



The Nature and Origin of the Rare Earth Element Mineralization in the Misery Syenitic Intrusion, Northern Quebec, Canada

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Abstract

The Misery syenitic intrusion in northern Quebec is host to a potentially important, recently discovered rare earth element (REE)-Zr-Nb prospect, containing significant concentrations of both light and heavy REEs, and is conspicuous on aeromagnetic maps as a well-defined, ring-shaped anomaly. Felsic syenite composed of idiomorphic perthite with interstitial mafic minerals, comprising fayalite, hedenbergite, ferropargasite and annite dominates the exposed outer part of the intrusion (the core is covered by Misery Lake). This unit is accompanied by ferrosyenite containing up to 50 vol % mafic minerals, including cumulate fayalite. The ferrosyenite, which occurs as amoeboid-like inclusions in the felsic syenite, is interpreted to have formed by fractional crystallization of ferromagnesian minerals, leaving behind a residual magma which produced the felsic syenites. This latter magma was progressively enriched in alkalis and silica, and only became saturated in ferromagnesian minerals at a very late stage of crystallization. The bulk of the REE mineralization was initially concentrated in pods and layers of fluorapatite that accumulated as a result of gravitational settling. The fluorapatite crystals were partly or completely replaced by britholite-(Ce), which further enriched the rocks in LREEs. Locally, thin quartz-fayalite dikes cut the felsic syenite. These dikes contain up to 10 vol % fergusonite-(Y) and 8 vol % zircon, and are interpreted to be products of an immiscible FeO-SiO₂-rich magma into which Zr, Nb, and HREEs were preferentially fractionated from the conjugate felsic syenite magma.

Introduction

ALTHOUGH rare-earth element (REE)-bearing minerals have been identified previously in fayalite-bearing syenites (Platt and Woolley, 1986; Yang et al., 2005; Shellnutt and Zhou, 2008), they have not been found in concentrations sufficient for them to constitute economic deposits, and consequently the processes of REE concentration in these rocks have received little attention. Most of the known rare-earth deposits, e.g., Bayan Obo, China (Yang et al., 2009); Maoniping, China (Xie et al., 2009); Mountain Pass, United States (Castor, 2008); Mount Weld, Australia (Lottermoser, 1990); Strange Lake, Canada (Salvi and Williams-Jones, 1996; Gysi and Williams-Jones, 2013); and Nechalacho, Canada (Sheard et al., 2012) are hosted by or genetically related to carbonatites and agpaite to hyperagpaite intrusions. As a result, the causes for the unusual REE enrichment in peralkaline rocks and carbonatites have been investigated in numerous studies. Some of these deposits, e.g., the carbonatite-hosted Mountain Pass deposit, are interpreted to be magmatic (Castor, 2008); others, like Bayan Obo, are interpreted to be hydrothermal, albeit involving fluids of carbonatitic origin (Smith, 2000; Xu et al., 2008). Yet others, e.g., Strange Lake and Nechalacho, are interpreted to have formed by a combination of both magmatic and hydrothermal processes (Boily and Williams-Jones, 1994; Salvi and Williams-Jones, 1996; Sheard et al., 2012; Gysi and Williams-Jones, 2013).

In this paper, we focus on an important prospect in northern Quebec where potentially large concentrations of REEs are hosted by fayalite-bearing syenitic intrusions. Rare-metal

mineralization was first discovered in the Misery syenitic intrusion in 2007 by Quest Rare Minerals Ltd. This led to a surface sampling program over the exposed part of the intrusion (much of it is covered by Misery Lake) that returned total rare earth oxide (TREO) concentrations in channel samples of up to 7.33 wt % over 1 m, including up to 1.07 wt % heavy rare earth oxides (HREO). This sample also contains 664 ppm Zr and 34.95 ppm Nb. Subsequent drilling by Quest Rare Minerals Ltd. intersected up to 2.40 wt % TREO over 1.80 m and 0.78 wt % TREO over 41.13 m; the HREO proportions of TREO are 13.2 and 15.2%, respectively (drill hole ML12017). These intervals also contain 1,879 ppm Zr and 124 ppm Nb and 3,956 ppm Zr and 363 ppm Nb, respectively.

On the basis of its aeromagnetic signature, the intrusion is interpreted to be a ring complex, only the outer part of which is exposed. The Misery intrusion is unusual for its enrichment in iron, partly as fayalite that locally forms cumulates, and partly as magnetite-apatite cumulates. The rare metal mineralization is concentrated in syenites rich in apatite, sodically metasomatized coarse-grained syenite, and quartz-fayalite dikes. This study evaluates the role of magmatic and hydrothermal processes in concentrating the REEs and associated rare metals.

Geologic Setting

The Nain Plutonic Suite

The Misery intrusion was emplaced in the southeastern sector of the Mistastin batholith (Petrella, 2011), which is part of the Nain Plutonic Suite, a group of anorthosite-jotunitite-mangerite-charnockite-granite rocks, collectively referred to as AMCG complexes (Emslie et al., 1994). These complexes,

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which crop out over an area of ~19,000 km² (Hill, 1988), straddle a suture that marks the boundary between the Paleoproterozoic Churchill Province and the Archean Nain Province (Emslie et al., 1994; Peck et al., 2010; Fig. 1). This structure, known as the Torngat Orogen, resulted from a collision between the two provinces between 1860 and 1740 Ma (Wardle et al., 1990; Ryan, 2000). The Nain Plutonic Suite was emplaced ~400 m.y. after the orogeny and was not affected by later tectonism (Ryan, 1990). Three major rock groups make up the Nain Plutonic Suite (Emslie et al., 1994). The two main groups, which occur in roughly equal proportions, are the anorthositic and granitic suites; the third group, comprising the remaining 10% of the suite, consists of troctolite, olivine gabbro, gabbroiorite, ferrodiorite, and other ferromagnesian rocks. A study of Nd and Sr isotope compositions by Emslie et al. (1994), and a more recent oxygen isotope study by Peck et al. (2010) concluded that the anorthosite originated from the mantle, and was affected by a deep crustal contaminant from either the Churchill or Nain Province, depending on the location of the plutons. The granitoid rocks of the Nain Plutonic Suite have A-type affinity, manifested by a high content of potassium and a high $Fe_t/(Fe_t + Mg)$ ratio. They were interpreted by Emslie et al. (1994) to be the products of high degrees partial melting of crustal rocks with little contribution

from the mantle, as their Nd and Sr isotope compositions are similar to those of the lower crust. The granitic plutons in the Nain Plutonic Suite are remarkably similar in respect to their major- and trace-element compositions, despite their large areal distribution. Solidus temperatures are estimated to have ranged from about 750° to 800°C, the total pressure to have been 3.5 kbar, and the f_{O_2} to have been 1 to 3 log units below the FMQ buffer (Berg, 1977; Emslie and Stirling, 1993).

The Mistastin batholith

The Mistastin batholith was emplaced within the Churchill Paleoproterozoic Province, and is composed mainly of rapakivi granites. With a surface area of 5,000 km² (Hill, 1988), the Mistastin batholith is the largest granitic intrusion in the region. The dominant rock types are a pyroxene-, olivine-bearing granite and monzonite, which were cut by a younger biotite-, hornblende-bearing granite (Emslie and Stirling, 1993). Based on its age of 1420 Ma (Emslie and Stirling, 1993), the Mistastin batholith is one of the oldest intrusions in the Nain Plutonic Suite; most of the other intrusions were emplaced between 1350 and 1290 Ma (Ryan, 1990). The Mistastin batholith was subsequently intruded by other igneous bodies, including the Misery syenitic intrusion and the Harp Lake gabbroic dike swarm. A satellite pluton of the Mistastin

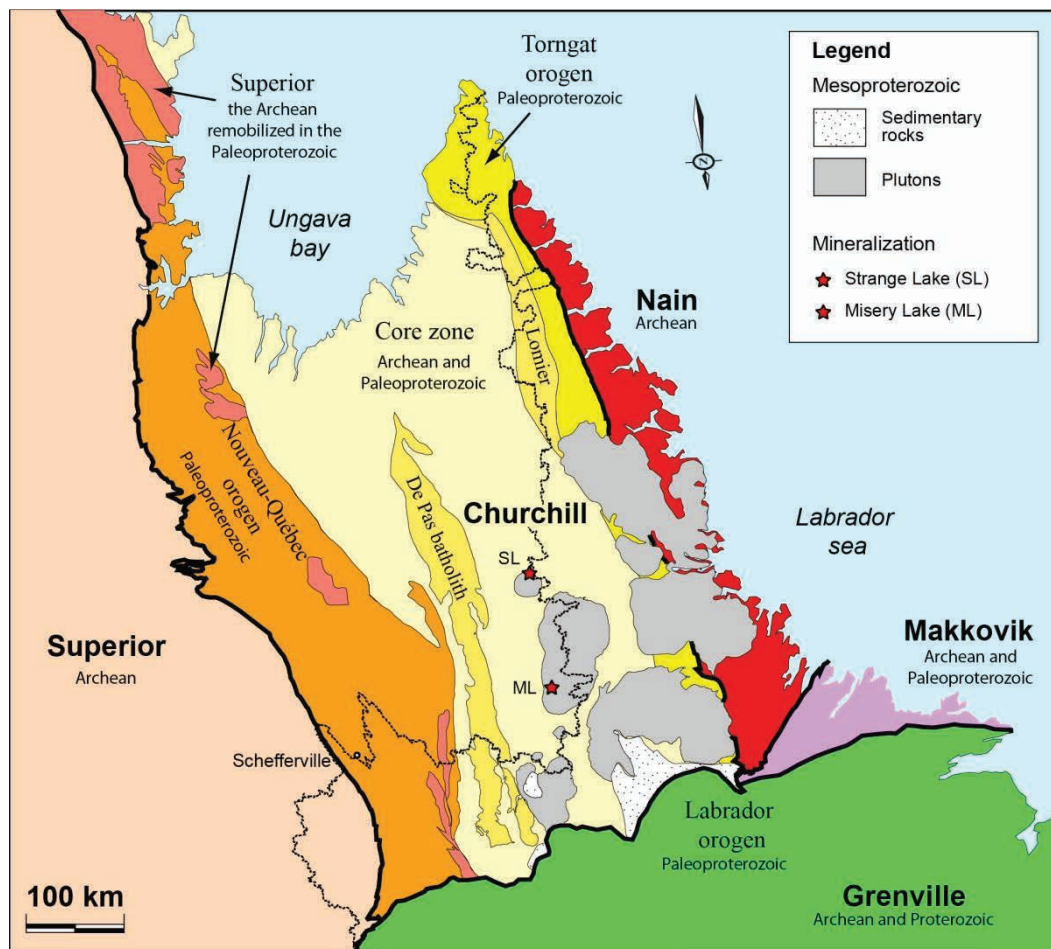


FIG. 1. Geologic map of the Churchill Province showing the location of the Misery syenitic intrusion prospect and the Strange Lake deposit (Hammouche et al., 2012).

batholith, the Napeu Kainiut quartz monzonite, was intruded by the Strange Lake peralkaline granite, which is the host to a large REE deposit, scheduled for exploitation in 2015. The Strange Lake granite has been dated at 1240 ± 2 Ma (Miller et al., 1997) and the Misery syenite at 1409.7 ± 1.2 Ma (David et al., 2012), based on radiometric determinations of U-Pb in zircon. The Harp Lake dikes have been dated at 1273 ± 1 Ma using radiometric determinations of U and Pb in baddeleyite (Cadman et al., 1993). Two ring-shaped intrusions that superficially bear similarities to the Misery intrusion, the Ramusio granite and the Juillet syenite were emplaced a few kilometres south of the Mistastin batholith (Fig. 2). They were thought to be contemporaneous with the Misery intrusion (Hammouche et al., 2012), but recently have been dated at 1481.7 ± 4.3 and 1479.7 ± 12.6 to -5.4 Ma, respectively, using U-Pb zircon geochronology (David et al., 2012).

