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ASSIMILATION OF COUNTRY-ROCK ILMENITE AND RUTILE IN THE SOUTH MOUNTAIN BATHOLITH, NOVA SCOTIA, CANADA

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Abstract

The South Mountain Batholith (SMB) of southwestern Nova Scotia is a peraluminous granitoid complex showing physical and chemical evidence of contamination by metasedimentary country-rocks of the Meguma Group. Some ilmenite grains in the granitic rocks are texturally and chemically similar to ilmenite grains in the country rocks, whereas other ilmenite grains in the granitic rocks appear to be texturally (more euhedral) and chemically (lower and less variable Mn contents) unique. Some rutile grains in the granitic rocks are texturally and chemically similar to rutile grains in the country rocks, whereas other rutile grains in the granitic rocks appear to be texturally and chemically similar to rutile grains in the country rocks, whereas other rutile grains in the granitic rocks appear to be texturally (more euhedral, possible cavity-fill) and chemically (higher Nb + Ta contents, oscillatory compositional zoning) unique. In the least evolved rocks of the SMB, ilmenite is magmatic and xenocrystic in origin, with cation exchange the probable reaction causing the assimilation of the xenocrysts, whereas rutile appears to be exclusively xenocrystic, remaining as the product of incomplete dissolution. In rocks from intermediate stages of evolution of the SMB, magmatic ilmenite and rutile are more abundant than xenocrystic ilmenite and rutile. In the most evolved rocks of the SMB, magmatic and xenocrystic ilmenite are absent from the mineral assemblage, probably through a combination of a peritectic reaction and dissolution, respectively, whereas most grains of rutile appear to be largely of magmatic origin, with some xenocrystic grains remaining after incomplete cation-exchange reactions.

Keywords: South Mountain Batholith, Nova Scotia, Meguma, xenolith, granite, ilmenite, rutile, texture, composition, dissolution, cation exchange.

Sommaire

Le batholite de South Mountain, situé dans le sud-ouest de la Nouvelle-Écosse, est un complexe granitique hyperalumineux comportant des évidences chimiques et physiques de contamination par les roches métasédimentaires du Groupe de Meguma. Certains grains d'ilménite dans le granite sont texturalement et chimiquement semblables aux grains d'ilménite dans les roches du groupe de Meguma, tandis que d'autres grains dans le granite semblent être texturalement (plus idiomorphes) et chimiquement (concentrations inférieures et moins variables en manganèse) uniques. Certains grains de rutile du granite sont texturalement et chimiquement semblables aux grains du granite semblent être texturalement (plus idiomorphes, possiblement remplissage de cavité) et chimiquement (contenu plus élevé de Nb + Ta, zonage compositionnel oscillatoire) uniques. Dans les roches les moins évoluées du SMB, l'ilménite est d'origine magmatique et aussi un xénocristal, avec assimilation des xénocristaux probablement par échanges cationiques, tandis que le rutile semble être exclusivement un xénocristal, avec dissolution incomplète des cristaux. Dans les roches les plus évoluées du SMB, l'ilménite magmatique et l'ilménite sous forme de xénocristaux sont absentes d'assemblage minéral, probablement à cause d'une réaction péritectique et de dissolution, respectivement, tandis que la plupart des grains de rutile semblen être d'origine magmatique, avec quelques xénocristaux restant suite à des échanges cationiques avortés.

Mots-clés: batholite de South Mountain, Nouvelle-Écosse, groupe de Meguma, xénolite, granite, ilménite, rutile, texture, composition, dissolution, échange de cations.

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INTRODUCTION

The ascent and emplacement of granitic magmas, by whatever mechanisms, probably involve some countryrock material crossing the contact into the magma. If so, the question becomes not *whether* a granitic rock is contaminated, but *to what extent* it is contaminated. Quantifying the extent of contamination is difficult because we can neither precisely know the composition of the contaminant, nor confidently know the composition of the uncontaminated granite. All we can know definitely is the composition of the contaminated granite, the mixture of the two unknowns.

