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GEOCHEMICAL EVOLUTION OF THE SOUTH MOUNTAIN BATHOLITH, NOVA SCOTIA: RARE-EARTH-ELEMENT EVIDENCE

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ABSTRACT

The South Mountain batholith (SMB), of Late Devonian – Early Carboniferous age (372–361 *Ma*), is an intrusive complex of peraluminous granodiorites, monzogranites (adamellites) and leucocratic monzogranites (leucoadamellites). La, Ce, Sm, Eu, Tb, Yb and Lu have been analyzed in 22 whole rocks and 13 mineral separates from the batholith, as well as in some pelites and quartz metawackes from the Meguma Group, which constitutes the principal country rock of the batholith. In the batholith, average values for Σ*REE*, La/Sm and Eu/Eu* all show a systematic decrease from granodiorite (104.2, 2.0, 0.47), to monzogranite (53.3, 1.6, 0.25), to leucocratic monzogranites (15.1, 1.1, 0.18), respectively. *REE* concentrations in the Meguma rocks are broadly similar to those in the granodiorites; therefore, the extent of complete assimilation of country rocks cannot be assessed, nor can partial assimilation of such material account for the observed decrease of La/Sm in the SMB. Also, on the basis of rare earths, partial melting of Meguma-like rocks is ruled out as a source for the SMB, as is a process of direct partial melting of any reasonable source material to produce the leucocratic monzogranites. Fractional crystallization of a mixture of plagioclase, biotite and zircon from the granodiorite can account for part of the decrease of Σ*REE*, La/Sm and Eu/Eu* in later rocks, and is in agreement with other models for the evolution of the SMB based on major and trace elements. The high degree of *REE* depletion cannot, however, be modeled solely on a process of fractional crystallization. Some greisenized rocks from the interior of the SMB show severe depletion in *REE*. Partitioning of *REEs* into late hydrothermal fluids as fluoride complexes may account for the magnitude of the decreases in Σ*REE*, La/Sm and Eu/Eu*. The importance of fluid transport relative to fractional crystallization probably increased during the cooling history of the batholith.

Keywords: granodiorite, monzogranite, leucocratic monzogranite, greisen, rare earths, trace elements, fractional crystallization, assimilation, fluid interaction, biotite, plagioclase, fluorite, South Mountain batholith, Nova Scotia.

SOMMAIRE

Le batholithe South Mountain (dévonien supérieur à carbonifère inférieur: 372-361 *Ma*) est un complexe de roches intrusives hyperalumineuses: granodiorites, monzogranites (adamellites) et monzogranites leucocrates (leucoadamellites). Nous avons déterminé les concentrations de La, Ce, Sm, Eu, Tb, Yb et Lu dans 22 roches, 13 concentrés de minéraux et quelques échantillons de roches encaissantes (pélites et métagrauwackes du groupe Meguma). Les valeurs moyennes des trois paramètres Σ terres rares, La/Sm et Eu/Eu* diminuent progressivement de la granodiorite (104.2, 2.0, 0.47) au monzogranite (53.3, 1.6, 0.25) d'une part, aux monzogranites leucocrates (15.1, 1.1, 0.18) d'autre part. Les roches du Meguma ressemblent *grosso modo* aux granodiorites au point de vue des terres rares. On ne peut donc évaluer le degré d'assimilation des roches encaissantes, ni attribuer à une contamination la chute du rapport La/Sm dans les roches différenciées du batholithe. D'après ces données, une fusion partielle de roches du type Meguma ne peut produire la suite de roches observées. Une fusion partielle directe des roches disponibles à la source ne peut expliquer les monzonites leucocrates. La cristallisation fractionnée d'un mélange plagioclase + biotite + zircon à partir d'un magma granodioritique explique, comme d'autres modèles, le comportement des éléments majeurs et en traces, et en outre rend partiellement compte de la chute de Σ terres rares, La/Sm et Eu/Eu* pendant l'évolution du batholithe. Toutefois, l'appauvrissement en terres rares est trop brutal pour que la cristallisation fractionnée en soit entièrement responsable. Certains greisens à l'intérieur du batholithe montrent l'élimination quasi-complète des terres rares. Le transfert de celles-ci en complexes fluorurés dans les fluides hydrothermaux tardifs pourrait expliquer l'appauvrissement observé; ce processus est probablement devenu plus important que la cristallisaaion fractionnée au cours du refroidissement du batholithe.

(Traduit par la Rédaction)

Mots-clés: granodiorite, monzogranite, monzogranite leucocrate, greisen, terres rares, éléments traces, cristallisation fractionnée, assimilation, interaction avec phase fluide, biotite, plagioclase, fluorine, batholithe South Mountain, Nouvelle-Ecosse.

INTRODUCTION

Geological setting

The South Mountain batholith (SMB) is a post-tectonic, peraluminous granodiorite–granite