The rocks immediately adjacent to the Misery intrusion comprise coarse-grained rapakivi granite and quartz monzonite. Both rock types are white to pale red in color, and contain large crystals of perthitic K-feldspar (up to 5 cm in length) mantled by a thin layer of plagioclase. Quartz forms

small, subrounded interstitial grains. There are also small proportions of ferromagnesian minerals (1–5 vol %), namely amphibole, minor fayalite and clinopyroxene, and trace proportions of apatite, fluorite and zircon. No obvious contact can be mapped between the rapakivi granite and the quartz monzonite. All that is observed is that the proportion of quartz decreases toward the Misery syenite.

The Misery Syenitic Intrusion

The Misery intrusion was discovered as a result of its expression as a very well defined, 6-km-wide, ring-shaped anomaly that is clearly observable on aeromagnetic maps (Dumont et al., 2010; Fig. 3). A geologic map of the Misery intrusion was prepared from mapping of outcrops during the summers of 2010 and 2011 and the logging of core drilled by Quest Rare Minerals Ltd. (Fig. 4). Unfortunately, the central part of the intrusion is not exposed because it is largely covered by Misery Lake and swamps. Away from the lake, the Misery rocks comprise two units. One of them is a ferrosyenite and the other comprises coarse-, medium-, and fine-grained felsic syenites; locally the coarse-grained syenite underwent sodic metasomatism in the form of albitization. Contacts with the host Mistastin granitoids are gradational and are marked by the disappearance of the plagioclase rim around alkali feldspar grains. The Misery syenites and the Mistastin granitoids were intruded by quartz-fayalite dikes, microgranite, and porphyritic quartz syenite dikes.

Ferrosyenite

In this paper, the term ferrosyenite refers to a dark gray-green (melanocratic), medium- to fine-grained syenite containing up to 50 vol % of ferromagnesian minerals. These minerals comprise idiomorphic yellow-green fayalite (~15 vol %), dark green hedenbergite (~15 vol %), black ferropargasite (~10 vol %), Ti-rich magnetite with ilmenite lamellae (~5 vol %), and annite (~5 vol %). All have compositions close to the iron endmembers of their respective solid-solution series. Idealized structural formulae for the minerals are listed in Table 1. Compositional data for them are reported in Tables 2 and 3. With the possible exception of ferropargasite and annite, the ferromagnesian minerals are primary. Fayalite, hedenbergite, and Ti-rich magnetite crystals all display idiomorphic shapes, and fayalite is usually rimmed by anhedral ferropargasite (Fig. 5A, B); the latter may be replaced by annite. The matrix between the ferromagnesian minerals is composed of micropertitic K-feldspar (Fig. 5A). Fayalite is commonly concentrated in cumulate layers which exhibit normal grading, i.e., the proportion of fayalite crystals decreases upward (Fig. 5B).

The ferrosyenite also contains 1 to 2 vol % primary idiomorphic zircon crystals, and fluorapatite. Two varieties of fluorapatite are observed, both comprising euhedral to subhedral crystals interpreted to be magmatic. However, the first variety (type 1) is unzoned, whereas the second variety (type 2) is strongly zoned, and the outer parts of its crystals usually have been replaced by britholite-(Ce) (Fig. 5C). To distinguish it from britholite-(Ce) discussed later, this variety is hereafter referred to as britholite-(Ce) 1. Both varieties of fluorapatite commonly occur as inclusions in pyroxene, amphibole, and less commonly fayalite, indicating that they started to crystallize early and continued to crystallize until a relatively late

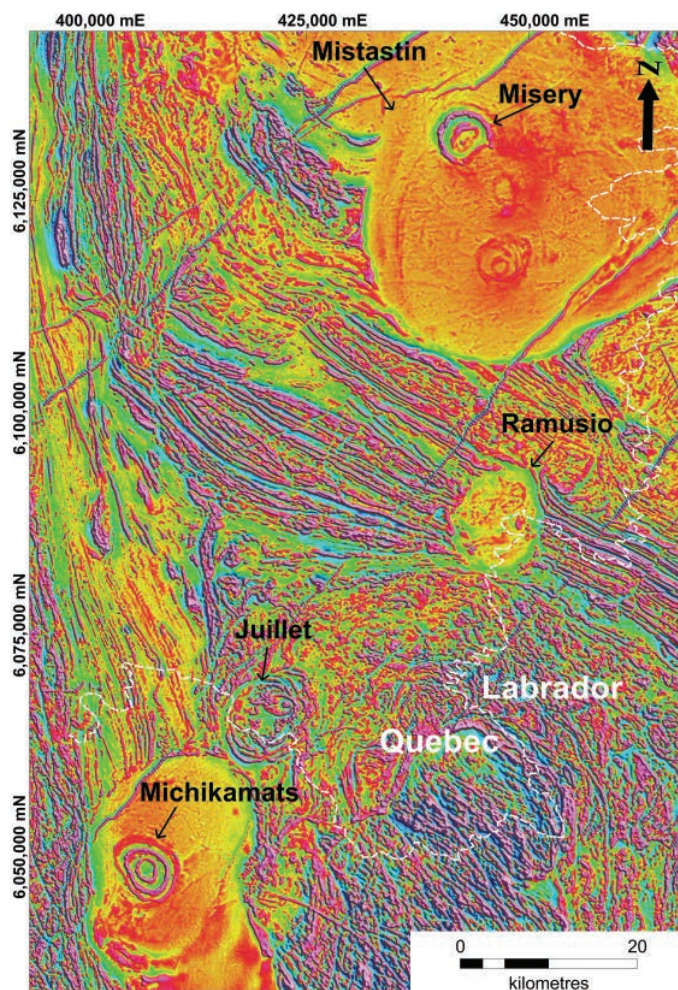


FIG. 2. A magnetic gradient map of the Churchill Province from Dumont et al. (2010). At least five intrusions can be seen on the map; Misery, Michikamats, and Juillet are syenites and Ramusio and Mistastin are granites (coordinates in NAD83, Zone20).

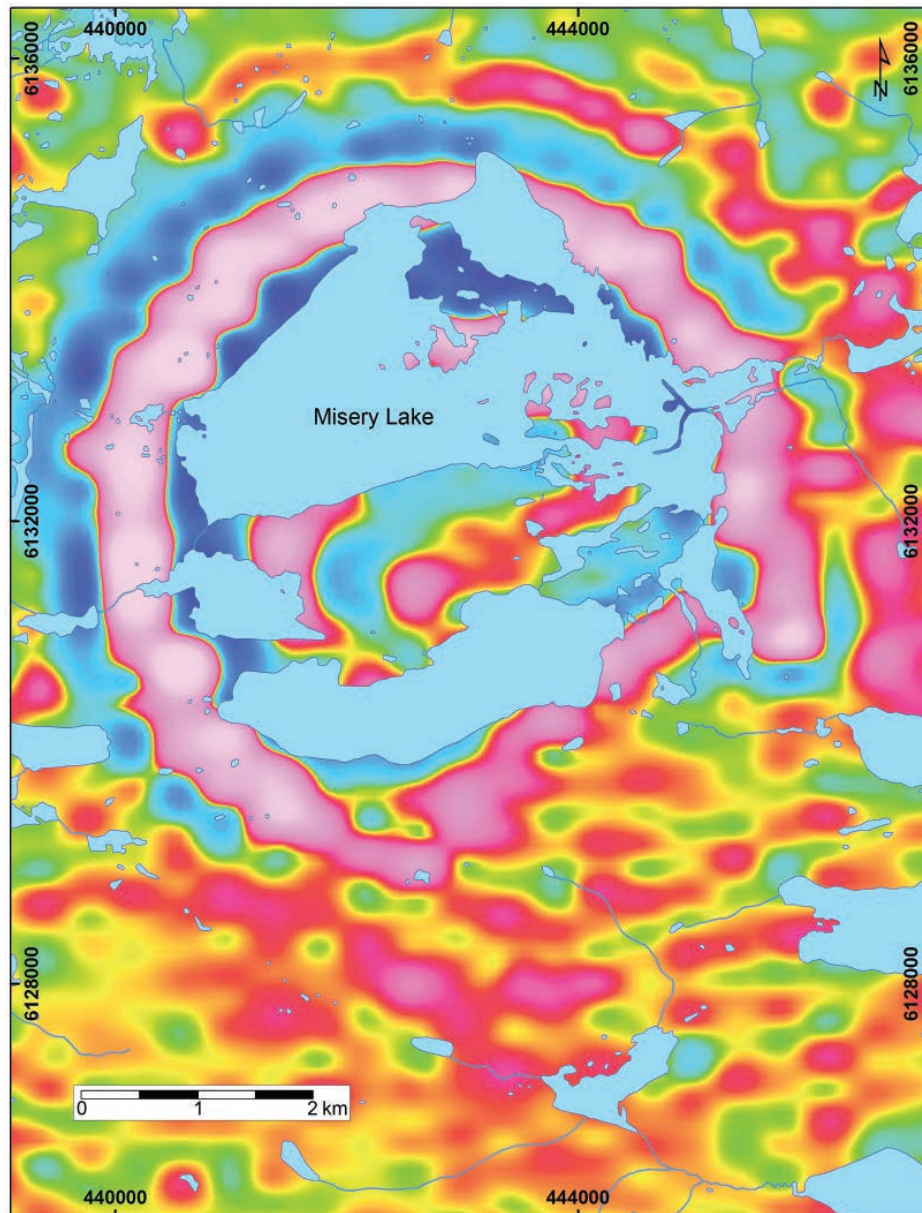


FIG. 3. First vertical derivative of the magnetic field of the Misery syenitic intrusion. Blue to yellow colors correspond to decreasingly negative nanoteslas per meter and yellow to pink colors to increasingly positive nanoteslas per meter. The pale blue areas are lakes.

stage. The composition of fluorapatite 1 is similar to the core of fluorapatite 2, suggesting that fluorapatite 2 continued to crystallize after fluorapatite 1.