The petrologically restricted (metapsammite, metapelite) rocks of the Cambro-Ordovician Meguma Group (Schenk 1997) form >90% of the perimeter of the late Devonian South Mountain Batholith (SMB). Considering the thickness of the Meguma Group (~10 km), these rocks probably form >>90% of the entire contact-surface of the batholith. Isotopic compositions (⁸⁷Sr/⁸⁶Sr, Clarke & Halliday 1980; ENd, Clarke et al. 1988; δ^{34} S, Poulson *et al.* 1991) show that the Meguma Group is not the source of the granitic magma, but whole-rock major-element compositions (Clarke et al. 2004) and Sr-Nd isotopic compositions (Clarke et al. 1988) provide chemical evidence that the parental magma for the SMB did undergo contamination with material from the enveloping Meguma Group. The lithological monotony of the country rocks places tight constraints on the mineralogy of the contaminant, but the overlap in the mineral assemblage between the country rocks and the batholith is nearly complete. The principal silicate (quartz, K-feldspar, plagioclase, biotite, cordierite, andalusite, muscovite, zircon), phosphate (apatite, monazite), sulfide (pyrite, pyrrhotite, chalcopyrite), and oxide minerals (ilmenite, rutile) of the granite also occur in the country rocks. Only the mineral textures and compositions can differ between the magmatic and metamorphic environments, but can the country-rock phases, in particular ilmenite and rutile, retain their distinctive textures or compositions in the granitic magma and still be recognizable as xenocrysts? Successful recognition of such xenocrysts would permit estimation of the amount of contamination; therefore, every oxide grain in the granitic samples needs careful scrutiny to texturally and chemically determine its origin as cognate or foreign. This paper is part of a broad program looking at all phases present in the SMB granitic rocks, including silicates and phosphates (Erdmann 2006), and sulfides (Samson & Clarke 2005).

Any given peraluminous granite may contain several genetic types of ilmenite and rutile, including: primary magmatic (crystallized directly from the silicate melt), peritectic (generated in melt-forming reactions in xenoliths), xenocrystic (including detrital and metamorphic), and secondary subsolidus (including products of exsolution, hydrothermal alteration of biotite, or oxidation). We have restricted our investigation to those oxide grains in the granites that are clearly *not* the products of any secondary subsolidus reactions.

In this paper, we investigate only the textural and chemical characteristics of the oxide minerals in the Meguma contaminant, observe the changes in these minerals in transitional xenoliths derived from the Meguma country rocks, and search for their xenocrystic equivalents in the granitic rocks of the SMB. At least in part, both ilmenite and rutile survive as xenocrysts in the granitic magma.

Methods

Samples of the Meguma Group country rocks come from the collections of Douma (1988) and Hicks (1996). They generally represent rocks of greenschist facies outside the thermal aureoles of the granites. All the xenolith samples come from localities in the batholith close to the contact with the country rocks. All xenoliths are clearly Meguma in derivation and present evidence of contact metamorphism up to sillimanite grade. For the granitic rocks of the SMB, we used the same compositionally controlled sample set as Pelrine (2003) and Carruzzo et al. (2005). We selected samples to cover the range of chemical evolution of the batholith as determined by the Sr + Zr differentiation index (Clarke et al. 2004). The least-evolved rocks in the batholith have Sr + $Zr \approx 475$ ppm, and the most evolved rocks have Sr + Zr less than 20 ppm. We divided the range of Sr + Zrvariation into five bins of equal Sr + Zr range. Figure 1 shows the locations of all samples.

As in Carruzzo et al. (2005), we used standard petrographic techniques (transmitted and reflected light microscopy) to locate and observe oxide minerals grains and to identify coexisting silicate phases. We utilized electron-microprobe analysis to determine the compositions of the ilmenite and rutile grains. The Dalhousie Regional Electron Microprobe Laboratory utilizes a JEOL JXA-8200 with five wavelength-dispersion spectrometers (WDS) (1.5 kV, 15 nA, 1 µm beam diameter, and 20-40-second counting times) to produce quantitative chemical analyses. We used synthetic standards: rutile for Ti, magnetite for Fe, Nb₂CoO₆ for Nb, Ta_2O_5 for Ta, and MnO_2 for Mn. In addition, we used semiquantitative energy-dispersive spectrometry (EDS) to obtain element-distribution maps and to identify the inclusions in the oxide phases.

RESULTS

Textures of ilmenite

Figure 2 shows the main textural types of ilmenite in the Meguma Group country rocks. We recognize three principal types: a variety characterized by abundant inclusions (Ilm M1), a variety with complex intergrowths with rutile (Ilm M2), and a variety with a



FIG. 1. Sample location map. Most Meguma country-rock samples are remote from the South Mountain Batholith (SMB). All Meguma xenolith samples are from close to the contact. Locations of South Mountain Batholith granite samples are chemically controlled.

"fingerprint" texture (Ilm M3). Ilmenite with textures morphologically similar to Ilm M1 and Ilm M2 also occur in the xenoliths and granite, but Ilm M3 appears to have no equivalents in the xenoliths or granites. A distinct, euhedral, inclusion-free textural type of ilmenite occurs in the xenoliths (Ilm X4) and granite (Ilm S4).