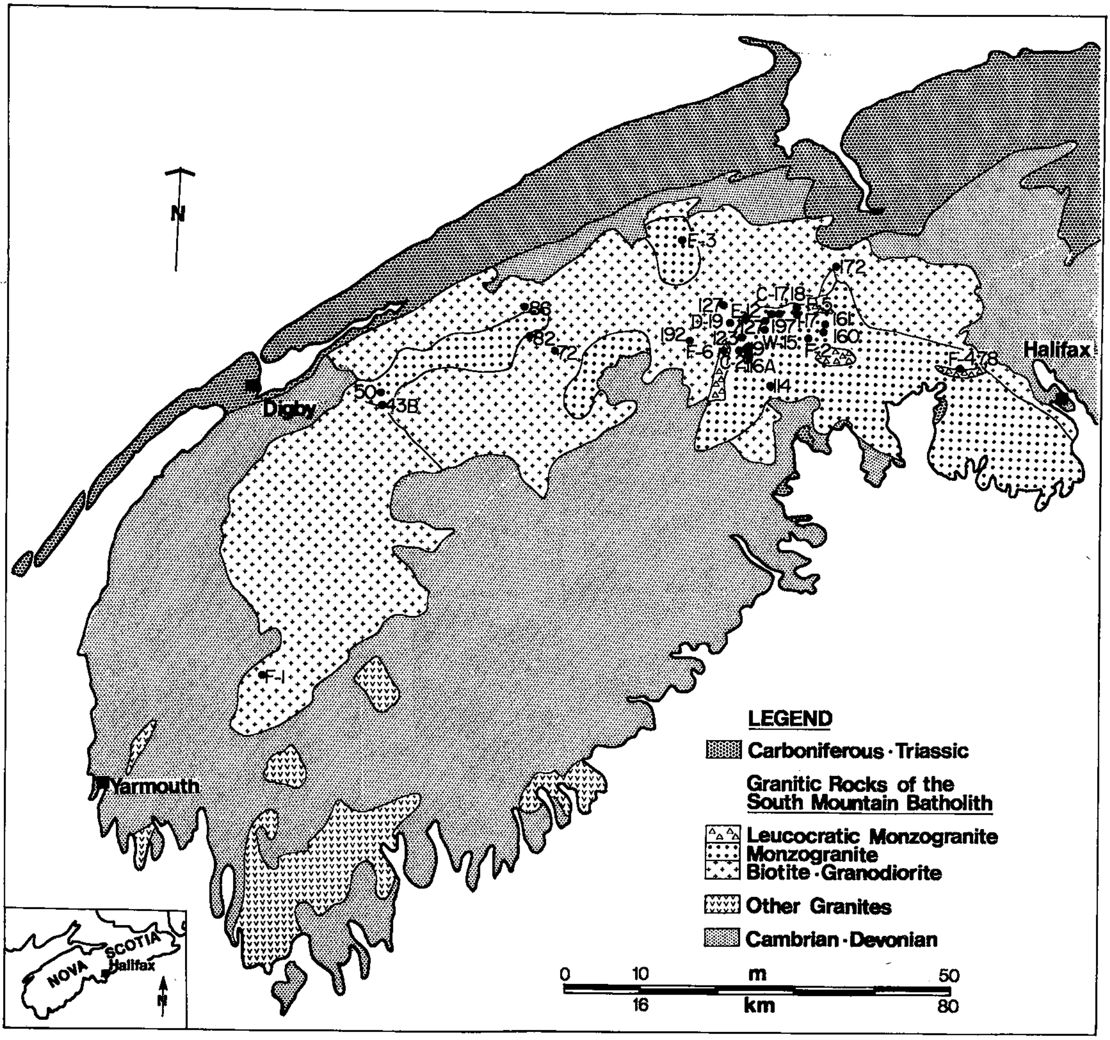

FIG. 1. Geological map of the central portion of the South Mountain batholith, Nova Scotia, showing the distribution of the major rock types and sample locations. Fluorite localities are prefixed by F.

complex that outcrops over a large area (10,000 km^2) of southwestern Nova Scotia (Fig. 1). It intrudes deformed, greenschist- to amphibolite-facies metawackes and metapelites of the Cambro-Ordovician Meguma Group; these are the oldest exposed rocks in southwestern Nova Scotia, and may exceed 10 km in thickness. Along its northwestern margin, the batholith also intrudes a sequence of metasedimentary and metavolcanic rocks ranging in age from Ordovician to Lower Devonian (Emsian) and known as the White Rock, Kentville, New Canaan and Torbrook Formations (Taylor 1969, Smitheringale 1973). These rocks were deformed and metamorphosed at the same time as the Meguma Group, *i.e.*, during the Acadian orogeny; in this part of Nova Scotia, the orogeny has been dated at 415–400 *Ma* (Reynolds & Muecke 1978).

The batholith is massive, undeformed and with locally discordant contacts, although the general shape of the batholith is broadly conformable with the regional trends of deformation in the country rocks. The frequency, sizes and shapes of country-rock xenoliths near the margins of the batholith suggest that the main mechanism of intrusion was stoping.

The batholith is unconformably overlain by coarse, subaerial clastic rocks of the Horton Group of Lower Carboniferous (Tournaisian) age; therefore, the time for intrusion, crystallization, uplift and erosion of the batholith is bracketed between Emsian and Tournaisian ages. Clarke & Halliday (1980) have reported Rb–Sr ages ranging from 372 to 361 *Ma* for various episodes of intrusion in the batholith.

Petrology of the batholith

The SMB generally consists of an envelope of biotite granodiorite into which are intruded a number of smaller, discrete bodies of biotite–muscovite monzogranite, porphyry (porphyritic monzogranite), leucocratic monzogranite, and dykes and irregular bodies of aplite, pegmatite and greisen. The more evolved rocks are associated with a gravity low (Garland 1953) centred over the town of New Ross. The greater volume of magma in this area appears to have been favorable for slow cooling, fractional crystallization, concentration of incompatible elements including Sn–W–Mo–Cu–U, and evolution of magmatic fluids (Charest 1976, Farley 1979). The rocks in the New Ross area show varying degrees of hydrothermal alteration, and most of the mineral showings of the SMB are located in this region.

Fractional crystallization of plagioclase and biotite has been advocated to explain the trends of major element chemical variation in the batholith (McKenzie & Clarke 1975). Clarke & Halliday (1980) also favored a closed-system fractional crystallization model over batch melting to explain variation in Rb and Sr concentrations. The present rare-earth element (*REE*) study examines in more detail the effects of fractional crystallization, country-rock contamination and hydrothermal fluids in the chemical evolution of the SMB.

ANALYTICAL PROCEDURES

The new trace-element data (*REE*s, Cs, Sc, Ta, Th, Hf) for this study were obtained by instrumental neutron-activation analysis (INAA) using a method first described by Gordon *et al.* (1968) and adapted as outlined by Gibson & Jagam (1980). Approximately 0.1 g of well-homogenized sample powder was irradiated in silica-glass ampoules at a flux of approximately 5 x 10^{13} n $cm^{-2}s^{-1}$ for 4–6 hours. Gamma-spectra from two 50 cm^3 coaxial Ge(Li) detectors (resolution of 2.2 keV FWHM for the 1332 keV of ^{60}Co) were accumulated with a 4096-channel analyzer. Full energy peak-areas were obtained by peak integration using linear background-subtraction on a PDP 12 computer or peak fitting with SAMPO (Routti & Prussin 1969) on a CDC 6400 computer.

Precision and accuracy of analyses attained in our laboratory may be judged from seven separate irradiations of standard rock G–2 reported by Ila *et al.* (1980). Precision varies from 2–5% for La, Ce, Sm, Eu, Lu, Cs, Hf, Sc and Th to 5–10% for Tb and 10–15% for Yb and Ta. The chondrite averages of Haskin *et al.* (1968) have been used for normalization of *REE* values.

Major element data and additional trace-element determinations for all the samples studied can be found in McKenzie & Clarke (1975), Charest (1976) and Farley (1979).