Ferrosyenite is interpreted to be the earliest intrusive phase as it occurs as inclusions in the coarse-grained syenite (Fig. 5D), which range in length from several centimeters to several meters (Fig. 6). The inclusions have amoeboid shapes, which frequently display re-entrants, suggesting that they have been plastically deformed. Commonly, they are oriented perpendicular to the contact between the Misery syenitic intrusion and the host Mistastin batholith. The contacts between the inclusions and the coarse-grained syenite are very sharp and generally are marked by an enrichment in coarser-grained ferromagnesian minerals within the inclusions. The shapes of the

inclusions suggest that they represent partly crystallized mafic magma that mingled with felsic magma.

Felsic syenites

The coarse-, medium-, and fine-grained felsic syenites have similar mineral assemblages, and vary only in texture and grain size. They consist mainly of perthitic K-feldspar crystals with minor proportions of ferromagnesian minerals (~5%). The minerals are the same as those in the ferrosyenite, except that alkali feldspar was the first major phase to crystallize, whereas in the ferrosyenite, alkali feldspar is an interstitial phase (Fig. 7A). In this type of syenite, the ferromagnesian minerals are interstitial phases. Fayalite, hedenbergite, and Ti-rich magnetite are rimmed by ferropargasite (Fig. 7B). In

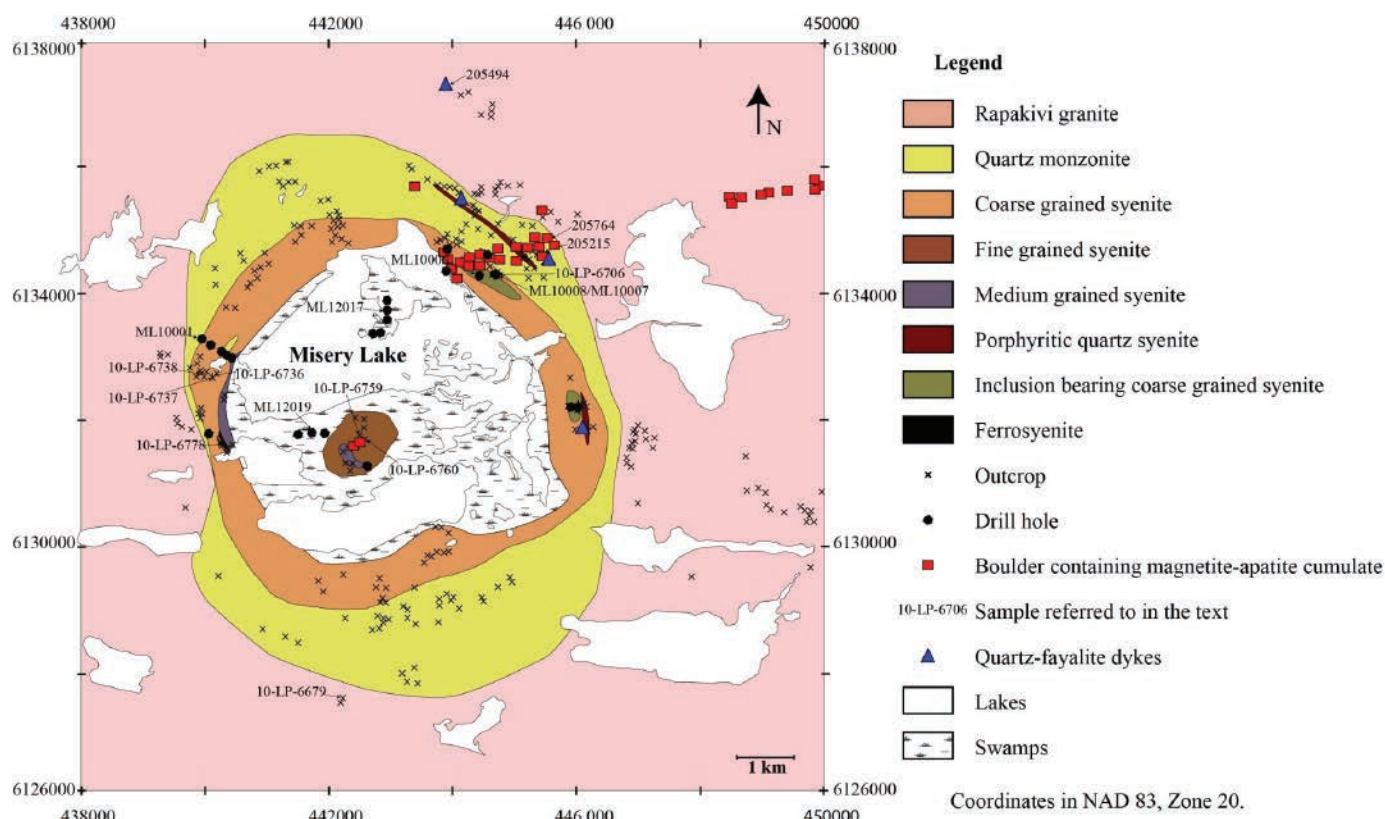


FIG. 4. Geologic map of the Misery syenitic intrusion.

a few samples that have higher alkali contents than normal, the amphibole is ferroedenite instead of ferropargasite (Table 3). The last major mineral to crystallize was annite, which locally replaced the ferropargasite. Quartz, zircon, fluorapatite 1, fluorite, columbite-(Fe), carbonate, and pyrite occur as accessory phases. The zircon crystals are zoned, usually have

an inherited core and may occur in thin (15 mm wide) layers interpreted to have formed by gravity settling or flow differentiation prior to crystallization of K-feldspar (Fig. 7C).

The coarse-grained syenite is characterized by centimetric crystals of ovoid perthite; ferromagnesian minerals fill the interstices between perthite crystals or occur in small clots

TABLE 1. List of Minerals Found in the Misery Syenitic Intrusion Together with Their Structural Formulae

Mineral	Formula	Mineral	Formula
<u>Silicates</u>		<u>Carbonates</u>	
Albite	Na(AlSi ₃ O ₈)	Bastnäsite-(Ce)	Ce(La,Ce)(CO ₃)F
Annite	KFe ₃ ²⁺ AlSi ₃ O ₁₀ (OH,F) ₂	Calcite	CaCO ₃
Arfvedsonite	Na ₂ (Fe ₄ ²⁺ Fe ³⁺)Si ₈ O ₂₂ (OH) ₂	Parisite-(Ce)	Ca(Ce,La) ₂ (CO ₃) ₂ F ₂
Astrophyllite	(K,Na) ₃ (Fe ²⁺ ,Mn) ₇ Ti ₂ Si ₈ O ₂₄ (O,OH) ₇	Synchysite-(Ce)	CaCe(CO ₃) ₂ F
Fayalite	Fe ₂ ²⁺ SiO ₄	<u>Sulfides</u>	
Ferropargasite	NaCa ₂ (Fe ₄ ²⁺ Al)Si ₆ Al ₂ O ₂₂ (OH) ₂	Chalcopyrite	CuFeS ₂
Hedenbergite	CaFe ²⁺ Si ₂ O ₆	Pyrite	FeS ₂
Microcline	K(AlSi ₃ O ₈)	Pyrrhotite	Fe _{1-x} S
Pyrochlore	(Na,Ca) ₂ Nb ₂ O ₆ (OH,F)	Sphalerite	ZnS
Quartz	SiO ₂	<u>Halide</u>	
Thorite	(Th,U)SiO ₄	Fluorite	CaF ₂
Willemite	ZnSiO ₄	<u>Oxides</u>	
Zircon	ZrSiO ₄	Magnetite	Fe ²⁺ Fe ³⁺ ₂ O ₄
<u>Phosphates</u>		Ilmenite	Fe ²⁺ TiO ₃
Fluorapatite	Ca ₅ (PO ₄) ₃ (OH,F)	Ti-rich magnetite	Fe(Fe,Ti) ₂ O ₄
Monazite	(Ce,La,Th)PO ₄	Fergusonite-(Y)	YNbO ₄
Britholite-(Ce)	Ca ₂ (Ce,Ca) ₃ (SiO ₄ ,PO ₄) ₃ (OH,F)	Columbite-(Fe)	Fe ²⁺ Nb ₂ O ₆

TABLE 2. Average Composition of Fayalite and Hedenbergite by Rock Type (FESY = ferrosyenite; FS = felsic syenite; Q-F = quartz-fayalite dikes) in the Misery Syenitic Intrusion

Mineral		Fayalite					Hedenbergite			
Rock type		FESY		FS		Q-F	FESY		FS	
Sample		10-Lp-673614 n = 6	ML10007- 30.8 n = 6	ML10001- 107 n = 8	ML10006- 46.15 n = 5	205494 n = 11	10-Lp-673614 n = 16	ML10007- 30.8 n = 1	ML10001- 107 n = 8	ML10006- 46.15 n = 13
SiO ₂	wt %	29.65	29.76	29.21	29.31	29.18	48.48	47.83	47.28	47.81
TiO ₂		b.l.	b.l.	b.l.	b.l.	b.l.	0.37	0.38	0.42	0.24
Al ₂ O ₃		b.l.	b.l.	b.l.	b.l.	b.l.	1.25	1.04	1.48	0.60
FeO		64.24	64.20	66.52	66.28	67.06	22.42	21.78	26.81	27.96
MnO		3.37	2.82	3.18	2.89	2.62	0.83	0.86	0.79	0.95
MgO		1.69	3.00	0.64	0.86	0.30	3.38	3.95	0.75	0.78
CaO		0.30	0.12	0.15	0.09	0.07	20.63	19.63	20.11	19.46
Na ₂ O		b.l.	b.l.	b.l.	b.l.	b.l.	1.09	0.75	1.10	0.94
K ₂ O		n.a	n.a	n.a	n.a	n.a	b.l.	b.l.	b.l.	b.l.
ZnO		0.16	0.12	0.13	0.31	0.75	0.05	0.16	0.04	0.10
NiO		0.02	0.01	b.l.	b.l.	b.l.	n.a	n.a	n.a	n.a
F		n.a	n.a	n.a	n.a	n.a	b.l.	b.l.	b.l.	b.l.
Cl		n.a	n.a	n.a	n.a	n.a	b.l.	b.l.	b.l.	b.l.
Total		99.50	100.05	99.86	99.76	100.02	98.52	96.39	98.77	98.84
Cations		O=4					O=6			
Si	apfu	1.00	0.99	0.99	0.99	0.99	1.98	1.98	1.96	1.98
Ti		b.l.	b.l.	b.l.	b.l.	b.l.	0.01	0.01	0.01	0.01
Al		b.l.	b.l.	b.l.	b.l.	b.l.	0.06	0.05	0.07	0.05
Fe ²⁺		1.80	1.78	1.88	1.87	1.90	0.71	0.75	0.93	0.96
Mn		0.10	0.08	0.09	0.08	0.08	0.03	0.03	0.03	0.03
Mg		0.08	0.15	0.03	0.04	0.01	0.24	0.24	0.05	0.05
Ca		0.01	0.00	0.01	0.00	0.00	0.90	0.87	0.89	0.88
Na		b.l.	b.l.	b.l.	b.l.	b.l.	0.08	0.06	0.09	0.08
K		n.a	n.a	n.a	n.a	n.a	b.l.	b.l.	b.l.	b.l.
Zn		0.00	0	0	0.01	0.02	b.l.	b.l.	b.l.	b.l.
Ni		b.l.	b.l.	b.l.	b.l.	b.l.	n.a	n.a	n.a	n.a
F		n.a	n.a	n.a	n.a	n.a	b.l.	b.l.	b.l.	b.l.
Cl		n.a	n.a	n.a	n.a	n.a	b.l.	b.l.	b.l.	b.l.
Mg#		0.04	0.08	0.02	0.02	0.01	0.25	0.24	0.05	0.05
Fa		91	89	94	94	95				
Hedenbergite		FESY	(Ca _{0.88} Fe _{0.06} ²⁺ Mn _{0.03} Mg _{0.02} Na _{0.01}) _{Σ1} (Fe _{0.72} ²⁺ Mg _{0.19} Al _{0.06} Ti _{0.01}) _{Σ0.98} Si _{2.02} O ₆							
		CSY	(Ca _{0.87} Na _{0.8} Mn _{0.03} Fe _{0.02} ²⁺) _{Σ1} (Fe _{0.85} ²⁺ Fe _{0.09} ³⁺ Mg _{0.05} Al _{0.01} Ti _{0.01}) _{Σ1} (Si _{1.97} Al _{0.04}) _{Σ2} O ₆							

