	(1.32)	(.91)	(.38)	(.49)	(.12)	(.43)					
MgO	12.66	13.85	13.79	15.41	13.99	14.35	12.39	10.84	10.44	11.80					
MnO	(.49) .50	(.62) .35	(.30) 1.05	(.37) .92	(1.39) .65	(.81) .78	(.20) .61	(.44) .74	(.13) .32	(.14) .29		•••		•••	
MIIO	(.05)	(.09)	(.08)	(.12)	(.08)	(.13)	(.03)	(.12)	(.05)	(.04)					
CaO	11.41	11.38	11.92	11.35	11.26	11.26	ŇΑ	NΑ	NA	NA					
N <sub>2</sub> O	(.26) 1.26	(.16) 1.44	(.03) 1.00	(.05) 1.03	(.27) .87	(.26) .81	00	.14	.09	.09					
$Na_2O$	(.08)	(.05)	(.10)	(.04)	(.35)	(.27)	.08 (.01)	(.02)	(.01)	(.02)					
$K_2O$	.65	.73	.51	.40	.30	.31	9.53	9.47	9.31	9.25					
г	(.09)	(.04)	(.05)	(.04)	(.09)	(.07)	(.15)	(.08)	(.17)	(.31)				•••	
F	.05 (.02)	.15 (.03)	.03 (.03)	.10 (.01)	.01 (.01)	.03 (.02)	.20 (.03)	.34 (.09)	.00 (.00)	.00 (.00)					
Cl	NA	NA	NA	NA	NA	NA	NA	.10	.21	.26			•••	•••	
	2.01	2.02	2.07	2.00	2.04	2.07	2.11	(.02)	(.03)	(.04)					
$H_2O^*$	2.01 (.01)	2.03 (.01)	2.07 (.02)	2.09 (.01)	2.06 (.03)	2.07 (.01)	3.66 (.04)	3.45 (.06)	3.65 (.06)	3.68 (.03)					
O = F, Cl		06	01	04	10	08	10	22	11	13		•••		•••	
- , -	(.01)	(.01)	(.01)	(.00)	(.04)	(.04)	(.01)	(.04)	(.02)	(.02)					
Total	99.59	99.95	101.38	100.97	100.20	100.42	98.70	98.38	98.02	98.41					
3.7	(.28)	(.24)	(.67)	(.34)	(.65)	(.54)	(.51)	(.97)	(1.20)	(.36)					1.0
V Co	369.2 57.1	408.5 75.6	354.5 46.5	•••	•••		100.6 25.0	161.4 26.6	503.0 57.1	412.8 118.3	218.4 40.0	26.1	.3 .2	15.2 1.4	1.8 .7
Ni	102.6	170.9	66.6				154.6	57.6	77.4	307.4	40.5		.7	3.3	2.8
Ba	44	133	136				514	2411	1086	2154	1593	239	238	279	276
Rb Cs	2.9 .16	9.4 .43	22.8 1.10			• • • •	40.1 .72	307.1 11.52	85.0 2.00	130.8 3.21	113.8 2.85	2.9 .14	13.6 .20	15.9 .48	9.0 .20
Sr	54	58	39				12	6	83	22	15	247	45	537	326
Y	88.3	205.2	259.0				1.1	38.1	47.7	50.5	51.9	.8	.4	1.1	.3
Nb Hf	24.64 3.33	37.26 4.60	22.10 5.25				9.42 .48	95.50 1.16	36.92 2.16	44.27 1.28	31.24 1.12	.34 .09	.53 .23	1.40 .12	.09 .03
Pb	2.8	3.2	4.1				10.0	2.9	6.5	16.3	2.6	7.2	2.1	5.4	3.8
Th	.76	6.58	.59				.12	6.21	1.20	1.22	1.95	.27	.20	1.65	3.8 .75
U	.34	.66	.54				.05	2.56	1.00	.48	.25	.11	.41	.85	.11
La Ce	22.9 77.2	41.7 144.0	28.8 118.3		•••		.4 1.2	56.1 101.2	15.4 47.6	9.9 34.2	10.5 31.2	5.3 7.5	1.4 2.0	6.4 8.8	4.4 6.2
Pr	12.5	24.8	22.4				.2	1.7	7.3	6.0	5.2	.7	.2	.8	.6
Nd	59.0	122.2	123.6				.6	36.5	33.0	30.6	26.2	2.2	.5	2.7	1.8
Sm	13.05 1.89	30.10 2.84	35.04 3.45				.30 .05	5.97 .40	7.48 1.35	8.16 .92	7.32 .77	.33	.16 .13	.45 .69	.28 .51
Eu Gd	13.75	2.84 31.87	39.04				.05	5.50	7.46	.92 8.15	7.54	.42 .25	.13	.35	.19
Tb	2.29	5.42	7.11	•••			.03	.92	1.25	1.41	1.36	.03	.01	.04	.02
Dy	14.63	34.85	46.19				.20	6.18	8.03	8.95	8.77	.16	.08	.24	.07
Ho Er	3.12 9.08	7.33 $20.72$	9.67 26.03		•••	•••	.04 .13	1.37 4.22	1.73 4.97	1.90 5.21	1.90 5.46	.03 .08	.01 .05	.04 .13	.01 .04
Tm	1.47	3.17	3.94				.03	.71	.81	.84	.89	.02	.03	.02	.04
Yb	9.54	19.41	23.57				.11	4.67	5.45	5.10	5.78	.07	.05	.12	.03
Lu	1.55	3.02	3.45		•••		.01	.73	.88	.79	.93	.01	.01	.02	.00