TABLE 1. RARE EARTH AND OTHER TRACE ELEMENTS IN THE SOUTH MOUNTAIN BATHOLITH

	Granodiorite (DI x TiO_2) > 30					Monzogranite 30 > (DI x TiO_2) > 10								Leucocratic Monzogranite 10 > (DI x TiO_2)						Greisen		
SAMPLE	M 72-82	M 72-86	M 72-72	M 72-192	M 72-172	M 72-127	M 72-50	M 72-161	M 72-119	M 72-160	M 72-43B	M 72-114	M 72-123	C-2	C-17	I-17	M 72-116A	C-18	M 72-197	W-15	D-19	E-12
La	34.3	34.5	30.3	27.8	24.0	19.8	24.4	21.2	13.6	13.7	11.3	8.39	2.60	4.46	4.77	2.71	2.93	2.42	1.99	0.274	7.13	6.89
Ce	77.9	72.9	65.1	60.7	53.5	47.5	52.9	53.0	34.9	32.2	28.3	21.4	7.74	13.9	14.2	7.85	6.45	6.63	5.74	0.506	19.8	20.1
Sm	9.65	9.41	7.90	7.74	5.56	5.62	7.33	6.54	4.59	4.66	4.48	4.13	2.00	2.24	1.80	1.53	2.06	1.12	1.22	0.344	3.45	3.33
Eu	0.87	1.36	1.43	1.28	0.87	0.88	0.71	0.56	0.40	0.33	0.50	0.17	0.085	0.069	0.171	0.103	0.092	0.082	0.081	0.07	0.233	0.265
Tb	0.74	1.27	1.07	0.91	0.81	0.70	0.66	0.61	0.48	0.63	0.53	0.46	0.23	0.34	0.37	0.31	0.15	0.29	0.31	**	0.51	0.42
Yb	1.25	4.17	2.70	3.49	2.51	1.93	0.74	1.35	1.35	1.13	0.29	0.79	0.56	0.81	0.44	0.81	0.23	0.54	0.46	0.126	0.72	1.47
Lu	0.15	0.57	0.41	0.53	0.41	0.36	0.15	0.22	0.19	0.17	0.074	0.15	0.10	0.15	0.087	0.125	0.053	0.075	0.066	0.03	0.16	0.18
Σ7REE	124.9	124.2	108.9	102.5	87.7	76.8	86.9	83.5	55.5	52.8	45.5	35.5	13.3	22.0	21.8	13.4	12.0	11.2	9.9	1.35	32.0	32.7
Eu/Eu*	0.31	0.45	0.56	0.53	0.48	0.60	0.32	0.29	0.29	0.22	0.36	0.13	0.14	0.09	0.27	0.19	0.15	0.19	0.18	---	0.21	0.25
Ba^x	491	672	732	616	618	429	418	341	200	141	301	66	28	34	68	72	16	n.d.	24	n.d.	99.6	75.0
Rb^x	221	172	148	144	136	174	272	324	299	410	268	532	620	608	720	409	660	847	816	1367	885	1534
Cs	12.9	13.0	9.00	10.6	7.53	14.9	15.6	23.0	18.9	26.7	17.9	30.1	32.9	17.7	33.3	19.0	33.1	48.5	40.7	91.2	38.7	53.2
Sc	4.93	12.0	12.7	12.2	7.93	8.51	4.32	4.75	3.86	3.49	2.37	2.52	2.12	3.11	2.73	1.83	1.74	2.91	3.13	1.46	2.11	3.23
Ta	2.56	2.46	2.08	1.13	2.00	1.39	2.65	2.11	2.13	3.56	2.54	3.16	3.88	6.93	7.16	4.43	5.46	10.5	6.48	9.09	6.47	3.46
Th	21.3	13.2	12.0	11.3	9.85	8.33	15.1	19.6	11.0	12.0	6.24	10.9	4.43	6.28	6.02	2.45	2.05	4.49	3.26	**	4.96	4.78
Hf	4.83	7.33	6.25	5.78	3.96	4.60	3.39	4.30	3.17	3.35	2.25	3.00	1.74	2.28	2.29	1.56	0.74	1.77	1.71	0.21	2.54	2.14
Zr^x	125	218	204	198	120	168	118	118	76	78	55	51	20	69	61	41	n.d.	43	35	2	70	73

n.d. = not determined All concentrations in parts per million. Ba, Rb and Zr values from McKenzie & Clarke (1975) and Charest (1976).
** below detection limit; x by X-ray fluorescence, remainder by INAA.

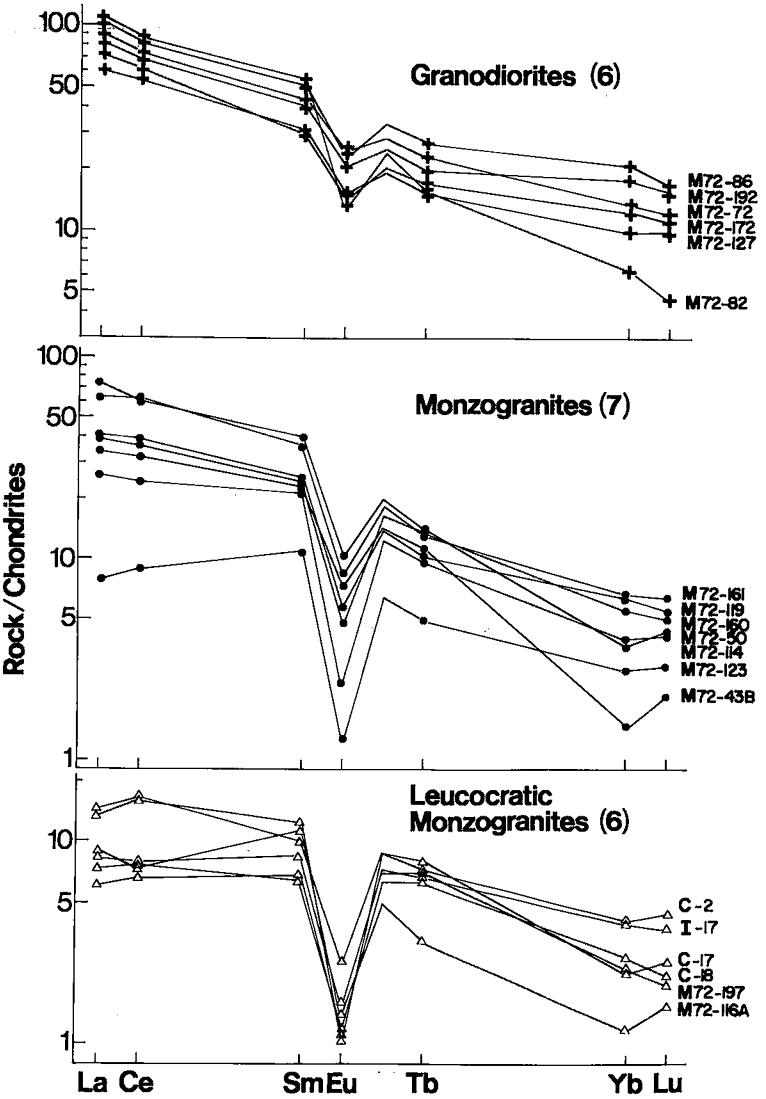

FIG. 2. Chondrite-normalized *REE* abundances in South Mountain batholith granitoid rocks: (a) granodiorites, (b) monzogranites and (c) leucocratic monzogranites. Groups (b) and (c) include porphyries, aplites and coarse, equigranular varieties.

ANALYTICAL RESULTS

The classification of samples into granodiorite, monzogranite (including porphyries) and leucocratic monzogranite (including some aplites) is based on the system of Streckeisen (1976). The trace-element concentrations for whole rock samples are reported in Table 1, in which the rocks are grouped according to the product of two chemical parameters that correlate well with Σ7*REE*, namely, TiO_2 (wt. %) and the Thornton–Tuttle differentiation index (DI). Petrographic and chemical groupings agree except for M72–82, which is petrographically a monzogranite but chemically a granodiorite.

The rare-earth-element compositions of all samples are shown in Figures 2 and 3. The granodiorites are characterized by high total rare-earths (average Σ7*REE* = 104.2 ± 19.4

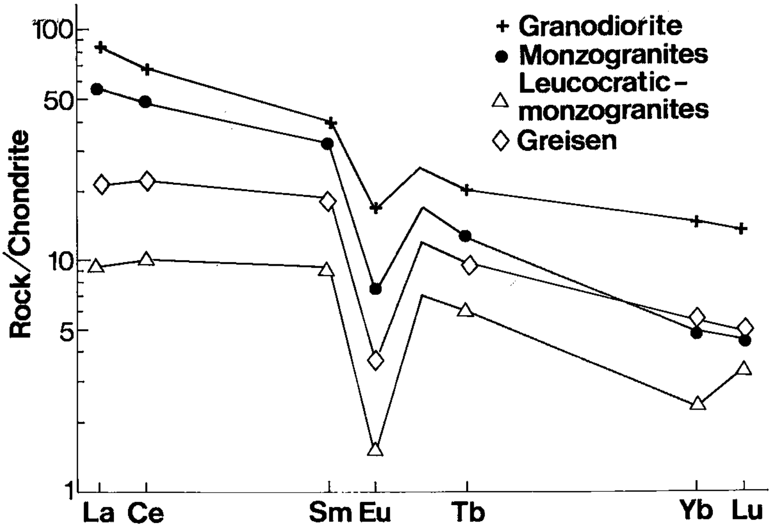

FIG. 3. Average chondrite-normalized *REE* abundances for granodiorites, monzogranites, leucocratic monzogranites and greisens from the South Mountain batholith, Nova Scotia.