Note: Total iron is expressed as FeO; n.a. = non analyzed; b.l. = below detection limit, which is as follows for oxides (wt %): Na, 0.03; F, 0.03; K, 0.03; Cl, 0.02; Fe, 0.04; Si, 0.06; Mg, 0.02; Ca, 0.03; Ti, 0.04; Mn, 0.4; Al, 0.02; Zn, 0.03; Cr, 0.03. Samples coordinates (UTM Nad83): 10-Lp-673614, 440191, 6132727; ML10007-30.8, 444635, 6134353 depth 30.8m; ML10001-107, 440150, 6133220, depth 107m; ML10006-46.15, 444420, 6134330, depth 46.15m; 205494, 443864, 6137247.

(1–5 cm wide). In the eastern part of the Misery intrusion, the coarse-grained syenite locally contains inclusions of ferrosyenite (described above), medium-grained syenite, and layers and pods of cumulate fluorapatite types 1 and 2 and magnetite. The layers, however, are best developed in glacially transported boulders that originated from an unknown location in the lake. They are closely spaced, range from a few cm up to about 15 cm in thickness and are continuous over the diameter of the boulders (up to 3 m; Fig. 7D). The fluorapatite crystals in the layers are idiomorphic but usually have corroded rims replaced by britholite-(Ce) 1, suggesting that they are dominantly of the fluorapatite 2 variety. In some cases, the fluorapatite cumulates have been replaced almost completely by britholite-(Ce) 1. In these samples, britholite-(Ce) 1 (after fluorapatite 2) commonly forms aggregates within a matrix of magnetite (Fig. 7E). It also occurs as inclusions in perthitic K-feldspar and biotite. A second type of britholite-(Ce), referred to as britholite-(Ce) 2, completely replaced an

unidentified rare-earth-enriched apatite-group mineral (Fig. 7F). Samples of the layer in the Discovery outcrop contain up to 5.24 wt % TREO, 0.11 wt % ZrO₂, and 0.10 wt % Nb₂O₅ (sample 10-LP-6737; Fig. 6). In the boulders, the corresponding concentrations range between 1.06 and 1.73 wt % TREO, 0.77 and 0.93 wt % ZrO₂, and 0.03 and 0.03 wt % Nb₂O₅ (samples 205767 and 205215). Representative compositions of the felsic syenites are listed in Tables 4, 5, and 6.

The medium-grained syenite is distinguished by oriented lath-shaped crystals of perthitic K-feldspar that impart a trachytic texture to the rock, and are commonly oriented parallel to the contact of the Misery intrusion with the granitoids of the Mistastin batholith. The ferromagnesian minerals are interstitial, and vary in proportion from 7 to 20 vol %. The fine-grained syenite also displays a strong magmatic lineation of the perthitic K-feldspar laths.

Locally, there are occurrences of coarse-grained syenite in which perthitic crystals were replaced by microcrystalline

TABLE 3. Average Composition of Amphibole and Mica by Rock Type (FESY = ferrosyenite; FS = felsic syenite; ASY = albitized coarse-grained syenite) in the Misery Syenitic Intrusion

Mineral		Ferropargasite			Ferroedenite	Arfvedsonite	Annite		
Rock type		FESY		FS	FS	ASY	FESY		FS
Sample		10-Lp-673614 n = 9	ML10007-30,8 n = 12	ML10001-107 n = 3	ML10006-46,15 n = 1	10-LP-6738 n = 11	10-Lp-673614 n = 5	ML10007-30,8 n = 4	ML10001-107 n = 1
SiO ₂	wt %	40.61	40.46	39.27	41.29	48.71	35.02	35.41	34.24
TiO ₂		1.98	2.17	0.41	2.24	0.70	4.44	3.85	4.62
Al ₂ O ₃		7.73	8.51	7.97	6.75	1.26	11.02	11.81	10.13
FeO		28.32	26.29	33.30	31.69	27.01	32.46	29.89	34.70
MnO		0.64	0.59	0.47	0.63	3.49	0.34	0.25	0.34
MgO		3.32	4.92	1.40	0.81	0.15	3.49	5.29	1.32
CaO		9.82	10.25	9.29	9.76	0.58	0.07	0.06	0.06
Na ₂ O		2.86	2.41	2.63	2.82	8.13	0.13	0.13	0.02
K ₂ O		1.64	1.57	1.85	0.63	1.93	9.29	9.67	9.53
ZnO		0.08	0.04	0.04	0.16	2.30	0.19	0.10	0.37
F		0.90	0.87	0.34	0.12	1.42	0.84	1.29	0.18
Cl		0.08	0.20	0.08	0.14	b.l.	0.04	0.06	0.00
Total		97.57	97.87	96.876	96.947	95.09	96.95	97.32	95.44
Cations		O=24				O=24	O=12		
Si	apfu	6.75	6.63	6.80	7.05	8.11	3.04	3.01	3.12
Ti		0.25	0.27	0.05	0.29	0.09	0.31	0.25	0.32
Al		1.51	1.64	1.63	1.36	0.25	1.15	1.18	1.09
Fe ²⁺		3.94	3.60	4.82	4.53	3.76	2.41	2.12	2.64
Mn		0.09	0.08	0.07	0.09	0.49	0.03	0.02	0.03
Mg		0.82	1.20	0.36	0.20	0.04	0.37	0.67	0.18
Ca		1.75	1.80	1.72	1.79	0.10	0.00	0.01	0.01
Na		0.92	0.76	0.88	0.93	2.63	0.02	0.02	0.00
K		0.35	0.33	0.41	0.14	0.41	1.05	1.05	1.11
Zn		0.01	0.00	0.01	0.02	0.28	0.01	0.01	0.02
F		0.48	0.45	0.19	0.06	0.75	0.20	0.35	0.05
Cl		0.02	0.06	0.02	0.04	0.00	0.01	0.01	0.00
Mg#		0.10	0.16	0.04	0.02	0.01	0.10	0.15	0.04
Ferropargasite	10-Lp-673614	FESY: (Na _{0.67} K _{0.35})Σ1.02(Ca _{1.75} Na _{0.25})Σ2(Al _{0.26} Ti _{0.22} Mg _{0.82} Fe _{3.93} ²⁺ Mn _{0.09})Σ5.36(Si _{6.75} Al _{1.25})Σ8O ₂₂ (F _{0.50} ,OH _{1.50})Σ2							
	ML10007-30,8	FESY: (Na _{0.56} K _{0.33})Σ0.89(Ca _{1.80} Na _{0.20})Σ2(Al _{0.27} Ti _{0.27} Mg _{1.20} Fe _{3.60} ²⁺ Mn _{0.08})Σ5.43(Si _{6.63} Al _{1.37})Σ8O ₂₂ (F _{0.50} ,OH _{1.50})Σ2							
	ML10001-107	FS: (Na _{0.61} K _{0.41})Σ1.02(Ca _{1.72} Na _{0.28})Σ2(Al _{0.48} Ti _{0.05} Mg _{0.36} Fe _{4.82} ²⁺)Σ5.74(Si _{6.80} Al _{1.20})Σ8O ₂₂ (F _{0.21} ,OH _{1.78})Σ2							
Ferroedenite	ML10006-46,15	FS: (Na _{0.72} K _{0.14})Σ0.86(Ca _{1.79} Na _{0.21})Σ2(Al _{0.41} Ti _{0.21} Mg _{0.20} Fe _{4.53} ²⁺ Mn _{0.09} Zn _{0.02})Σ5.54(Si _{7.05} Al _{0.95})Σ8O ₂₂ (F _{0.10} ,OH _{1.90})Σ2							
Arfvedsonite	10-LP-6738	PSY: (Na _{0.73} K _{0.41})Σ1.14(Na _{1.89} Ca _{0.11})Σ1.2(Fe _{3.76} ²⁺ Mn _{0.49} Al _{0.36} Zn _{0.28} Ti _{0.09} Mg _{0.04})Σ5.02Si _{8.11} O ₂₂ (OH _{1.25} F _{0.75})Σ2							

albite. This rock also contains secondary astrophyllite (6 vol %) and arfvedsonite (composition reported in Table 3) after inferred ferropargasite and strongly zoned, idiomorphic zircon crystals (5 vol %), which have fractured rims and locally, fractured cores (Fig. 8A, B). This sodically metasomatized syenite also contains several REE-rich minerals, including an anhydrous mineral (orange to brown in plane polarized light), which occurs as aggregates of very small crystals interstitial to zircon and albite or in pseudomorphs (Fig. 8A-C). This mineral has a composition similar to that of britholite-(Ce), based on the similarity of their EDS spectra. The pseudomorphs may represent former apatite and comprise up to 3 vol % of the sodically altered coarse-grained syenite. The other REE-bearing minerals are fluorocarbonates, mainly bastnäsite-(Ce), which occur as small, ovoid-shaped inclusions in perthite and ferromagnesian silicate minerals. Parisite-(Ce) and synchysite-(Ce) are observed mainly as replacements of the inferred britholite-(Ce) (Fig. 8D). The compositions of the REE-fluorocarbonate minerals are reported in Table 7. Finally, this rock also contains small crystals of columbite-(Fe), an unidentified Nb-, LREE-rich calcium silicate and

primary monazite-(Ce). Samples of this rock type returned up to 0.18 wt % TREO, 3.20 wt % ZrO₂ and 4.53 wt % Nb₂O₅ (sample 10-LP-6738).