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS OF ILMENITE GRAINS IN THE COUNTRY ROCKS (M), XENOLITHS (X), AND GRANITES (S), SOUTH MOUNTAIN BATHOLITH, NOVA SCOTIA

Text. Sample	Ilm M1 -D-048 -1	Ilm M2 29e /6	Ilm M3 11D-D -079 -4	Ilm X1 E465A -2	Ilm X2 E437 -9	Ilm X4 E430W -3	Ilm S1 A11 -2286 -8	Ilm S2 D05 -0016 -2	Ilm S4 A11 -3002 -5
TiO	53.41	52.65	53.42	53.07	53.25	53.49	54.74	53.90	53.00
Nb ₂ O ₅	0.05	0.09	0.37	0.02	0.07	0.04	0.13	0.12	0.11
Ta ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
FeO	38.34	25.06	42.98	41.23	41.71	42.03	43.10	22.28	42.96
MnO	8.54	22.63	3.62	5.61	4.50	4.91	4.53	24.07	3.54
Total	100.34	100.44	100.39	99.93	99.52	100.48	102.51	100.38	99.66

Compositions are reported in wt.%.

Compositions of ilmenite

Table 1 contains some representative results of analyses of ilmenite. Ilmenite grains from the Meguma country rocks, xenoliths and SMB have approximately the same Mn compositional range (0 to 20 wt.%) (Fig. 3). All three populations show that relatively few grains have compositions in the range of 12 to 16 wt.% Mn. Many ilmenite grains show no chemical zoning, and others have a rim that is Mn-rich (maximum 2.5 wt.% MnO, average <0.5 wt.% MnO), greater than the core.The minor-element concentrations (Zr, Hf, Nb, Ta, Sn, W, U, Th, Zn, Y) in ilmenite grains are, for the most part, below detection limits for the analytical method used.

Textures of rutile

Figure 4 illustrates the four principal textures of rutile in the Meguma Group country rocks: an anhedral to subhedral poikilitic variety (Rt M1), a variety in complex intergrowth with ilmenite (Rt M2 is equivalent to Ilm M2), an anhedral variety with a distinctive "fingerprint" texture (Rt M3), and a blocky, subhedral, inclusion-poor (Rt M4) represented by a single grain

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in sample 11E–D–188. Textural type Rt M1 does not appear to have an equivalent in the xenoliths, but may be represented by Rt S1 in the granites. The Rt M2 and Rt M3 varieties appear to have textural equivalents in the xenoliths (Rt X2 and Rt X3) and the granites (Rt S2 and Rt S3), respectively. Although texturally similar in shape and types of inclusions, Rt M4 is probably not related to the distinctive oscillatory zoned Rt S4, or to the cavity-fill(?) Rt S5, in the granites.

Compositions of rutile

Table 2 contains some representative results of analyses of rutile grains. Figure 5 illustrates the compositional variation in rutile in the Meguma country rocks,

the xenoliths, and the granites. All Meguma country rocks and xenoliths have rutile compositions with (Nb + Ta) concentrations less than 0.6 wt.% that trend toward increasing (Fe + Mn) values. The rutile grains in granites have compositions that overlap significantly with those from the country rocks and xenoliths, but they trend toward much higher concentrations of (Nb + Ta).

DISCUSSION

Textures of ilmenite

Given that the purpose of this investigation is to search for oxide xenocrysts in the SMB, a comprehen-

Textural Features	anhedral to subhedral poikilitic with round inclusions	anhedral elongate poikilitic grains complexly intergrown with rutile	anhedral to subhedral poikilitic with fingerprint/net texture and oriented inclusions	subhedral to euhedral inclusion-poor or inclusion- free
Meguma	Im M1 abundant 275 μm Sample 11D-D-048 Inclusions: Qtz, Pl, Cal, Kfs or Ms	JTEL CAP 15.40 and 15.40 June 10.10 Ilm M2 rare 250 µm Sample 109D Inclusions: Qtz, Pl, Cal, Ap	RECEIPTION TO A REPORT OF THE	N/A
Xenoliths	LEU LOF 15.00 200 200 200 200 200 200 200 200 200	JOL COF 15.40 LLOB JAN ROLLAN Ilm X2 rare 310 µm Sample E437 Inclusions: Qtz, Cal	N/A	JID. CHP 15.40 st.800 18-BG1tes Ilm X4 common 110 µm Sample E430W
SMB	LEL CHE 15.00 cm 3 the Felice Ilm S1 rare 350 μm Sample A11-2286 Bin 2 Inclusions: Qtz, Bt, Kfs or Ms	Tot core 15.80 and 100 Ferture Ilm S2 rare 150 μm Sample D05-0016 Bin 3 Inclusions: Qtz	N/A	JER. COM 15.40 +199 TRAN ROLLOW Ilm S4 abundant 300 µm Sample A14-0007 Bin 3

FIG. 2. Textures of ilmenite grains in country rocks of the Meguma Group, in xenoliths of the Meguma Group in the SMB, and in the granitoid rocks of the South Mountain Batholith.