ppm) and relatively small negative europium anomalies (average $Eu/Eu^* = 0.47 \pm 0.09$). As shown in Figure 2a, the chondrite-normalized patterns are broadly similar and show marked *LREE* enrichment (average $La/Sm = 2.04$). Sample M72–82 deviates from the "normal" pattern; its major element chemistry and some trace-element characteristics suggest that it is transitional between granodiorites and monzogranites. By comparison, the monzogranites have intermediate rare-earth concentrations (average $\Sigma 7REE = 53.3 \pm 25.9$ ppm) and a larger negative europium anomaly (average $Eu/Eu^* = 0.25 \pm 0.09$). The patterns are broadly similar to each other (Fig. 2b) but show more within-group variation than the granodiorites, and also are less *LREE*-enriched (average $La/Sm = 1.55$). Finally, the leucocratic monzogranites have the lowest *REE* concentrations (average $\Sigma 7REE = 15.1 \pm 5.4$ ppm) and the largest negative europium anomalies in the SMB (average $Eu/Eu^* = 0.18 \pm 0.06$). The patterns are generally similar (Fig. 2c) and show virtually no *LREE* enrichment ($La/Sm = 1.05$).

In the vicinity of New Ross, several mineral deposits are associated with greisenized monzogranite and leucocratic monzogranite (including aplite and pegmatite). The greisens are essentially quartz–phengite assemblages with minor amounts of other phases (Farley 1979) that occur in joints or associated with minor intrusions.

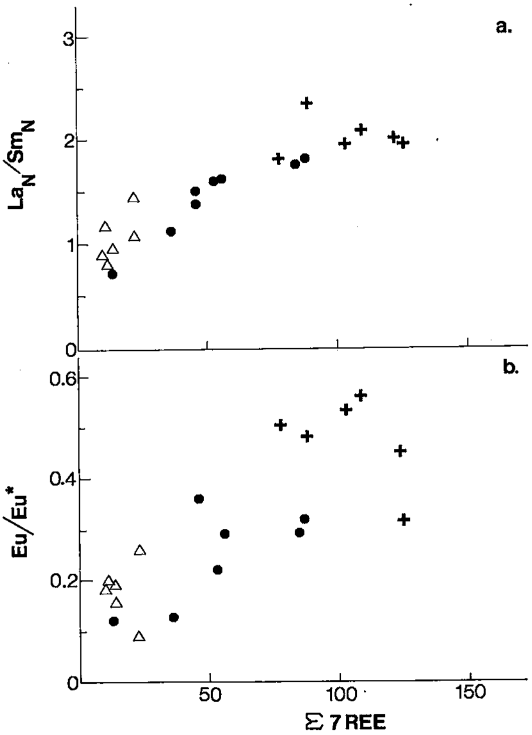

FIG. 4. Variation of La/Sm and Eu/Eu* with total ($\Sigma 7REE$) rare-earth content for all granitoid rocks of the South Mountain batholith. Symbols as in Figure 3.

Three greisen samples were analyzed in this study, two of which had rare-earth and trace-element contents similar to the considerably less-altered monzogranite and leucocratic monzogranite precursor rocks (Table 1, Fig. 3). The third sample (W15) is a phengite–quartz–siderophyllite–tourmaline–topaz–rutile–fluorite–copper sulfide greisen whose *REE*, Ba, Zr, Hf, Sc and Th concentrations are significantly below those of even the most depleted leucocratic monzogranite, whereas it is strongly enriched in alkali elements such as Li, Rb and Cs. This sample provides evidence of the ability of late fluid phases to modify significantly the trace-element concentrations of late-stage rocks in the SMB. For comparison, the averages of the major groupings of rock are shown in Figure 3, which shows the very clear trend of *decreasing* total *REE* from early granodiorites (372 *Ma*; Clarke & Halliday 1980), to later monzogranites (366 *Ma*) and leucocratic monzogranites (361 *Ma*). At the same time, the negative Eu anomaly increases in magnitude, and the relative light *REE* enrichment (La/Sm) decreases (Fig. 4). Two of the greisen samples are not distinguishable from their igneous precursors, but sample W15 (Table 1, Fig. 3) is markedly different.

Some of the other trace elements show covariations with the *REE*s that are thought to be significant, although sometimes poorly defined. Ba, Zr, Hf, Sc and Th all show a positive correlation with $\Sigma 7REE$ (Fig. 5) and are significantly depleted in the late-stage leucocratic monzogranites. The alkalis (Li, Rb, Cs) and Ta, on the other hand, show a negative correlation and are strongly enriched in the highly differentiated rocks (Fig. 5).

The role of Ta is particularly notable. Nb, Ta

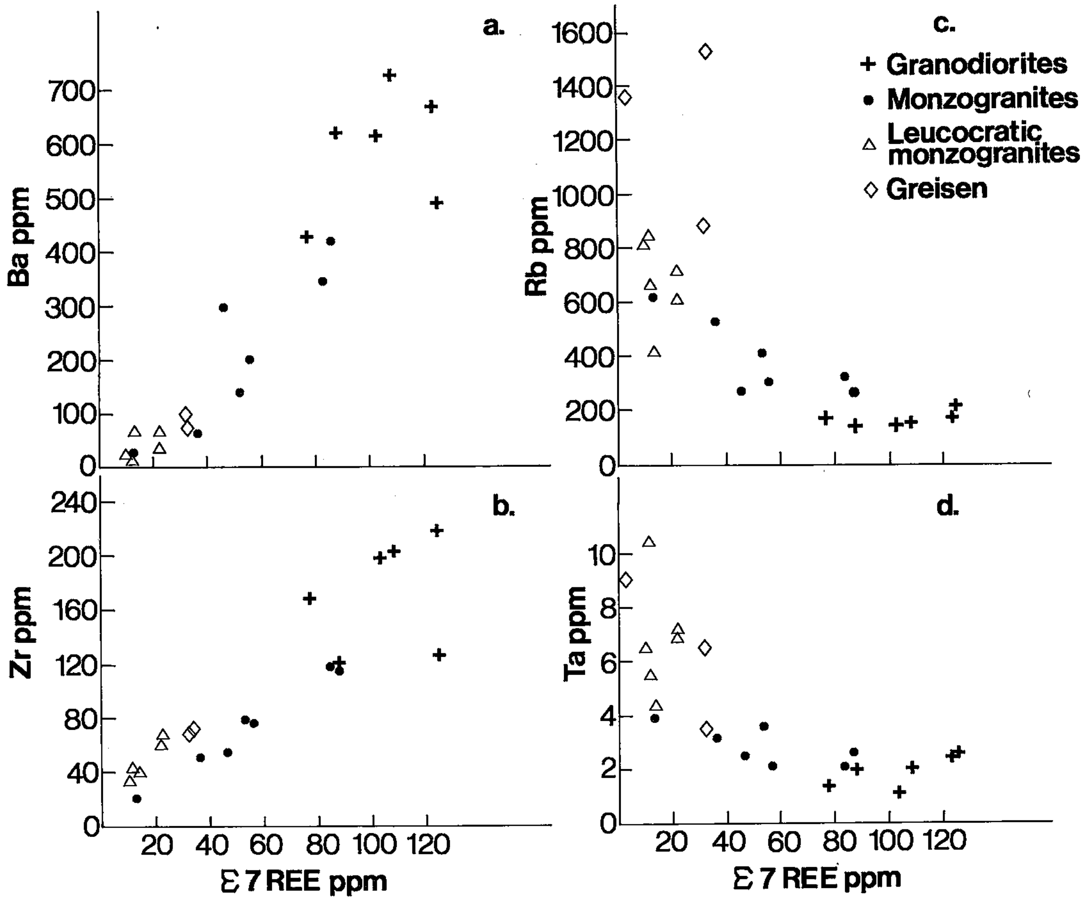

FIG. 5. Covariation of selected trace elements with total *REE* content for all granitoid rocks of the South Mountain batholith.