Note. Major oxides and halogens are in weight percent; trace elements are in parts per million. Major element data are averages ( $1\sigma$  SD in parentheses) of three to 10 individual analyses. Asterisk =  $H_2O$  calculated on the basis of 23 (O, OH) for amphibole and on the basis of OH = 2 - (Cl + F) for biotite. Am = amphibole, Bi = biotite, Pl = plagioclase. Average major element compositions are not calculated for plagioclase because zoning renders average values not meaningful. RC = Ruth Creek, HP = Hannegan Peak, CM = Copper Mountain.



**Figure 6.** Comparison of amphibole and biotite compositions from enclaves, host granitoids, and medium-K series (MKS) samples. Note that enclave-host mineral pairs from each pluton define a chemically distinct cluster and that they have no significant overlap with data from MKS plutons. The MKS data are from Tepper (1991), average enclave and granitoid data are given in table 5.

curately the compositions of interstitial liquids involved in the exchange process. For elements that concentrate in early-formed minerals, interstitial melt concentrations would have been significantly lower than is implied by whole rock analyses. Thus, the lack of enclave enrichment in P and Zr compared with other HFSE probably reflects sequestering of these elements in early-formed apatite and zircon crystals in the host granitoid magma. Conversely, greater than predicted enrich-

ments in an enclave should occur where growth of minerals in the enclave during diffusion enhanced the transfer of elements from the felsic liquid. The high levels of  $\rm K_2O$  and Rb in enclave 92–16, which contains abundant biotite oikocrysts, illustrate this phenomenon.

The close correspondence in major element chemistry between mafic enclave and granitoid host minerals from each pluton indicates that the enclave minerals maintained equilibrium with an interstitial enclave liquid that was continually evolving, through differentiation and chemical exchange, to become increasingly similar in bulk composition to the granitoid host liquid. This type of progressive mineral reequilibration has been recognized in other studies of enclaves (Dorais et al. 1990) and plutonic rocks (Helz 1979). In comparison, trace element equilibration between minerals in the enclaves and minerals in the host granitoid evidently proceeded more slowly. The tendency for major elements to reequilibrate more rapidly than trace elements has also been noted in hightemperature metamorphic recrystallization (Vannucci et al. 1993).