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FIG. 3. Ilmenite compositions in the Meguma country rocks, xenoliths, and granitic rocks of the South Mountain Batholith. The range of ilmenite compositions is similar in all three populations.

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Textural Features	anhedral to subhedral poikilitic with subround inclusions	anhedral elongate poikilitic grains complexly intergrown with ilmenite	anhedral to subhedral poikilitic with fingerprint/net texture and oriented inclusions	anhedral to euhedral, inclusion-free, oscillatory zoned (S4) or cavity fill (S5)
Meguma	Het (49-95-80' st.20) Ter feiter Rt M1 abundant 220 μm Sample 109D Inclusions: Qtz, Kfs or Ms	Rt M2 abundant 250 µm Sample 109D Inclusions: Qtz, Pl, Cal, Ap	TCL COP 15.6V (CE 16.4 CG) TCL COP 15.6V (CE 16.4 CG) TR M3 abundant 400 μm Sample 11D-D-079 Inclusions: Qtz, Pl, Kfs or Ms, Bt, Chl, Cal	Rt M4 rare 45 μm Sample 11E-D-188
Xenoliths	N/A	Rt X2 rare 310 µm Sample E436G Inclusions: Rt Cal	ADD. COPE 15.6W state TRANSITISM Rt X3 rare 400 μm Sample E433C Inclusions: Otz Chl. Cal	N/A
SMB	Rt SI rare 390 µm Sample D12-0099 Bin 2	All Constant 2.3 Can All Constant 2.3 Can	Rt S3 rare 280 µm Sample A15-0075 Bin 4 Inclusions: Qtz, Bt	At S4 abundant 100 μm Sample A16-1256 Bin 5

FIG. 4. Textures of rutile grains in country rocks of the Meguma Group, in xenoliths of the Meguma Group in the SMB, and in the granitoid rocks of the South Mountain Batholith.

sive textural classification of ilmenite in the country rocks is necessary. The problem then becomes one of recognizing those textural types, or their modified versions, in the granite. Figure 2 illustrates the three principal types of ilmenite in the Meguma country rocks. Within the contact aureole of the batholith, an ilmenite-forming reaction, perhaps $Chl + Rt \rightarrow Bt + Ilm$, may go to completion, so that Ilm M1 and Ilm M2 may

simply represent different stages of this reaction. Xenoliths of the Meguma Group rocks contain three textural types of ilmenite: Ilm X1 is morphologically similar to Ilm M1, Ilm X2 is morphologically similar to Ilm M2, and Ilm X4 appears to be new and, judging from the euhedral shape, it may be related to the formation of partial melt in the xenoliths (either primary magmatic, or peritectic, related to the incongruent melting of titaniferous biotite). The granitic rocks of the SMB contain many textural varieties of ilmenite, two of which may be derived from the country rocks: Ilm S1 with its rounded inclusions is morphologically similar to Ilm M1, and Ilm S2 with its associated rutile is similar to Ilm M2. Otherwise, the most strongly euhedral grains are the ones most likely to be primary magmatic in origin.

Compositions of ilmenite

Ilmenite grains from the Meguma country rocks, Meguma xenoliths, and SMB have approximately the same compositional range, from 0 to 20% Mn (Fig. 3). Clearly, with this high degree of overlap, the Fe and Mn contents cannot serve as a discriminant for the origin of ilmenite in the granites. Significantly, however, the Fe + Mn content of the ilmenite appears to be independent of the stage of chemical evolution of the SMB. Figures 6a and 6c show that considerable variation in MnO and MnO/(MnO + FeO) occurs among ilmenite grains within single samples of granite (columns of points at constant Sr + Zr). Most of this variation comes from separate grains in single samples, rather than from zoning within single grains. The erratic compositional variation of ilmenite as a function of whole-rock differentiation index (Sr + Zr) is in sharp contrast to the systematically decreasing MnO content, and systematically increasing MnO/(MnO + FeO) in the whole-rock compositions (Figs. 6b, d). Thus, although the MnO/(MnO + FeO) of the whole rocks increases systematically throughout the batholith, the composition of the ilmenite does not. Furthermore, the wide range of ilmenite compositions in a single rock indicates disequilibrium with the granitic melt.