TABLE 2. RARE EARTH AND OTHER TRACE ELEMENTS IN MINERALS FROM THE SOUTH MOUNTAIN BATHOLITH

	Plagioclase		Biotite				Fluorite							
SAMPLE #	M 72-127	M 72-137	M 72-72	M 72-72†	M 72-172	M 72-172†	F-1	F-2	F-3	F-4	F-5	F-6	F-7	F-8
La	18.9	11.2	64.9	57.8	51.3	32.2	2.75	2.31	1.26	1.01	3.46	0.131	0.234	1.40
Ce	31.8	20.6	117.9	105.8	90.1	58.9	11.3	10.7	2.31	2.21	6.84	0.205	0.522	4.17
Nd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10.2	14.2	2.68	1.29	3.75	**	0.463	3.13
Sm	2.99	1.38	15.4	14.4	12.3	8.12	4.98	7.71	1.03	0.441	0.683	0.274	0.171	1.33
Eu	2.10	2.44	0.286	0.283	0.244	0.193	1.67	0.335	0.192	0.031	0.049	0.006	0.017	0.090
Tb	0.45	0.25	1.32	1.67	1.16	0.94	1.85	1.71	0.424	0.110	0.114	0.127	0.059	0.355
Yb	0.77	0.40	2.82	4.33	3.07	3.24	7.38	1.66	1.60	0.204	0.275	0.140	0.228	0.401
Lu	0.12	0.06	0.48	0.72	0.642	0.57	0.97	0.20	0.25	0.029	0.048	0.017	0.032	0.047
Σ7REE	57.1	36.3	203.1	185	158.8	104.2	30.9	24.6	7.07	4.04	11.5	0.90	1.26	7.79
Eu/Eu*	2.20	5.21	0.07	0.07	0.07	0.08	0.78	0.12	0.41	0.19	0.22	0.05	0.26	0.18
Ba	352	209	1565	1677	1554	1499	395	299	86.2	24.8	29.3	29.4	17.7	80.4
Cs	2.74	2.81	34.2	33.6	41.1	43.1	0.10	0.13	0.04	0.07	0.02	0.08	0.03	0.15
Sc	0.38	0.12	64.8	65.6	62.9	64.2	0.20	0.04	0.01	0.04	0.01	0.03	0.02	0.06
Ta	**	**	5.76	5.43	5.54	5.54	**	0.04	**	0.04	**	0.02	**	0.04
Th	3.59	0.60	28.3	23.5	19.5	11.0	0.11	0.57	0.11	0.55	0.10	0.11	0.10	0.40
Hf	3.08	0.81	14.0	13.8	5.68	3.83	0.15	0.16	0.11	0.18	0.14	0.14	0.14	0.19

n.d. = not determined. All concentrations in parts per million. † = partial removal of included apatite and zircon.
** = below detection limit.

and the *REE*s are usually concentrated together in late-stage granitic pegmatites and muscovite granites (Boyle 1974). In the SMB, Nb does not vary significantly with differentiation (Charest 1976), whereas Ta increases and *REE*s decrease.

McKenzie & Clarke (1975) suggested that closed-system fractional crystallization of plagioclase and biotite could account for much of the major element variation in the SMB. To test this model, we separated plagioclase and biotite from four different rocks and analyzed them for *REE* and other trace elements (Table 2). The plagioclase mineral separates contained some quartz, and the values in Table 2 have been corrected for this impurity on the assumption that the quartz contained no *REE*s. As is normal for plagioclase in granitoid rocks, the Σ7*REE* is low and Eu/Eu* ratios greater than unity (positive). The biotite separates were analyzed both with poikilitic inclusions of apatite and zircon and with at least some of these enclosed phases removed. Those samples with apatite and zircon partly removed have lower Σ7*REE*, Hf and Th. In the modeling calculations the naturally occurring biotite–apatite–zircon composite was used.

Fluorite is an important constituent of some leucocratic monzogranites, aplites, greisen zones and hydrothermal veins in the SMB. Specimens of fluorites from veins in granitic hosts from seven localities in the SMB (Fig. 1) were separated, checked optically to be free from inclusions and analyzed for their trace-element contents (Table 2). Their low Hf, Th, Sc and Ta contents indicate that most of the *REE*s do not reside in impurities of zircon, xenotime, monazite or allanite, but are probably incorporated into the fluorite structure. Furthermore, the *REE* patterns of these *REE*-rich accessory phases are unlike those observed in the fluorites. The fluorites show a wide range of Σ7*REE* concentrations and, in some cases, the fluorite Σ7*REE* content exceeds that of the granitic host rocks.

The chondrite-normalized patterns of the fluorites (Fig. 6) generally show enrichment of the middle *REE*s relative to the *LREE* and *HREE*, probably a reflection of their ionic size relative to the Ca position in the fluorite structure, with the exception of a well-developed negative Eu anomaly. Strong negative Eu anomalies are not a generally observed feature of fluorites (*e.g.*, Grappin *et al.* 1979); their petrogenetic significance will be discussed in the following section.

Fluorine complexing has been suggested as a means of mobilizing rare earths, uranium (Kimberly 1978) and tin (Barsukov & Kuril'chikova 1966), and of separating Ta from Nb (Parker & Fleischer 1968). The fluorites with the highest concentrations of *REE*s, particularly *HREE*s, (F1–F3, Table 2) are associated with important Sn and U mineralization in the SMB. The remainder of the fluorites in Table 2 occur in apparently barren hydrothermal veins. The potential for using *REE* contents of fluorites in geochemical prospecting is obvious.

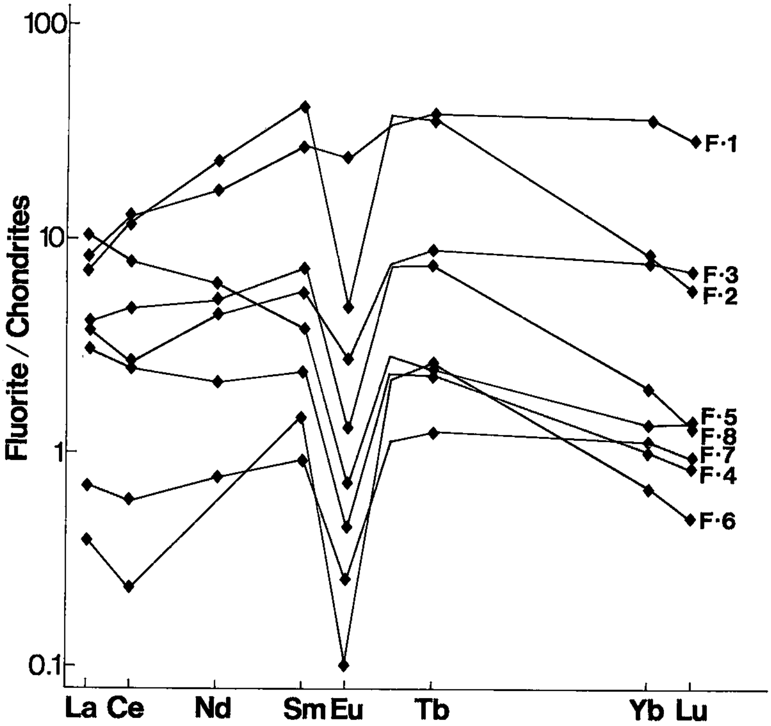

FIG. 6. Chondrite-normalized *REE* abundances in fluorites from the South Mountain batholith.