### **Origins of Enclave Apatite Chemistry**

The acicular habit of enclave apatite crystals is commonly attributed to rapid growth following undercooling of the enclave against the host (Wyllie

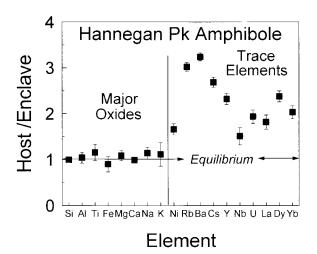
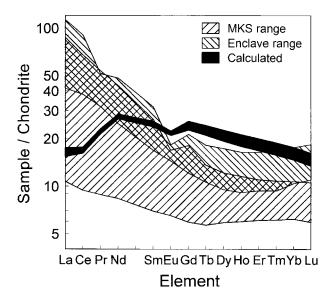


Figure 7. Comparison of amphibole compositions from Hannegan Peak enclave (CB92-08) and host (CB92-7b). Data and uncertainty for major oxides  $(2\sigma)$  are from table 5. Trace element error bars are based on assumption of 20% analytical uncertainty. Note that while there are no significant differences in major oxide chemistry, the host amphiboles contain higher trace element abundances.



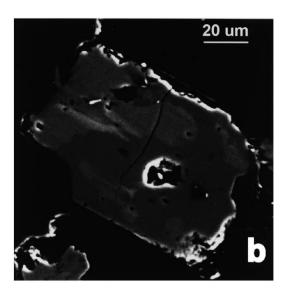
Comparison of REE patterns of Hannegan Peak enclaves with medium-K series (MKS) samples and with calculated compositions for enclaves in which equilibrium was attained between enclave minerals and the granitoid host magma. Data for enclaves are from tables 2, 3; MKS data (14 samples from five stocks) are from Tepper (1996). Host equilibrated compositions calculated using enclave modal data, host REE compositions for 82-135, and crystal/liquid distribution coefficients (for andesitic-dacitic liquids) are from Tepper et al. (1993) and Watson and Green (1981). Note that the enclaves have consistently higher HREE contents than do the MKS samples and REE patterns that differ markedly from the concave-downward patterns calculated for enclaves in which the minerals have equilibrated with the granitoid host magma.

et al. 1962). However, chemical diffusion is several orders of magnitude slower than thermal diffusion, and this raises the question of how these apatite crystals, if they grew on chilling of the enclave magma, acquired REE patterns that reflect not only chemical communication with a hostlike felsic melt but also precipitation of other enclave minerals. One explanation is that early-formed acicular apatites may have reequilibrated with and been mantled by material that grew from the evolving interstitial melt. This explanation is supported by the high REE contents of enclave apatites, which imply equilibration with liquids that were considerably more evolved than the bulk enclave compositions. Growth over an extended time interval also accounts for the fact that apatite REE and Y contents reflect the modal abundances of other minerals in the rock, particularly amphibole, and is supported by backscattered electron images of apatite grains in Ruth Creek enclave 92–16, some of which contain REE-poor cores with thick REE-enriched rims (fig. 9a). The lack of variation in REE pattern among different size fractions of apatite separated from the same sample (fig. 5b) suggests that even early-formed apatite cores may have reequilibrated. On the basis of experimentally determined REE interdiffusion rates (Cherniak 2000), the time required for an apatite crystal with a 20- $\mu$ m radius to attain the REE pattern of an external reservoir ranges from about 150 yr at 900°C to about 80,000 yr at 700°C, which is well within the time-scale for longevity of a granitic magma system (Koyaguchi and Kaneko 1999).

An alternative explanation for the REE patterns of enclave apatites is that deuteric fluids have modified them. Ward et al. (1992) document remobilization of REE during hydrothermal alteration of granite that resulted in redistribution of REE into secondary alteration minerals but no change in whole rock REE abundances, and indeed, backscattered electron images of apatite grains from Hannegan Peak and Copper Mountain reveal anastomosing veins and patchy zoning suggestive of metasomatic alteration (fig. 9b). However, because apatite incorporates MREE more readily than LREE (Watson and Green 1981), it is difficult to account for LREE enrichment in an enclave apatite by redistribution of REE from other enclave minerals that have lower La/Sm<sub>N</sub>. In Hannegan Peak enclave 92-08, for example, the apatite has higher La/Sm<sub>N</sub> (5.6) than does the amphibole (La/Sm<sub>N</sub> = 1.1) or biotite  $(La/Sm_N = 1.3)$ , which leaves plagioclase  $(La/Sm_N = 8.9)$  as the only major phase capable of contributing to LREE enrichment of the apatite. However, plagioclase REE concentrations are so low that 30%-40% of all plagioclase-hosted La would need to be transferred in order to raise apatite La contents by 10%, and petrographic evidence for such extensive alteration of plagioclase is completely absent.