Porphyritic quartz-syenite dikes

Northwest-oriented porphyritic quartz-syenite dikes intruded the coarse-grained syenite in the eastern part of the Misery syenitic intrusion and in the adjacent quartz-monzonite (Fig. 4). These dikes are dark gray to green in color, porphyritic, and fine to medium grained. The phenocryst phase is perthitic K-feldspar (1–2 cm long), which comprises up to 10 vol % of the rock. The groundmass is composed of small crystals of K-feldspar, plagioclase, quartz, fayalite, and minor ferropargasite and hedenbergite. The ferromagnesian minerals, especially fayalite, are unaltered and display ovoid shapes. The accessory minerals are apatite, zircon, and fluorite.

Quartz-fayalite dikes

Narrow dikes (up to 10 cm wide, Fig. 9A) containing up to 2.27 wt % TREO (including 1.1 wt % HREO), 2.56 wt % ZrO₂, and 1.48 wt % Nb₂O₅ cut the coarse-grained syenite

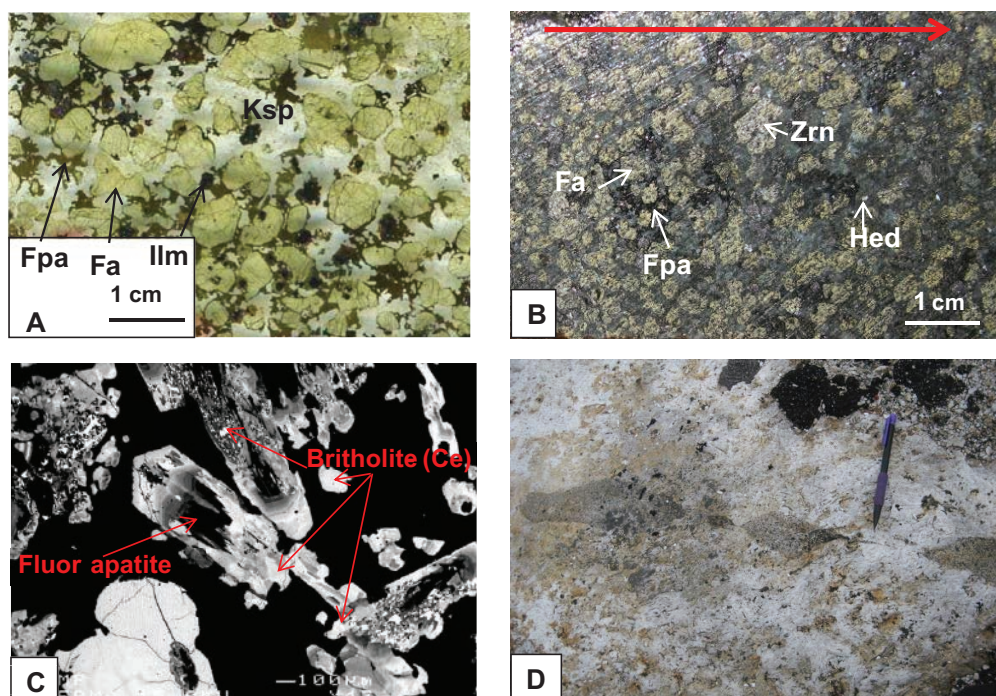


FIG. 5. (A) Photograph of ferrosyenite in thin section showing fayalite (Fa) crystals rimmed by ferropargasite (Fpa; sample ML10007-30.08). (B) Fayalite cumulate in core from diamond drill hole ML10007 at a depth between 30.93 and 31 m (the red arrow identifies the direction of decreasing depth). (C) Backscattered electron image of compositionally zoned fluorapatite crystals partly replaced by britholite-(Ce) in ferrosyenite (sample 205447). (D) Photograph of ferrosyenite inclusions in coarse-grained syenite (Outcrop 2011-036).

and quartz-monzonite parallel to the contact between them, in the eastern part of the Misery intrusion (Fig. 4). They have also been found within rapakivi granite, 1.5 km north of the Misery intrusion. The dikes are composed mainly of roughly equal proportions of interlocking quartz and fayalite crystals (this suggests that the two minerals crystallized at the same

time) varying in diameter from 1 mm to 2 cm (Fig. 9B, C). Idiomorphic fergusonite-(Y) and zircon crystals (zircon is typically zoned; Fig. 9D) make up a significant proportion of the rock, ~ 2 and 3 vol %, respectively (thereby explaining the high rare metal content of the dikes), and occur either as inclusions in fayalite (Fig. 9B, C) or at the contacts

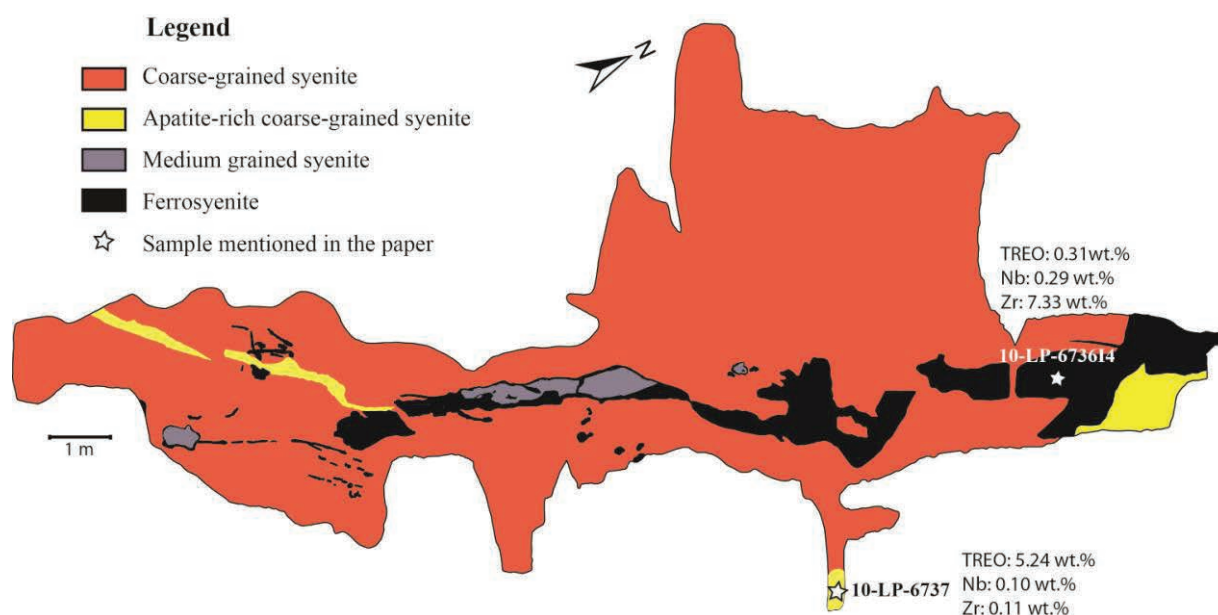


FIG. 6. Sketch of the "discovery outcrop" showing relationships among the different lithological units listed in the legend.

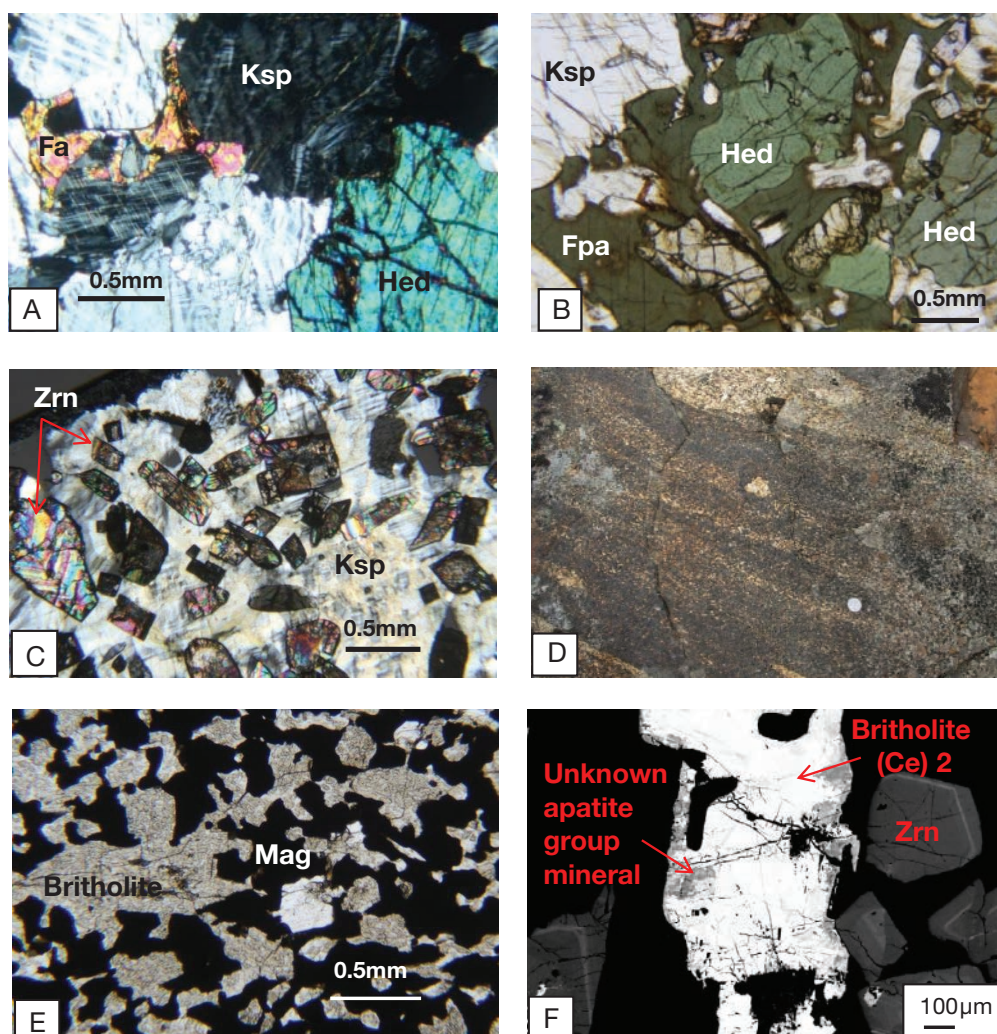


FIG. 7. (A) Photomicrograph of coarse-grained syenite in cross polars showing interstitial fayalite and hedenbergite (Hed) among crystals of perthitic K-feldspar (Ksp; sample 10-LP-6762). (B) Photomicrograph of coarse-grained syenite in plane-polarized light showing fayalite and hedenbergite crystals rimmed by ferropargasite (Fpa; sample 2011-015). (C) Photomicrograph in cross polars showing coarse-grained syenite containing a cumulate layer of zoned zircon (Zrn) crystals with inherited cores. They are poikilitic in a perthite crystal (sample ML10001-91.73). (D) Photograph of a boulder containing apatite-magnetite-rich layers. The scale is indicated by a 25 cent coin. (E) Photomicrograph in plane-polarized light of apatite crystals almost entirely replaced by britholite-(Ce) 1 intergrown with magnetite (Mag; sample 205162). (F) Backscattered electron image of type 2 britholite-(Ce) and zoned zircon (Zrn) in coarse-grained syenite (sample 205130).

between quartz and fayalite crystals (Fig. 9D). The crystals of fergusonite-(Y) and zircon are surrounded by radial fractures filled with a material similar in composition to fayalite. The composition of the fergusonite-(Y) is reported in Table 7. Small ovoid grains of magnetite and quartz also occur within the fayalite and are interpreted to represent the products of the partial decomposition of the fayalite (Fig. 9B). Small proportions of thorite, astrophyllite, fluorite, an unidentified LREE-, Fe-, and Nb-rich silicate mineral and trace amounts of K-feldspar in some samples complete the mineralogy of the quartz-fayalite dikes.