DISCUSSION

As stated in the Introduction, the purpose of this trace-element study is to provide further insight into the processes that controlled the chemical evolution of the SMB. These processes are known to be fractional crystallization, for which there is considerable major- and trace-element evidence (McKenzie & Clarke 1975), assimilation of country rocks (Clarke & Halliday 1980) and late-stage modification by fluid phases, for which there is evidence such as reddened granites, greisen zones and very low K/Rb ratios in the vicinity of New Ross (McKenzie 1973, Charest 1976, Farley 1979). Each of these three processes will now be examined in the light of the currently available rare-earth and other trace element data. Since younger plutons in the batholith have higher Rb, Cs and Li, but not *REE*s) than the older concentrations of magmatophile elements (*e.g.*, phases of intrusion, a batch-melting model for the origin of the SMB will not be considered here.

Fractional crystallization

As noted earlier, the trend of *REE* concentrations in the SMB is downward with increasing differentiation index and decreasing age (Fig. 3). As a test of the fractional crystallization model, plagioclase and biotite analyses (Table 2) were combined in various ratios and subtracted in various amounts from average SMB magma in an attempt to match the *REE* pattern of average late-stage rock (weighted mean of average monzogranites and average leucocratic monzogranite in the ratio 4:1).

Two of the typical models are presented in Figure 7. The first involved only plagioclase (M72–137) and biotite (M72–72) in roughly equal amounts, representing a 52.5% cumulate from the average SMB magma. (This plagioclase-, biotite-rich "cumulate" would be petrologically similar to the granodiorite.) After removal of the fractionating phases, the residual magma should approximate that of the average late-stage magma in the batholith. As can be seen from Figure 7, the fit is erratic, being acceptable for La and Eu but unsatisfactory for all other elements, especially the *HREE*s, which become enriched rather than depleted in later differentiates. An improvement to the *HREE*s is achieved by adding 3% zircon (Hanson 1978)

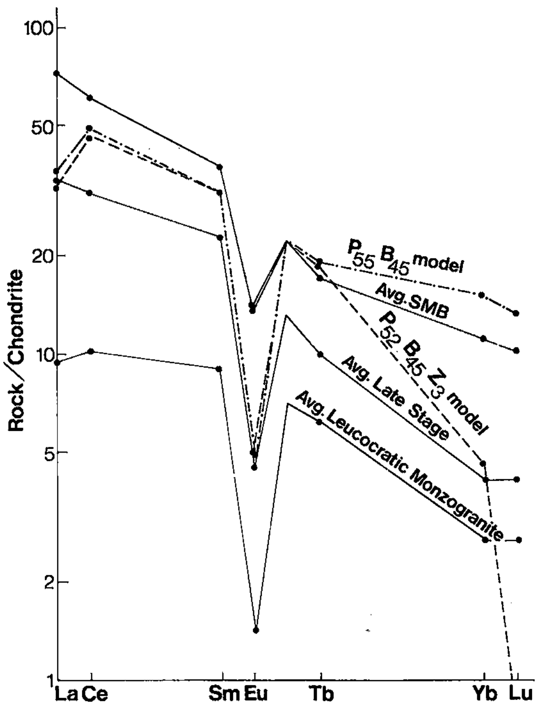

FIG. 7. Results of modeling rare earths by fractional crystallization. Two model compositions are shown: (1) removal of 55% plagioclase and 45% biotite ($P_{55}B_{45}$) from average SMB magma to model the average late-stage composition and (2) removal of 52% plagioclase, 45% biotite and 3% zircon ($P_{52}B_{45}Z_3$) from average SMB to model the average late-stage composition. In general, the fits are poor for the average late-stage composition; this process certainly could not be extended to account for the highly depleted leucocratic monzogranites.

to the fractionating assemblage, *i.e.*, in addition to that already poikilitically enclosed in the biotite. For this assemblage, the fit is reasonable for La, Eu and Yb (*i.e.*, one light, one middle and one heavy rare-earth element) but in general the fit is poor.

The acceptability of such a model becomes questionable if one considers the Zr–Σ*REE* correlation observed in Figure 5, since zircon crystallization should rapidly deplete Zr (major component) relative to *REE*s (trace component). The observed correlation can only be established during fractional crystallization if zircon crystallized concomitantly with a nearly equivalent amount of a phase in which *REE*s are also major constituents, such as monazite or allanite. Moreover, such a model would require the simultaneous crystallization of zircon and monazite or allanite in nearly constant proportions. In our view this is an unlikely situation, since phosphorus shows no systematic decrease in the SMB crystallization sequence, whereas Zr decreases progressively.

The limitations of such modeling are the fixed compositions of phases, fixed proportions of phases and simple subtraction of the cumulate in a single batch. Moreover, mass-balance calculations indicate that > 50% of the *REE*s in the granodiorites must reside in accessory phases (see also Condie & Lo 1971). A more dynamic model might involve a range of mineral compositions, variable proportions of phases, a variation in the style of crystallization (equilibrium *versus* fractional, or Rayleigh *versus* batch), and a greater consideration of accessory phases, but such refinements would probably not greatly alter the conclusions reached below.

Two conclusions arise from these modeling attempts. First, by refining the fractionation model, it may be possible to account for the derivation of average late-stage rocks from average SMB magma by the subtraction of plagioclase and biotite, although the amounts removed are large. Secondly, the difference between average late-stage rocks (weighted strongly in favor of monzogranite) and average leucocratic monzogranites (Fig. 7) is even greater than the difference between average late-stage rocks and the average SMB composition. Whereas removal of plagioclase and biotite may account for some of the *REE* depletion in the early stages of the batholith, the reduced modal amounts of these minerals in monzogranites and leucocratic monzogranites and the much greater *REE* differences involved make it a wholly unsatisfactory mechanism to account for the late-stage variation. Another process is indicated.

The other trace elements (Table 1) similarly show changes in concentration from granodiorites to monzogranites that can be explained by a process of fractional crystallization. However, the accelerated enrichments or depletions in these elements from the monzogranite to leucocratic monzogranite stages of evolution require another explanation.