In summary, the REE patterns of apatite crystals from these enclaves appear to reflect growth from and reequilibration with a hybridized melt that had acquired chemical characteristics of the granitoid host magma by liquid-liquid diffusion. This hybridization may have begun before formation and dispersal of individual enclaves, but other trace element features of enclave apatite that correlate with the modal mineralogy of an individual hand sample (e.g., HREE depletion in apatite from amphibole-rich enclave 92–04) developed later, probably after entrainment. Deuteric alteration has obscured magmatic zoning and caused some intracrystalline redistribution of REE in apatite grains





**Figure 9.** Backscatter electron images of zoned apatite crystals. Brighter areas have higher REE contents. *a*, Acicular apatite in Ruth Creek enclave 92–16 that contains a wide REE-enriched rim. *b*, Patchy zoning suggestive of subsolidus alteration in Hannegan Pass enclave 92–08.

from Hannegan Peak and Copper Mountain enclaves, but this process does not appear to have significantly modified REE patterns.

### Discussion

The chemical characteristics of the enclaves analyzed in this study can be associated with three stages in their evolution. (1) Enclave major element chemistry (except for Na and K) appears largely to

reflect the bulk compositions of basaltic and basaltic andesite magmas that were emplaced beneath (in a stratified system) or into the host granitoid. Preservation of major element chemistry is a consequence of the slow diffusion of Si, which rate limits the redistribution of other major elements excluding the alkalis. (2) Enclave trace element chemistry, particularly the concave-upward REE patterns that parallel those of the host granitoids, originated by diffusive exchange between coexisting mafic and felsic liquids. This exchange probably occurred across the mafic-felsic interface of a stratified magma system before formation and dispersal of individual enclaves. Because this exchange mainly affected trace elements, there is a decoupling of major element chemistry (and mineralogical mode) from trace element abundance. (3) Major oxide compositions of enclave minerals, with the exception of plagioclase cores, reflect postdispersal equilibration with a hybridized interstitial melt. Because of this process, enclave minerals are nearly identical in major element composition to their counterparts in the host granitoids.

Chemical exchange between a mafic magma and a felsic magma through a liquid-liquid diffusion process requires that the mafic magma remains well above its solidus and in physical contact with the felsic magma for an extended interval of time. Such diffusion is unlikely to be effective after a mafic enclave has been entrained within its felsic host and has undergone significant crystallization. The most likely setting for chemical equilibration at high temperature would be at the mafic-felsic interface in a stratified magma body, where a high mass ratio of mafic liquid to felsic liquid would maintain elevated temperatures.

The results of this study indicate that even enclave apatite crystals with acicular habits indicative of rapid cooling are unlikely to have trace element characteristics consistent with crystallization from an uncontaminated mafic magma. Zoning textures and REE patterns in this case point to growth from or reequilibration with an interstitial melt that had already been modified by exchange with the host granitoid and by crystallization of other enclave minerals. The presence of early-formed acicular apatites, which imply rapid cooling and crystallization, would appear to conflict with geochemical arguments for prolonged coexistence of mafic and felsic liquids. However, this paradox can be explained if thermal equilibration of the mafic and felsic liquids is achieved at high temperature. A tholeiitic basalt may be only 50% crystallized at 950°C and only 80% crystallized at 900°C (Blundy and Sparks 1992). Thus, a mafic liquid that underwent rapid cooling to temperatures of 900°–950°C could contain apatite crystals with an acicular habit and could at the same time retain a significant volume of interstitial melt that could communicate chemically with the adjacent felsic magma.

The enclaves that show the greatest chemical similarity to MKS rocks, and by inference the least interaction with the host, are those from the most felsic pluton, Ruth Creek, where large thermal and rheological contrasts between enclave and host may have inhibited chemical exchange. However, even in this case, the REE patterns of enclave apatite separates show the influence of the host granitoid. Plagioclase, particularly the calcic cores of enclave phenocrysts, appears to be the mineral most likely to preserve an early record of enclave magma chemistry. Apatite inclusions within early-formed plagioclase crystals would also be promising targets.