Microgranite

The microgranite forms centimetric dikes, which were exposed only in one drill core from the eastern part of the intrusion. They cut the host quartz-monzonite next to the

coarse-grained syenite over an area ~1 m wide. The rock is dark gray, very fine-grained, and consists mainly of quartz and K-feldspar, which impart a granophyric texture. Ferromagnesian minerals, mainly biotite and amphibole, comprise ~1 vol % of the rock. On the basis of its optical properties, the amphibole is interpreted to be hornblende.

Bulk Rock Chemistry

Outcrop and drill core samples from 14 holes drilled by Quest Rare Minerals in 2010 and 2011 were analyzed for their bulk rock composition. The analyses were carried out by Acme Analytical Laboratories Ltd. in Vancouver. Major elements were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and trace elements by inductively coupled plasma-mass spectrometry (ICP-MS). The samples were subjected to lithium metaborate-tetraborate fusion and

TABLE 4. Major Element Composition of Representative Samples from the Misery Syenitic Intrusion and Host Mistastin Granitoids

Rock type	Mistastin granite		Mistastin monzonite	Ferro-syenite	Coarse-grained syenite	Medium-grained syenite	Fine-grained syenite	Porphyritic quartz syenite	Micro-granite	Quartz-fayalite dyke	Albitized pegmatitic syenite	Apatite cumulate in pegmatitic syenite	Magnetite-, apatite-rich layers
	Sample	wt %											
Sample	10-LP-6676	69.37	68.65	43.16	62.39	63.69	63.90	61.15	73.93	65.94	60.42	31.86	38.22
	442396	14.50	14.96	3.94	16.06	17.57	16.48	17.29	12.55	3.11	11.40	8.33	3.4
	UTMX	3.74	3.20	32.45	5.23	3.64	5.36	5.68	2.08	19.52	10.97	1.76	40.22
UTMY	6125412	3.74	3.20	1.95	0.08	0.03	0.07	0.27	0.05	0.08	0.23	0.09	1.43
		1.39	1.23	11.84	2.35	1.25	1.10	1.96	0.81	0.64	0.28	25.40	8.91
		3.55	3.71	1.77	5.63	7.48	7.63	5.76	4.14	1.07	8.95	3.06	1.29
		6.07	6.08	1.07	5.80	4.91	4.53	6.16	4.86	1.24	0.62	3.04	0.96
		0.33	0.29	1.81	0.31	0.10	0.15	0.43	0.06	0.20	0.30	0.04	2.359
		0.06	0.05	0.37	0.06	<0.01	<0.01	0.16	0.03	0.04	0.04	18.46	0.35
		0.07	0.05	1.03	0.14	0.08	0.11	0.14	0.04	0.62	0.86	0.10	1.251
		99.22	98.75	99.39	98.05	98.75	99.33	99.00	98.55	92.46	94.07	92.14	96.31
		0.40	0.90	-0.80	1.00	1.20	0.60	0.60	0.54	0.01	1.30	1.10	2.07
		0.9639	0.8579	0.9433	0.9849	0.9918	0.9871	0.9546	0.9765	0.9959	0.9795	0.9514	0.9657

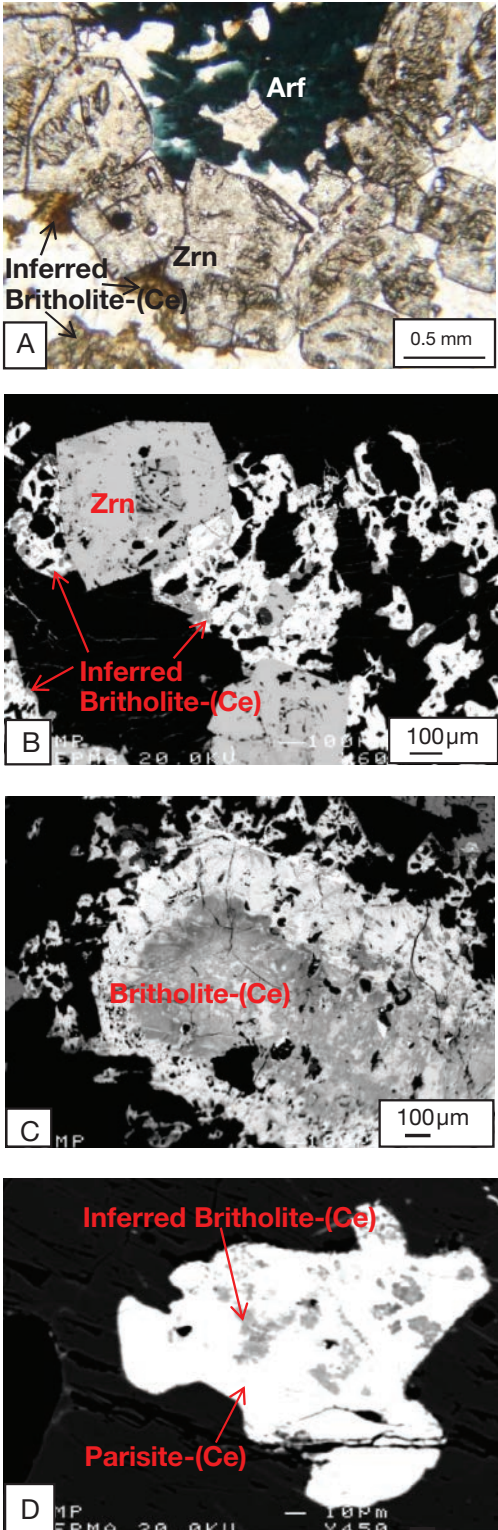


FIG. 8. (A) Photomicrograph in crossed polars showing arfvedsonite (Arf), zircon (Zrn), and inferred britholite-(Ce) in albitized coarse-grained syenite (sample 10-LP-6738). (B) Backscattered electron image of albitized coarse-grained syenite containing zircon crystals, and interstitial inferred britholite-(Ce) (sample 10-LP-6738). (C) Backscattered electron image showing a zoned crystal of britholite-(Ce) in albitized syenite; the light outer part has a higher REE content than the core (sample 10-LP-6738). (D) Backscattered electron image of the inferred britholite-(Ce) (light gray) replaced by parasite-(Ce) (white; sample 10-LP-6738).

TABLE 6. Rare-Earth Element Composition of Representative Samples from the Misery Syenitic Intrusion and Host Mistastin Granitoids

Rock type	ML10008-														Magnetite-, apatite-rich layers
	Mistastin granite	Mistastin monzonite	Ferro- syenite	Coarse- grained syenite	Medium- grained syenite	Fine- grained syenite	Porphyritic quartz syenite	Micro- granite	Quartz- fayalite dyke	Albitized pegmatitic syenite	Apatite cumulate in pegmatitic syenite	205215			
Sample	10-LP-6676	10-LP-6679	10-LP-673614	10-LP-6706	10-LP-6759	10-LP-6760	10-LP-6778	138,9	205494	10-LP-6738	10-LP-6737	205215			
Sc	10	9	1,001	14	3	31	50	8	21	11	6	205			
Y	83.1	92.6	332.1	199.1	61.6	57	82.2	202	5,632	880.2	3,940	1,046			
La	164	218.9	495.6	364	15.1	13.7	154.4	97.1	1,660	278	9,508	2,690			
Ce	349	417.7	1,107.30	717.9	27.7	33	358.9	189	4,750	531.1	20,945.30	6,150			
Pr	37.99	45.79	141.04	70.91	3.11	4.1	41.78	20.4	580	48.82	21,96.23	700			
Nd	131	154.2	525	215	10.4	15.1	148.7	75.7	2,380	132.9	8,095	2,470			
Sm	21	21.89	82.69	34.04	2.42	3.18	23.49	17.1	678	24.34	1,194.43	402			
Eu	3.01	3	2.25	1.83	0.15	0.16	2.05	0.55	13.1	1.23	34.58	8.2			
Gd	16.36	17.1	67.14	27.68	2.79	3.14	17.95	16.1	686	25.14	945.17	276			
Tb	2.74	2.77	10.81	5.15	0.57	0.66	2.98	3.3	143	6.96	136.8	42.7			
Dy	15.54	15.9	65.77	31.68	4.14	4.58	16.41	25	951	71.99	828.57	246			
Ho	2.97	3.13	13.07	6.92	1.03	1.1	3.17	5.5	201	23.3	147.59	48			
Er	8.99	9.25	39.9	22.71	3.58	3.97	9.1	19.4	604	110.4	395	138			
Tm	1.28	1.43	6.52	3.52	0.65	0.87	1.36	3.34	86.3	25.09	53.23	19.8			
Yb	8.43	9.69	51.94	26.06	5.09	8.64	9.23	24	540	205.18	293.22	126			
Lu	1.27	1.45	9.88	4.33	0.88	1.92	1.45	4.11	83.6	34.32	35.47	19.6			
TREO	0.09	0.11	0.31	0.18	0.01	0.01	0.09	0.08	2.27	0.18	5.24	1.73			