Four possible explanations might account for the erratic compositional variation of ilmenite in single samples, and across the differentiation spectrum of the SMB. (i) If $f(O_2)$ increases in the late stages of crystal-

lization (Wang et al. 2001), the amount of ferrous iron available may decrease by oxidation to ferric iron, and then Mn²⁺ could substitute for the depleted Fe²⁺ in the melt to maintain ilmenite crystallization. (ii) The partition coefficients for Mn and Fe vary significantly as a function of falling temperature or increasing H2O content of the magma, giving rise to a wide range of ilmenite compositions in the very latest stages of crystallization of the interstitial melt. (iii) The partition coefficients for Mn and Fe do not vary significantly in the latter stages of crystallization, and the increase in Mn is a normal function of nucleation and crystallization at the very last stages of fractional crystallization. (iv) The granite contains an array of ilmenite compositions similar to that in the country rocks because the ilmenite grains in granite are mainly xenocrysts (in combination with primary magmatic grains) randomly derived from the Meguma Group.

All four of these explanations are possible, but the first one is unlikely because we avoided sampling rocks that show any obvious signs of oxidation. Also, although no data exist for partitioning of Fe and Mn between silicate melt and ilmenite as a function of temperature, other systems do not exhibit strong dependences on temperature, and so, the second explanation is similarly unlikely. If the ilmenite grains appeared late in the magmatic crystallization sequence and were unable to communicate with each other to achieve chemical equilibrium, the third explanation could potentially account for the variability in ilmenite composition in a single rock. Indeed, the higher MnO content of the rim of some ilmenite grains is consistent with formation at the last stages of fractional crystallization. The fourth explanation can elegantly account for the coincidence of ilmenite compositions in country rock and granite. If correct, some of the xenocrysts may have recrystallized or annealed somewhat, but probably have undergone little overall compositional change. If true, the presence

 TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF RUTILE GRAINS IN THE COUNTRY ROCKS (M),

 XENOLITHS (X), AND GRANITES (S), SOUTH MOUNTAIN BATHOLITH, NOVA SCOTIA

Texture Sample	Rt M1 105d-1 -1	Rt M2 109d-1 -1	Rt M3 128-4 -4	Rt M4 11E-D -188-1	Rt X2 E436G -18	Rt X3 E433C -5	Rt S1 D12-099 -1	Rt S2 D12-3072 -12	Rt S3 A15-0075 -2	Rt S4 A16-1256 -3	Rt S5 D12-0042 -7
	-	·	•				^ 				
TiO ₂ wt.%	98.58	98.05	100.40	98.17	99.88	98.07	97.02	100.16	97.89	98.64	97.92
Nb ₂ O ₅	0.19	0.06	0.17	0.36	0.28	0.45	0.98	0.41	0.63	0.00	0.52
Ta ₂ O ₅	0.01	0.00	0.00	0.14	0.00	0.00	0.14	0.09	0.11	0.00	0.12
FeO	0.33	0.56	0.59	0.28	0.42	1.23	0.42	0.19	1.25	0.01	0.19
MnO	0.04	0.07	0.21	0.00	0.02	0.04	0.05	0.00	0.00	0.00	0.01
MgO	0.01	0.01	0.00	0.02	0.00	0.00	0.03	0.01	0.01	1.41	0.03
Y ₂ O ₃	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.73	0.00
ZrO_2	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.18	98.75	101.38	99.24	100.63	99.79	98.64	100.86	99.89	100.79	98.79



FIG. 5. Rutile compositions in the Meguma country rocks, Meguma xenoliths, and South Mountain Batholith. High Nb + Ta concentrations characterize some, but not all, rutile grains in the granitic rocks.

of significant amounts of xenocrystic ilmenite in granitic rocks has implications for the origin of ilmenite-series granites (Ishihara 1977, 2004). This classification of granites, based on the amount of Fe–Ti oxides and the ratio of magnetite to ilmenite, might say more about contamination effects than source properties.