Recognition that enclave-host interactions at different stages in the history of a granitic magma body have distinct chemical signatures suggests the potential to use enclave chemistry to gain insight into the nature and timing of mafic magma inputs. Enclaves with whole rock REE patterns indicative of liquid-liquid diffusion imply protracted high-temperature interaction between mafic and felsic liquids and may be indicative of stratified magmatic systems at mid- to lower crustal depths. At shallower levels, where heat loss is more rapid, enclave chemistry even in stratified systems may be dominated by fractional crystallization (e.g., Wiebe et al. 1997). The extent to which enclave minerals equilibrate with the granitoid host will depend on

the cooling history of the host. In the epizonal plutons examined in this study, cooling was sufficiently rapid to preserve trace element contrasts between enclave and host minerals but not fast enough to preserve major oxide differences in mineral chemistry that are observed in volcanic systems (e.g., Stimac et al. 1990). Enclaves with cumulate-like REE patterns resulting from trace element equilibration between enclave minerals and host granitoid melt (e.g., Blundy and Sparks 1992) point to faster solidification of the enclave, such as by dike injection and disaggregation, followed by slow cooling of the host. Better knowledge of diffusion rates for the elements and minerals of interest would permit a more quantitative estimation of the timescale of enclave formation and the cooling history of the host pluton. With these potential applications of enclave petrology in mind, the most useful information may come not from enclaves in conspicuous trains but rather from the more scattered and hybridized ones that have experienced a longer history of interaction with the granitoid host.

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### REFERENCES CITED

- Allen, C. M. 1991. Local equilibrium of mafic enclaves and granitoids of the Turtle pluton, southeast California: mineral, chemical, and isotopic evidence. Am. Mineral. 76:574–588.
- Bateman, R. 1995. The interplay between crystallization, replenishment and hybridization in large felsic magma chambers. Earth Sci. Rev. 39:91–106.
- Blundy, J. D., and Sparks, R. S. J. 1992. Petrogenesis of mafic inclusions in granitoids of the Adamello massif, Italy. J. Petrol. 33:1039–1104.
- Boynton, W. V. 1984. Cosmochemistry of the rare earth elements: meteorite studies. *In* Henderson, P., ed. Rare earth element geochemistry. New York, Elsevier, p. 63–114.
- Cherniak, D. J. 2000. Rare earth element diffusion in apatite. Geochim. Cosmochim. Acta 64:3871–3885.
- Didier, J., and Barbarin, B., eds. 1991. Enclaves and granite petrology. Amsterdam, Elsevier.

- Dorais, M. J.; Whitney, J. A.; and Rhoden, M. F. 1990. Origin of mafic enclaves in the Dinkey Creek pluton, central Sierra Nevada batholith, California. J. Petrol. 31:853–881.
- Flinders, J., and Clemens, J. D. 1996. Non-linear dynamics, chaos, complexity and enclaves in granitoid magmas. Trans. R. Soc. Edinb. Earth Sci. 87:217–223.
- Frost, T. P., and Mahood, G. A. 1987. Field, chemical, and physical constraints on mafic-felsic magma interaction in the Lamarck granodiorite, Sierra Nevada, California. Geol. Soc. Am. Bull. 99:272–291.
- Helz, R. T. 1979. Alkali exchange between hornblende and melt: a temperature sensitive reaction. Am. Mineral. 64:953–965.
- Holden, P.; Halliday, A. N.; and Stephens, W. E. 1987. Neodymium and strontium isotope content of microdiorite enclaves points to mantle input to granitoid production. Nature 330:53–56.