Assimilation of Meguma rocks

Partially digested xenoliths, clearly of Meguma origin, are a common feature of the marginal granodiorites of the SMB. In addition, the frequent occurrence of ghost-like patches, mafic schlieren, lacey sulfide "screens", xenocrystic garnet (and cordierite?), coupled with abnormally

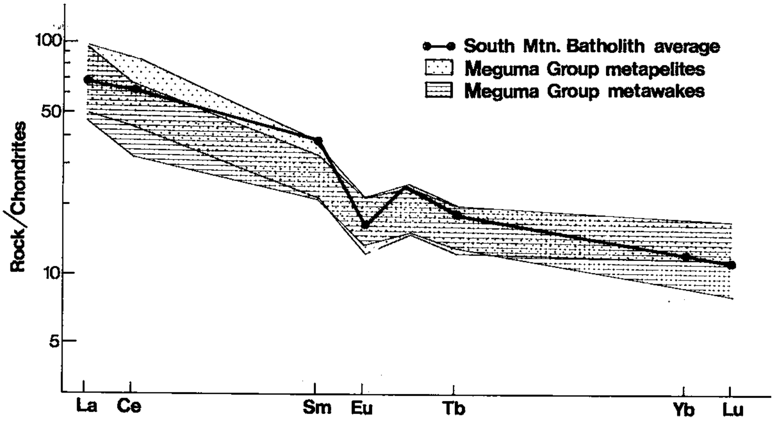

FIG. 8. Chondrite-normalized *REE* abundances of the estimated average composition of the South Mountain batholith compared with the composition of Meguma Group metapelites and metawackes. Compositional ranges plotted for the metasediments represent the mean ± 1σ based on 18 analyzed metapelites and 28 metawackes (data from Liew 1979 and Muecke, unpubl. data).

high aluminum (Jamieson 1974) and radiogenic strontium (Clarke & Halliday 1980) contents in these marginal rocks, points to total (or near-total) assimilation of many more xenolithic blocks.

Liew (1979) and Muecke (unpubl. data) have analyzed the *REE* content of lithological subdivisions in the Meguma Group. For each element determined, the restricted range of variation in Meguma rocks brackets the composition of the average SMB (Fig. 8), and therefore total assimilation of such material will not have a large effect on the overall *REE* composition of the batholith. Of course, those xenoliths that are only partly assimilated will contribute more or less than the average SMB composition, depending on the phases involved, the distribution coefficients and whether or not equilibrium is attained. However, no addition of such a partial melt to the average SMB magma could account for the observed change in *REE*s from granodiorite to monzogranite to leucocratic monzogranite.

Clarke & Halliday (1980) have shown that, although the SMB magma underwent chemical modification along its margins at the time of intrusion, once a relatively thin granodiorite margin had crystallized, the rest of the variation in $^{87}Sr/^{86}Sr$ could be explained by closed-system fractional crystallization. The average SMB magma may have undergone very little *REE* modification as a result of total assimilation during the initial phase of intrusion. At a later stage, when some monzogranite plutons intruded beyond the granodiorite envelope into Meguma rocks, further assimilation may have served to retard the general downward trend of *REE*s in the SMB. Since *REE*s decrease even more rapidly from the monzogranite to leucocratic monzogranite stages, further contamination probably was not an important process in the chemical evolution of the batholith.

Role of fluids

Products of the late stages of crystallization of the SMB show abundant evidence of the importance of aqueous fluids in the evolution and modification of the rocks. Pegmatite and aplite formation, greisenization, albitization, polymetallic mineralization (Sn–W–Mo–Cu–U) and "reddening" of phases are mainly found associated with the leucocratic monzogranites. All these phenomena are thought to be closely related to late-magmatic stages of the batholith rather than postmagmatic processes. Fluorite and topaz are important minor constituents in many of the late-stage rocks and also occur as vein minerals. Geochemical expressions of these processes include strong enrichments in alkalis (Li, Rb, Cs), Sn, Ta and F, as well as unusually low K/Rb (≃30–40) and Th/U (≃0.35) ratios.

The predominance of fluorine-bearing species among vein minerals and as minor constituents in late-stage rocks strongly suggests that fluorine-enriched aqueous fluids played an important role in the late-magmatic stage of the batholith.

Bandurkin (1961), Mineyev *et al.* (1966) and Balashov & Krigman (1975) have suggested that carbonate and fluoride anionic complexes are the most effective means of stabilizing and mobilizing *REE*s in aqueous solutions at the magmatic stage. The strong partitioning of *REE*s into CO_2-rich fluids at elevated T and P, probably as a result of complexing, has been experimentally verified by Wendlandt & Harrison (1979). Equivalent evidence for *REE* behavior in the presence of fluorine-rich aqueous solutions is still sparse, but preliminary experimental data by Flynn and Burnham (1978) suggest that fluoride is effective as a complexer of *REE*s under magmatic conditions.

However, there is strong, indirect evidence of *REE* mobility in fluorine-rich fluids. Rare-earth mineralization is frequently encountered in high-temperature greisen deposits in close association with fluorite (Bandurkin 1961). Grappin *et al.* (1979) have investigated fluorite deposits genetically related to granitic rocks and found considerable *REE* enrichment in the fluorites (up to 200x chondritic) and positive Eu anomalies. They attributed the *REE* character of the fluorites to the interaction of fluorine-rich hydrothermal solutions with feldspars in the associated granites. Alderton *et al.* (1980) attributed the mobility of *REE*s during hydrothermal and supergene alteration of granites from southwestern England to the presence of fluorine in the alteration fluids and the stability of *REE* fluoride complexes.

Although crystal fractionation of combinations of major and minor mineral phases from a granodioritic parent magma may account for the reduction of *REE* content observed in the monzogranites, it is difficult to envisage how this process could account for the very low concentrations found in the leucocratic monzogranites. The evidence for the interaction of the latter with a fluorine-rich aqueous fluid leads us to conclude that fluoride-complexing of the *REE*s into an aqueous phase became the dominant fractionation mechanism during the late magmatic stage. Although our data on greisen zones are still limited, in at least one case *REE* concentrations approach detection limits and are significantly lower than any probable parent material. Removal of the *REE*s by the greisenizing solutions appears to be a feasible mechanism for producing such abnormally low *REE* concentrations in an acidic rock. The increasingly negative Eu anomaly in the late-stage rocks is probably also a function of the partitioning of *REE*s into the fluid phase, rather than a reflection of feldspar fractionation. Experiments by Flynn and Burnham (1978) on chloride-bearing systems, consisting of an aqueous fluid phase and granitic melt, have demonstrated a strong preferential incorporation of Eu into the fluid phase (*i.e.*, positive Eu anomaly). We postulate a similar Eu enrichment for fluoride-bearing or mixed fluoride–chloride fluids and suggest that the removal of this fluid constitutes the main mechanism of Eu depletion observed in the late-stage rocks of the SMB.

The fluorite samples are clearly one sink for *REE*s mobilized in the late hydrothermal fluids. Unfortunately, neither the distribution coefficients of *REE*s between silicate melt and hydrothermal solution nor the distribution coefficients between hydrothermal fluid and fluorite is known. It is, therefore, not possible to estimate either absolute or relative amounts of *REE*s removed from the late magmas in hydrothermal fluids. However, the fluorite data do indicate that these solutions mobilized the *REE*s, probably as fluoride complexes.

The unusual negative Eu anomalies in the *REE* patterns of the fluorites have no obvious explanation in terms of crystal chemistry. Instead, they may be related to the compositions of the hydrothermal fluids, which in turn were derived from magmas depleted in Eu through extensive fractional crystallization of plagioclase. Thus, we regard the negative Eu anomalies in the fluorites as broadly reflecting the Eu depletion in the source magmas of the SMB at the time of their formation.

CONCLUSIONS

Successively younger intrusive phases of the South Mountain batholith, as defined by field relations (McKenzie & Clarke 1975) and Rb/Sr geochronology (Clarke & Halliday 1980), are characterized by decreasing $\Sigma 7$*REE*, La/Sm and Eu/Eu*. In addition, Ba, Sc, Th, Hf and Zr decrease and Rb, Cs and Ta increase from older to younger intrusive rocks.