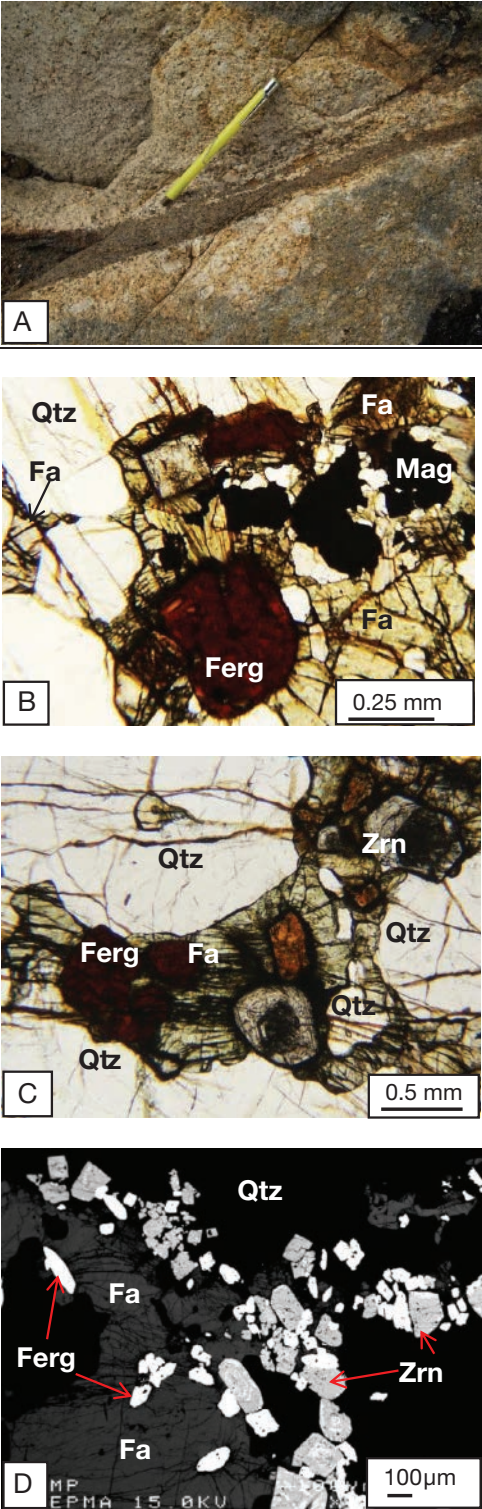


FIG. 9. (A) Photograph of a quartz-fayalite dike (outcrop 2011-042). (B) Photomicrograph of a quartz-fayalite dike in plane polarized light showing magnetite (Mag) and a euhedral crystal of fergusonite-(Y) surrounded by quartz (Qtz) and fayalite (Fa) (sample 205494). (C) Photomicrograph of a quartz-fayalite dike in plane polarized light showing intergrown quartz and fayalite and idiomorphic fergusonite-(Y) (Ferg) and zoned zircon (sample 205123). (D) Backscattered image showing an aggregate of zoned zircon and unzoned fergusonite-(Y) crystals at the contact between quartz and fayalite crystals in a quartz-fayalite dike (sample 205494).

TABLE 7. Average Composition (wt %) of Fergusonite-(Y), Columbite-(Fe), and REE Fluorocarbonates in the Misery Syenitic Intrusion

	Fergusonite-(Y) n = 22	Columbite-(Fe) n = 13	Bastnaesite-(Ce) n = 8	Parisite-(Ce) n = 4	Synchysite-(Ce) n = 3
ZrO ₂	n.a.	n.a.	b.l.	b.l.	b.l.
SiO ₂	0.74 ± 0.67	b.l.	b.l.	b.l.	b.l.
HfO ₂	n.a.	n.a.	b.l.	b.l.	b.l.
TiO ₂	0.26 ± 0.10	1.22 ± 0.19	n.a.	n.a.	n.a.
FeO	1.93 ± 0.25	19.81 ± 0.74	b.l.	b.l.	b.l.
Al ₂ O ₃	n.a.	n.a.	b.l.	b.l.	b.l.
MgO	n.a.	n.a.	b.l.	b.l.	b.l.
P ₂ O ₅	n.a.	n.a.	0.26 ± 0.43	2.01 ± 3.86	0.06 ± 0.07
UO ₂	1.14 ± 0.31	b.l.	n.a.	n.a.	n.a.
ThO ₂	1.66 ± 0.56	b.l.	0.50 ± 0.70	0.50 ± 0.62	0.13 ± 0.12
CaO	1.54 ± 0.61	0.10 ± 0.19	1.64 ± 1.24	6.20 ± 3.37	11.05 ± 0.10
F	n.a.	n.a.	6.43 ± 1.06	3.98 ± 2.56	5.74 ± 0.64
Y ₂ O ₃	20.53 ± 1.95	b.l.	1.02 ± 1.37	0.66 ± 0.49	0.77 ± 0.30
Nb ₂ O ₅	44.64 ± 0.89	74.53 ± 0.64	n.a.	n.a.	n.a.
Ta ₂ O ₅	0.87 ± 0.09	1.95 ± 0.43	n.a.	n.a.	n.a.
La ₂ O ₃	n.a.	n.a.	21.31 ± 2.74	17.68 ± 2.20	14.87 ± 0.54
Ce ₂ O ₃	4.67 ± 1.55	b.l.	34.29 ± 3.96	31.17 ± 1.92	29.47 ± 0.53
Pr ₂ O ₃	0.96 ± 0.27	b.l.	3.23 ± 0.38	3.31 ± 0.53	3.34 ± 0.13
Nd ₂ O ₃	5.37 ± 0.93	b.l.	9.15 ± 1.40	10.89 ± 2.82	11.26 ± 0.57
Sm ₂ O ₃	1.62 ± 0.18	b.l.	0.52 ± 0.29	0.82 ± 0.45	1.01 ± 0.05
Eu ₂ O ₃	0.28 ± 0.06	b.l.	b.l.	b.l.	b.l.
Gd ₂ O ₃	3.85 ± 0.45	b.l.	0.38 ± 0.27	0.51 ± 0.27	0.65 ± 0.06
Dy ₂ O ₃	3.52 ± 0.72	b.l.	0.11 ± 0.18	0.09 ± 0.08	0.15 ± 0.05
Er ₂ O ₃	1.98 ± 0.47	b.l.	0.07 ± 0.12	0.02 ± 0.02	b.l.
Tm ₂ O ₃	0.26 ± 0.14	b.l.	n.a.	n.a.	n.a.
Yb ₂ O ₃	1.48 ± 0.31	b.l.	0.05 ± 0.10	b.l.	b.l.
CO ₂	n.a.	n.a.	23.75 ± 3.83	23.82 ± 5.17	23.91 ± 0.66
Total	97.33	98.14	100.00	100.00	100.00

Note: n.a. = not analyzed; b.l. = below detection limit which, are as follows for oxides (wt %): Zr. 0.11; Si. 0.06; Hf. 0.10; Ti. 0.04; Fe. 0.04; Al. 0.02; Mg. 0.02; P. 0.04; U. 0.04; Th. 0.06; Ca. 0.03; F. 0.03; Y. 0.07; Nb. 0.06; Ta. 0.14; La. 0.04; Ce. 0.04; Pr. 0.13; Nd. 0.11; Sm. 0.07; Eu. 0.02; Gd. 0.07; Dy. 0.08; Er. 0.05; Tm. 0.05; Yb. 0.06.

nitric acid digestion. Compositions of these samples are presented in Tables 4, 5, and 6.

The compositions of the Misery syenites, their host granitoids, and the microgranites define two trends on an alkali versus silica diagram (Fig. 10A, B). Two of the rock types described above plot in the granite field: the Mistastin granitoids (group 2) and the microgranite dikes (group 4). By contrast, Misery syenites (group 1) plot in a field ranging from syenite to syenogabbro. The last group (group 3), which is intermediate in composition between Misery syenite and Mistastin granitoids, is interpreted to be the product of hybridization of Misery syenite and Mistastin granitoid. This interpretation is supported by the observations that the samples forming group 3 are all located along the eastern contact between the Mistastin granitoids and the Misery syenite, and that this contact is gradational.

The trend formed in Figure 10A by Misery syenites can be subdivided into subgroups a and b, where a represents the ferrosyenites and b the fine- to coarse-grained felsic syenites. These subgroups are interpreted to reflect fractional crystallization and the extraction of ferromagnesian minerals from a parental syenitic magma. The ferrosyenite represents the extracted fraction, and the most alkali- and silica-rich syenite the evolved liquid. Quartz-fayalite dikes plot beyond the limit of the diagram at high silica and low alkali concentration. Further insight into the relationship of the quartz-fayalite dikes

to the Misery syenites and Mistastin granitoids is provided by Figure 11, in which Zr/Ti is plotted versus Nb/Y, with the former parameter representing the degree of magma evolution and the latter the alkalinity. From this diagram, it is evident that the quartz-fayalite dikes (assuming that they are igneous; see discussion below) represent the most evolved rock unit analyzed (Zr/Ti) but that their alkalinity (Nb/Y) is similar to that of the syenites and Mistastin granitoids; the syenites and the granitoids are broadly coincident in the field of alkali rhyolite.

Although the Misery syenites and Mistastin granitoids have quite different major element compositions, their trace-element compositions are relatively similar (Fig. 12A; Tables 5, 6). Both suites of rocks are enriched in La and Th and depleted in Sr, Pb, Ba, and Eu. However, the Zr, Hf, and Yb concentrations present positive anomalies in the syenites and not in the granitoids. Among the syenites, the principal difference is that the ferrosyenite is more enriched in the REEs, Zr, and Hf than the other syenites (Fig. 12A). The REE profiles for the Misery syenites and Mistastin granitoids are also fairly similar (Fig. 12B). Both display a similar LREE enrichment and a negative Eu anomaly. However, the ferrosyenites show a progressive enrichment in the HREEs (Er to Lu), whereas the MREE and HREE parts of the profiles are relatively flat for the syenites and the Mistastin granitoids. The absolute concentrations of the REEs are also higher in both the

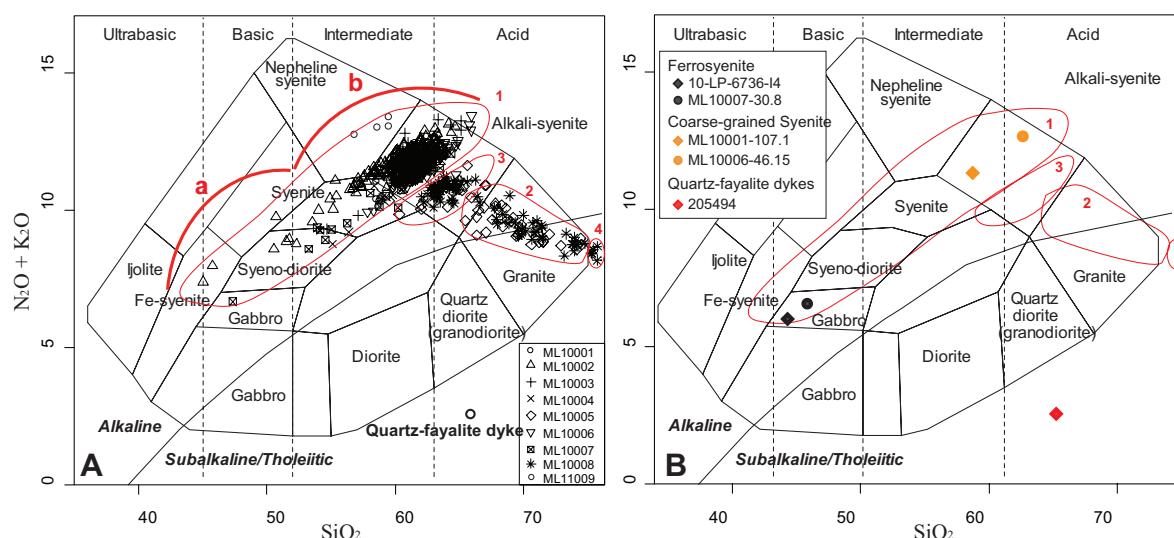


FIG. 10. (A) A plot of total alkalis vs. silica (TAS) with the igneous classification of Cox et al. (1979) superimposed. The diagram shows the distribution of rock compositions from nine drill holes collared in Misery syenite and/or Mistastin granitoid. Misery syenites are subdivided into two groups: ferrosyenite (a) and fine- to coarse-grained syenite (b). The four groups of rocks (fields 1 to 4), namely Misery syenites, Mistastin granitoids, quartz-monzonite, and microgranite dikes, have been distinguished based on their petrographic characteristics. The quartz-fayalite dikes plot beyond the limits of this diagram. (B) Total alkalis vs. silica (TAS) with the igneous classification of Cox et al. (1979) superimposed showing the composition of four samples for which the composition of the ferromagnesian minerals was analyzed (Tables 2, 3).