- Irving, A. J., and Frey, F. A. 1984. Trace element abundances in megacrysts and their host basalts: constraints on partition coefficients and megacryst genesis. Geochim. Cosmochim. Acta 48:1202–1221.
- Koyaguchi, T., and Kaneko, K. 1999. A two-stage thermal evolution model of magmas in continental crust. J. Petrol. 40:241–254.
- Leake, B. E. 1978. Nomenclature of amphiboles. Mineral. Mag. 42:533–563.
- Metcalf, R. V.; Smith, E. I.; Walker, J. D.; Reed, R. C.; and Gonzales, D. A. 1995. Isotopic disequilibrium among commingled hybrid magmas: evidence for a two-stage magma mixing: commingling process in the Mt. Perkins pluton, Arizona. J. Geol. 103:509–527.
- Nicholls, I. A., and Harris, K. L. 1980. Experimental rare earth element partition coefficients for garnet, clinopyroxene and amphibole coexisting with andesitic and basaltic liquids. Geochim. Cosmochim. Acta 44: 287–308.
- Orsini, J.-B.; Cocirta, C.; and Zorpi, M.-J. 1991. Genesis of mafic microgranular enclaves through differentiation of basic magmas, mingling, and chemical exchange with their host granitoid magmas. *In* Didier, J., and Barbarin, B., eds. Enclaves and granite petrology. Amsterdam, Elsevier, p. 445–465.
- Reid, J. B., Jr.; Evans, O. C.; and Fates, D. G. 1983. Magma mixing in granitic rocks of the central Sierra Nevada, California. Earth Planet. Sci. Lett. 66:243–261.
- Ryerson, F. J., and Hess, P. C. 1978. Implications of liquidliquid distribution coefficients to mineral-liquid partitioning. Geochim. Cosmochim. Acta 42:921–932.
- Stimac, J. A.; Pearce, T. H.; Donnelly-Nolan, J. M.; and Hearn, B. C. 1990. The origin and implications of undercooled andesitic inclusions in rhyolites, Clear Lake volcanics, California. J. Geophys. Res. 95:17,729– 17,746.
- Tabor, R. W.; Haugerud, R. A.; Booth, D. B.; and Brown, E. H. 1994. Preliminary geologic map of the Mount Baker 30-by-60 minute quadrangle, Washington. U.S. Geol. Surv. Open-File Rep. OF-94–403, scale 1:100,000.
- Tepper, J. H. 1991. Petrology of mafic plutons and their role in granitoid genesis, Chilliwack batholith, North

- Cascades, Washington. Ph.D. thesis, University of Washington, Seattle, 307 p.
- ——. 1996. Petrology of mafic plutons associated with calc-alkaline granitoids, Chilliwack batholith, North Cascades, Washington. J. Petrol. 37:1409–1436.
- Tepper, J. H.; Nelson, B. K.; Bergantz, G. W.; and Irving, A. J. 1993. Petrology of the Chilliwack batholith, North Cascades, Washington: generation of calcalkaline granitoids by melting of mafic lower crust with variable water fugacity. Contrib. Mineral. Petrol. 113:333–351.
- Vannucci, R.; Shimizu, N.; Piccardo, G. B.; Ottolini, L.; and Bottazzi, P. 1993. Distribution of trace elements during breakdown of mantle garnet: an example from Zabargad. Contrib. Mineral. Petrol. 113:437–449.
- Vernon, R. H. 1991. Interpretation of microstructures of microgranitoid enclaves. *In* Didier, J., and Barbarin, B., eds. Enclaves and granite petrology. Amsterdam, Elsevier, p. 277–291.
- Ward, C. D.; McArthur, J. M.; and Walsh, J. N. 1992. Rare earth element behavior during evolution and alteration of the Dartmoor granite, SW England. J. Petrol. 33:785–815.
- Watson, E. B. 1976. Two-liquid partition coefficients: experimental data and geochemical implications. Contrib. Mineral. Petrol. 56:119–134.
- ——. 1982. Basalt contamination by continental crust: some experiments and models. Contrib. Mineral. Petrol. 80:73–87.
- Watson, E. B., and Green, T. H. 1981. Apatite/liquid partition coefficients for the rare earth elements and strontium. Earth Planet. Sci. Lett. 56:405–421.
- Wiebe, R. A. 1993. The Pleasant Bay layered gabbrodiorite, coastal Maine: ponding and crystallization of basaltic injections into a silicic magma chamber. J. Petrol. 34:461–489.
- Wiebe, R. A.; Smith, D.; Sturm, M.; King, E. M.; and Seckler, M. S. 1997. Enclaves in the Cadillac Mountain granite (coastal Maine): samples of hybrid magma from the base of the chamber. J. Petrol. 38:393–423.
- Wyllie, P. J.; Cox, K. G.; and Biggar, G. M. 1962. The habit of apatite in synthetic systems and igneous rocks. J. Petrol. 3:238–243.

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