In contrast, the most strongly euhedral, most "magmatic looking" grains of ilmenite (euhedral, no inclusions, no intergrowths with rutile) in each bin (the grain in Bin 2 is anomalous) show a much lower and more regular increase in MnO and Mn/(Mn + Fe) with chemical evolution of the batholith (Fig. 7), consistent with their origin as grains that crystallized from, and in equilibrium with, the silicate melt. For instance, Sasaki *et al.* (2003) related such regular increase in the MnO content of ilmenite to differentiation in the Tono pluton in Japan.

Textures of rutile

Again, given that the purpose of this investigation is to search for oxide xenocrysts in the SMB, a comprehensive textural classification of rutile in the country rocks is also necessary. Then the problem becomes one of being able to recognize those textural types, or the modified versions of those textural types, in the granite. Figure 4 illustrates the four principal types of rutile in the Meguma country rocks. Within the contact aureole of the batholith, the ilmenite-forming reaction may in some cases go to completion, so that rutile disappears from the country-rock assemblage and is therefore not available as a xenocryst. The most common type of rutile in the country rocks, Rt M1, does not occur in the xenoliths we examined. Two of the other types of rutile in the country rocks are distinctive for their association with ilmenite (Rt M2), and for their "fingerprint" texture (Rt M3).

Type Rt M4 is a unique single grain. Figure 4 shows that in the xenoliths, Rt X2 with its association with ilmenite is similar to Rt M2, and that Rt X3 with its "fingerprint" texture is similar to Rt M3. The granitic rocks of the SMB contain many textural varieties of rutile, three of which arguably may be derived from the country rocks: Rt S1 may be a recrystallized version of Rt M1, Rt S2 shows the same association with ilmenite

TABLE 3. DETERMINATION OF THE ASSIMILATION REACTION OPERATING AT EACH STAGE IN THE CHEMICAL EVOLUTION OF THE SOUTH MOUNTAIN BATHOLITH

Granite-evolution stage	Ilmenite xenocryst	Rutile xenocryst
Bin 1	cation exchange	dissolution
Bin 2	cation exchange	dissolution
Bin 3	cation exchange	cation exchange
Bin 4	cation exchange	cation exchange
Bin 5 and pegmatites	dissolution	cation exchange

as does Rt M2, and Rt S3 has the same "fingerprint" texture as Rt M3. The granitic rocks also contain two distinct textural types of rutile, many grains of which show oscillatory zoning with respect to Nb and Ta concentration, thus that appear to be primary and magmatic (Rt S4), or grains that appear to have grown in late-stage cavities in the solidifying rock (Rt S5).

Compositions of rutile

Carruzzo et al. (2005) suggested that the SMB magma was undersaturated with respect to rutile early in its differentiation history, and achieved saturation only in Bins 3-5 of the middle and later stages of chemical evolution. Thus, except for one highly anomalous sample (D13-2095) in Bin 1, magmatic rutile is absent from the most primitive bins (1 and 2) of the SMB; only xenocrystic rutile occurs in these early-stage rocks. Otherwise, virtually all the compositional points in Figure 5c are from Bins 3–5 and late pegmatites. Rutile compositions from the country rocks and xenoliths have concentrations of (Nb + Ta) lower than 0.6 wt.%. The dashed black line on Figure 5 separates rutile of magmatic origin (right side) from rutile of indeterminate xenocrystic or magmatic origin (left side). Thus, chemical compositions can serve to identify some grains of magmatic rutile (or possibly xenocrysts that have reequilibrated), but cannot assist in identifying xenocrysts with any degree of confidence.

Contamination of the South Mountain Batholith according to the oxide minerals

Pelrine (2003) demonstrated that ilmenite became saturated in the granitic magma from its earliest stage (Bin 1) to at least its penultimate stage (Bin 4). Carruzzo *et al.* (2005) showed that primary magmatic rutile did not begin to crystallize from the SMB magma until Bin 3, and then continued to crystallize until the latest pegmatites. We use the flowchart of Clarke (2007) to determine the likely reaction that such oxide mineral contaminants entering the SMB magma would undergo (Table 3).

Thus, throughout most of the crystallization history of the SMB, ilmenite xenocrysts must have undergone Fe \rightleftharpoons Mn cation-exchange reactions in order to achieve chemical equilibrium with the silicate melt and its grains of primary magmatic ilmenite. Given the wide range of Fe–Mn contents of ilmenite in the country rocks and the granites (Figs. 3, 6), the wide range of ilmenite compositions in a single sample of granite, and the lack of correlation between ilmenite Fe/Mn and whole-rock Fe/Mn, we deduce that, if many of the ilmenite grains are xenocrysts, this cationexchange reaction must be sluggish. This finding needs to be reconciled with the crystal structure and specific processes of Fe \rightleftharpoons Mn exchange in ilmenite (Wilson *et al.* 2004), but the apparent failure to equilibrate is in



FIG. 6. Ilmenite compositions in the SMB as a function of chemical evolution of the batholith. The erratic variation in ilmenite compositions as a function of differentiation in the SMB is in contrast to the systematic variation in whole-rock compositions.

contrast to subsolidus exchange-reaction experiments between garnet and ilmenite (Feenstra & Engi 1998), in which the ilmenite attained chemical equilibrium.