Fractional crystallization, assimilation of country rock and interaction with deuteric aqueous fluid were all considered as mechanisms to account for the variation in *REE* and trace-element geochemistry. Fractional crystallization of plagioclase and biotite can largely explain the derivation of average late-stage rocks from the average SMB magma, but cannot explain the large chemical differences between the monzogranites and leucocratic monzogranites. Since the average *REE* compositions of the SMB and Meguma host rocks are very similar, wholesale assimilation of country rocks by the SMB magma cannot produce the observed *REE* variation during the cooling history of the SMB. Also, partial melting of Meguma-like material would be most unlikely to have given rise to the average SMB magma. Finally, the large changes in *REE* and trace-element geochemistry were examined as possible products of late-stage interaction between the magma, late-stage fluids and solid granitic rocks. The occurrence of substantially *REE*-depleted greisen zones and somewhat *REE*-enriched fluorite veins attests to the high mobility of *REE*s at a late stage in the evolution of the batholith. If fluorine-rich fluids also removed *REE*s from the late-stage magmas, the same mechanism may account for the substantial *REE* depletions in the leucocratic monzogranites. The existence of large volumes of *REE*-depleted rocks in the SMB suggests that there may be associated *REE*-rich mineral deposits yet to be found.

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REFERENCES

ALDERTON, D.M.H., PEARCE, J.A. & POTTS, P.J. (1980): Rare earth mobility during granite alteration: evidence from southwest England. *Earth Planet. Sci. Lett.* **49**, 149-165.

BALASHOV, YU.A. & KRIGMAN, L.D. (1975): The effects of alkalinity and volatiles on rare-earth separation in magmatic systems. *Geochem. Int.* **12**(6), 165-170.

BANDURKIN, G.A. (1961): Behavior of the rare earths in fluorine-bearing media. *Geochem.*, 159-167.

BARSUKOV, V.L. & KURIL'CHIKOVA, G.YE. (1966): On the forms in which tin is transported in hydrothermal solutions. *Geochem. Int.* **3**, 759-764.

BOYLE, R.W. (1974): Elemental associations in mineral deposits and indicator elements of interest in geochemical prospecting (revised). *Geol. Surv. Can. Pap.* **74-75**.

CHAREST, M.H. (1976): *Petrology, Geochemistry and Mineralization of the New Ross Area, Lunenburg County, Nova Scotia.* M.Sc. thesis, Dalhousie Univ., Halifax, N.S.

CLARKE, D.B. & HALLIDAY, A.N. (1980): Strontium isotope geology of the South Mountain batholith, Nova Scotia. *Geochim. Cosmochim. Acta* **44**, 1045-1058.

CONDIE, K.C. & LO, H.H. (1971): Trace element geochemistry of the Louis Lake batholith of early Precambrian age, Wyoming. *Geochim. Cosmochim. Acta* **35**, 1099-1110.

FARLEY, E.J. (1979): *Mineralisation at the Turner and Walker Deposits.* M.Sc. thesis, Dalhousie Univ., Halifax, N.S.

FLYNN, R.T. & BURNHAM, C.W. (1978): An experimental determination of rare earth partition coefficients between a chloride containing vapor phase and silicate melts. *Geochim. Cosmochim. Acta* **42**, 685-701.

GARLAND, G.D. (1953): Gravity measurements in the Maritime Provinces. *Dom. Obs. Publ.* **16**(7), 105-275.

GIBSON, I.L. & JAGAM, P. (1980): Instrumental neutron activation analysis of rocks and minerals. *In* Neutron Activation Analysis in the Geosciences (G.K. Muecke, ed.). *Mineral. Assoc. Can. Short Course Handbook* **5**, 109-131.

GORDON, G.E., RANDLE, K., GILES, G.G., CORLISS, J.B., BEESON, M.H. & OXLEY, S.S. (1968): Instrumental activation analysis of standard rocks with high-resolution γ-ray detectors. *Geochim. Cosmochim. Acta* **32**, 369-396.

GRAPPIN, C., TREUIL, M., YAMAN, S. & TOURAY, J.C. (1979): Le spectre des terres rares de la fluorine en tant que marqueur des propriétés du milieu de dépôt et des interactions entre solutions minéralisantes et roches sources. Exemple pris dans le district de la Marche occidentale (France). *Mineral. Deposita* **14**, 297-309.

HANSON, G.N. (1978): The application of trace elements to the petrogenesis of igneous rocks of granitic composition. *Earth Planet. Sci. Lett.* **38**, 26-43.

HASKIN, L.A., HASKIN, M.A., FREY, F.A. & WILDEMAN, T.R. (1968): Relative and absolute terrestrial abundances of the rare earths. *In* Origin and Distribution of the Elements (L.H. Ahrens, ed.). Pergamon, Oxford, England.

ILA, P., JAGAM, P. & MUECKE, G.K. (1980): Reactor-detector calibration for routine instrumental neutron activation analysis of geological materials. *J. Radioanal. Chem.* **57**, 147-155.

JAMIESON, R.A. (1974): *The Contact of the South Mountain Batholith near Mt. Uniacke, N.S.* B.Sc. thesis, Dalhousie Univ., Halifax, N.S.

KIMBERLEY, M.M. (1978): High-temperature uranium geochemistry. *In* Uranium Deposits: their Mineralogy and Origin (M.M. Kimberley, ed.). *Mineral. Assoc. Can. Short Course Handbook* **3**, 101-104.

LIEW, M.Y.C. (1979): *Geochemical Studies of the Goldenville Formation at Taylor Head, Nova Scotia.* M.Sc. thesis, Dalhousie Univ., Halifax, N.S.

MCKENZIE, C.B. (1973): *Petrology of the South Mountain Batholith, Nova Scotia.* M.Sc. thesis, Dalhousie Univ., Halifax, N.S.

——— & CLARKE, D.B. (1975): Petrology of the South Mountain batholith, Nova Scotia. *Can. J. Earth Sci.* **12**, 1209-1218.

MINEYEV, D.A., DIKOV, YU.P., SOBOLEV, B.P. & BORUTSKAYA, V.L. (1966): Differentiation of rare earth elements under supercritical conditions. *Geochem. Int.* **3**, 357-359.

PARKER, R.L. & FLEISCHER, M. (1968): Geochemistry of niobium and tantalum. *U.S. Geol. Surv. Prof. Pap.* **612**.

REYNOLDS, P.H. & MUECKE, G.K. (1978): Age studies on slates: applicability of the $^{40}Ar/^{39}Ar$ stepwise outgassing method. *Earth Planet. Sci. Lett.* **40**, 111-118.

ROUTTI, J.T. & PRUSSIN, S.G. (1969): Photopeak method for the computer analysis of gamma-ray spectra from semiconductor detectors. *Nucl. Instr. Meth.* **72**, 125-142.

SMITHERINGALE, W.G. (1973): Geology of parts of Digby, Bridgetown and Gaspereau Lake map-areas. *Geol. Surv. Can. Mem.* **375**.

STRECKEISEN, A.L. (1976): To each plutonic rock its proper name. *Earth Sci. Rev.* **12**, 1-33.

TAYLOR, F.C. (1969): Geology of the Annapolis–St. Mary's Bay map-area, Nova Scotia. *Geol. Surv. Can. Mem.* **358**.

WENDLANDT, R.F. & HARRISON, W.J. (1979): Rare earth partitioning between immiscible carbonate and silicate liquids and CO_2 vapour: results and implications for the formation of light rare earth-enriched rocks. *Contr. Mineral. Petrology* **69**, 409-419.

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