Two factors mitigate against any occurrence of xenocrystic rutile in the early stages of the SMB. First, the ilmenite-forming reaction in the metamorphic aureole eliminates much of the country-rock rutile before it reaches the granitic magma (R + M1 is entirely absent in the xenoliths we investigated), and second, any rutile that does become a xenocryst is undersaturated in the early SMB magma and should undergo a dissolution-assimilation reaction. Nevertheless, rutile does occur in the earliest stage (Bin 1) of evolution of the SMB, and we can recognize its xenocrystic character only by its texture and not its composition. As an example, both oxide phases in the Rt S2 ilmenite-rutile grain in Sample D12-3072 (Fig. 4) in Bin 3 should undergo cation-exchange reactions in an attempt to reach equilibrium with the primary magmatic grains of ilmenite and rutile. As previously mentioned, the Fe \rightleftharpoons Mn exchange reaction may be sluggish in ilmenite, but likewise the $4(Nb + Ta) + \Box \rightleftharpoons 5Ti$ reaction in rutile may be slow.

The partition coefficients of Mn and Fe between the two main Fe–Mn–Mg minerals of the granite, biotite and ilmenite, should vary systematically throughout the batholith. Theoretically, at least, only one ilmenite composition can be in equilibrium with the biotite, and only one rutile composition can be in equilibrium with the melt, so that all the others may be xenocrysts. Provided that all the biotite grains are magmatic, any misaligned tie-lines between coexisting biotite and ilmenite would help to identify the ilmenite grains that are xenocrystic.

CONCLUSIONS

Many chemical and mineralogical parameters shed light on the contamination story for the SMB, including major elements (Clarke *et al.* 2004), Sr–Nd isotopic ratios (Clarke *et al.* 1988), cordierite (Erdmann *et al.* 2004), and sulfides (Samson & Clarke 2005). In this paper, we examine the oxide minerals for the information they may carry about the extent of contamination.

1. Texturally, we can identify some ilmenite and rutile grains in the SMB that are xenocrystic in origin. In particular, the distinctive grains of inclusion-rich ilmenite, the rutile–ilmenite intergrowths, and the "fingerprint"-textured rutile appear to be foreign constituents in the granite. The simplest explanation for the textural similarity of ilmenite and rutile in the granite and country rocks is that the grains in the granite are country-rock xenocrysts.



FIG. 7. Primary compositions of magmatic ilmenite. The ilmenite grains that appear to be magmatic (euhedral shapes, no inclusions, no intergrowths with rutile) generally show systematic increases in MnO and MnO/(MnO + FeO) with differentiation.

2. Chemically, the systematic variation of MnO and MnO/(MnO + FeO) in the whole rocks of the batholith, but the erratic variation of these parameters in the suite of ilmenite, suggests that the ilmenite grains are not equilibrated and may, therefore, be xenocrysts. Rutile grains with high (Nb + Ta) are identifiable as primary and magmatic, but no distinctive chemical parameter characterizes the country-rock grains.

3. The process of dissolution appears to be a more effective assimilation-reaction than cation exchange for ilmenite xenocrysts in late-stage granitic magmas (Bin 5), whereas the opposite is true for ilmenite xenocrysts in earlier-stage magmas (Bins 1–4). Alternatively, Bin 5 rocks received no contaminants, but Sr–Nd isotopic evidence suggests otherwise.

4. For rutile, texturally xenocrystic grains are recognizable in Bin 1, and chemically xenocrystic grains with low (Nb + Ta) are recognizable in Bins 3–5; thus neither form of assimilation (dissolution in Bin 1, or cation exchange in Bins 3–5) seems to work very efficiently for this oxide phase. Dissolution of xenocrystic rutile in Bin 2 appears to have been effective.

5. Given that texturally identifiable ilmenite and rutile xenocrysts occur in the SMB, a *minimum* quantitative estimate of the amount of contamination in the SMB now requires knowledge of the proportion of *surviving* xenocrystic ilmenite or rutile relative to magmatic ilmenite or rutile (*i.e.*, total ilmenite or rutile minus magmatic ilmenite or rutile).

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References

- CARRUZZO, S., CLARKE, D.B., PELRINE, K.M. & MACDONALD, M.A. (2006): Texture, composition, and origin of rutile in the South Mountain Batholith, Nova Scotia. *Can. Mineral.* 44, 715-729.
- CLARKE, D.B. (2007): Assimilation of xenocrysts in granitic magmas: principles, processes, proxies, and problems. *Can. Mineral.* 45, 5-30.
- CLARKE, D.B. & HALLIDAY, A.N. (1980): Strontium isotope geology of the South Mountain Batholith, Nova Scotia. *Geochim. Cosmochim. Acta* 44, 1045-1058.
- CLARKE, D.B., HALLIDAY, A.N. & HAMILTON, P.J. (1988): Neodymium and strontium isotopic constraints on the origin of the peraluminous granitoids of the South Mountain Batholith, Nova Scotia. *Chem. Geol.* **73**, 15-24.
- CLARKE, D.B., MACDONALD, M.A. & ERDMANN, S. (2004): Chemical variation in Al₂O₃-CaO-Na₂O-K₂O space: controls on the peraluminosity of the South Mountain Batholith. *Can. J. Earth Sci.* **41**, 785-798.
- DOUMA, S.L. (1988): Preliminary report on the metamorphic history of the Meguma Group metasediments in eastern Nova Scotia: regional and contact metamorphism. *Nova Scotia Dep. Nat. Resources, Rep.* ME 1988-1.
- ERDMANN, S. (2006): Country-Rock Contamination in the South Mountain Batholith. Ph.D. thesis, Dalhousie Univ., Halifax, Nova Scotia.
- ERDMANN, S., CLARKE, D.B. & MACDONALD, M.A. (2004): Origin of chemically zoned and unzoned cordierites from the South Mountain and Musquodoboit Batholiths, Nova Scotia. *Trans. Roy. Soc. Edinb.: Earth Sci.* **95**, 99-110.

- FEENSTRA, A. & ENGI, M. (1998): An experimental study of the Fe–Mn exchange between garnet and ilmenite. *Contrib. Mineral. Petrol.* 131, 379-392.
- HICKS, R.J. (1996): Low-Grade Metamorphism in the Meguma Group, Southern Nova Scotia. M.Sc. thesis, Dalhousie Univ., Halifax, Nova Scotia.
- ISHIHARA, S. (1977) The magnetite-series and ilmenite-series granitic rocks. *Mining Geol.* 27, 293-305.
- ISHIHARA, S. (2004): The redox state of granitoids relative to tectonic setting and earth history: the magnetite–ilmenite series 30 years later. *Trans. Roy. Soc. Edinb.: Earth Sci.* 95, 23-33.
- PELRINE, K.M. (2003): Ilmenite–Pyrophanite and Niobian Rutile in the South Mountain Batholith, Nova Scotia. B.Sc. Honours thesis, Dalhousie Univ., Halifax, Nova Scotia.
- POULSON, S.R., KUBILIUS, W.P. & OHMOTO, H. (1991): Geochemical behavior of sulfur in granitoids during intrusion of the South Mountain Batholith, Nova Scotia, Canada. *Geochim. Cosmochim. Acta* 55, 3809-3830.
- SAMSON, H.R. & CLARKE, D.B. (2005): Assimilation of country-rock sulphide minerals in the South Mountain Batholith, Nova Scotia, Canada. Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr. 30, 170.
- SASAKI, K., NAKASHIMA, K. & KANISAWA, S. (2003): Pyrophanite and high Mn ilmenite discovered in the Cretaceous Tono pluton, NE Japan. *Neues Jahrb. Mineral.*, *Monatsh.*, 302-320.
- SCHENK, P.E. (1997): Sequence stratigraphy and provenance on Gondwana's margin; the Meguma Zone (Cambrian to Devonian) of Nova Scotia, Canada. *Geol. Soc. Am., Bull.* 109, 395-409.
- WANG, RU-CHENG, WANG, D.-Z., ZHAO, G.-T., LU, J.-J., CHEN, X.-M. & XU, S.-J. (2001): Accessory mineral record of magma–fluid interaction in the Laoshan I- and A-type granitic complex, eastern China. *Phys. Chem. Earth* (A) 26, 835-849.
- WILSON, N.C., MUSCAT, J., MKHONTO, D., NGOEPE, P.E. & HARRISON, N.M. (2005): The structure and properties of ilmenite from first principles. *Phys. Rev.* B71, 075202-1 -075202-9.
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