ferrosyenites and felsic syenites than in the granitoids (Fig. 12B; Table 7). In Figure 12C and D, we show the chondrite-normalized trace elements distributions and REE profiles of the three rock units that are the current targets of exploration. Their trace element profiles are roughly similar to those of weakly mineralized syenites except for the fluorapatite cumulates, which are strongly depleted in Nb and Ta, and also in Zr and Hf. We attribute the latter to the dominance of apatite-group minerals in these rocks and the fact that Nb, Ta, Zr, and Hf do not easily substitute into the crystal structures of

these minerals. Each of the REE-enriched rock units displays a distinctive REE profile (Fig. 12D). The sodically metasomatized coarse-grained syenite displays a trend of decreasing enrichment in LREEs from La to Sm and a trend of increasing enrichment in the HREEs from Gd to Yb. By contrast, the fluorapatite cumulate unit is enriched in LREEs and shows a trend of increasing depletion in the HREEs with increasing atomic number of the REEs. Finally, the quartz-fayalite dike unit is relatively depleted in LREEs and shows a relatively constant enrichment in the HREEs.

Mineral Chemistry

Mineral compositions were determined using a JEOL JXA-8900L electron microprobe equipped with five WDS spectrometers and a Si(li) EDS detector at McGill University. Spot analyses, using wavelength-dispersive spectrometry (WDS), were carried out on ferromagnesian minerals and feldspars at 30 kV with a 5- μm beam diameter and a 20-nA beam current, and on apatite-group minerals and the REE fluorocarboxates at 20 kV with a 30-nA beam current and a 10- μm beam diameter. A 3- μm beam diameter with a 30-nA beam current at 20 kV was used for zircon, columbite-(Fe), and fergusonite-(Y). The data reduction was performed using a ZAF correction procedure.

Ferromagnesian minerals

Ferromagnesian minerals were analyzed in coarse-grained syenite (samples ML10001-107 and ML10006-46.15), ferrosyenite (samples 10-LP-653614 and ML10007-30.8), a quartz-fayalite dike (sample 205494), and sodically metasomatized coarse-grained syenite (sample 10-LP-6738). The corresponding bulk rock compositions, except that of the metasomatically altered coarse-grained syenite, are illustrated in Figure 10B. Because the compositions of the ferromagnesian minerals in

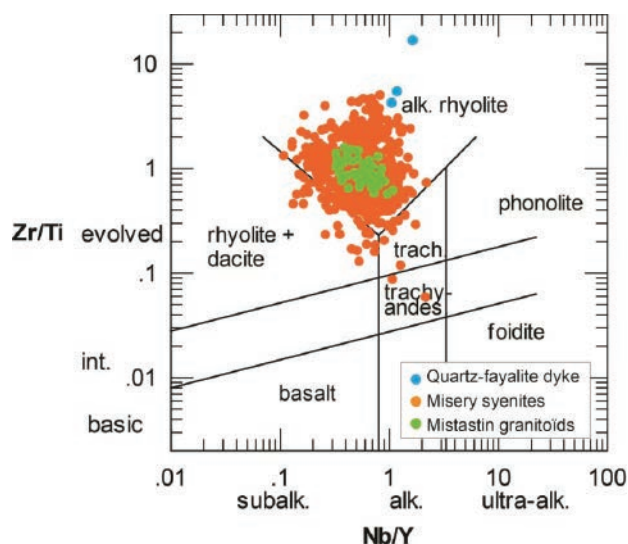


FIG. 11. A plot of Nb/Y vs. Zr/Ti from Pearce (1996) modified after Winchester and Floyd (1977). The diagram emphasizes the difference in composition between the Misery syenites (orange), the host Mistastin granitoids (green), and the quartz-fayalite dikes (blue).

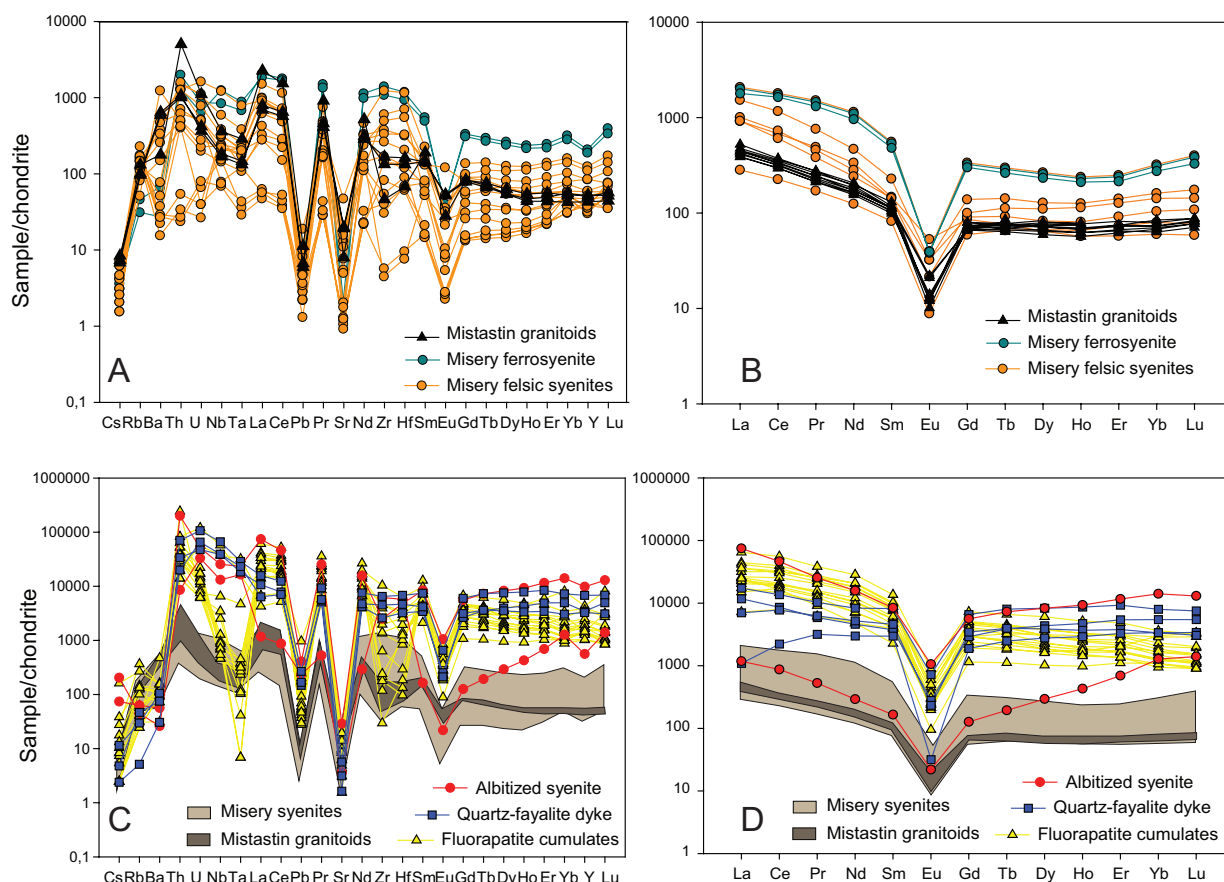


FIG. 12. Representative chondrite-normalized trace element diagrams for the various Misery and Mistastin rock units. (A) A spider diagram illustrating the trace element distribution in the Mistastin granitoids (black triangles), Misery ferrosyenite (blue circles), and Misery felsic syenites (orange circles). (B) An REE diagram for the same rock types. (C) A spider diagram illustrating the trace element distribution for Mistastin granitoids, Misery syenites and REE-mineralized facies: the red circles correspond to albitized syenite ($n = 2$), the yellow triangles to fluorapatite cumulates ($n = 7$), and the blue rectangles to quartz-fayalite dike ($n = 3$). (D) An REE diagram for rock types in C.

the fine-, medium-, and coarse-grained syenites are indistinguishable, they are grouped together under the label “felsic syenite.” The results of the analyses of the different ferromagnesian minerals highlight a number of important differences between the ferrosyenite, felsic syenite, and quartz-fayalite dikes.

The fayalite is slightly richer in iron in the felsic syenite (Fa_{94}) than it is in the ferrosyenite (from Fa_{89} to Fa_{91}) and even richer in Fe in the quartz-fayalite dikes (Fa_{95}). It is correspondingly richer in Mg in the ferrosyenite than in the felsic syenite and is poorest in Mg in the quartz-fayalite dikes. This is consistent with the ferrosyenite and quartz-fayalite dikes representing the least and most evolved magmas, respectively. However, the Mn content of the fayalite in the three units is very similar (Table 2).

Observations made for fayalite also apply to hedenbergite in the ferrosyenite and felsic syenites. In the latter, hedenbergite contains an average of 2.69 wt % less Mg and 5.14 wt % more Fe than in the ferrosyenite (Table 2). As is evident from Figure 13, hedenbergite evolved from a more magnesian- and calcium-enriched variety in the ferrosyenite to a nearly Mg-free variety in the felsic syenite. Significantly, the hedenbergite of sample ML10006-46.15 (Fig. 13), which has

a composition in the augite field close to the wollastonite-ferrosilite tie-line, is from a rock that has one of the highest bulk rock SiO_2 and alkali contents of all the syenites analyzed, making it among the most evolved of these syenites (Fig. 10B).

The composition of the amphibole in both the felsic syenite and the ferrosyenite is very close to that of ferropargasite, except for sample ML10006-46.15, which has a composition closer to that of ferroedenite (Fig. 14; Table 3). As is the case for fayalite and hedenbergite, ferropargasite in the felsic syenite is richer in Fe (an avg of 5.74 wt %) and less enriched in Mg (2.98 wt %) than in the ferrosyenite. Furthermore, the higher the bulk rock content of alkalis, the higher is the content of Fe in the corresponding amphibole. However, amphibole in both rock types has similar concentrations of Mn. Curiously, F is more concentrated in ferropargasite in the ferrosyenite than in ferropargasite or ferroedenite in the felsic syenite, and this comparison applies even to the most evolved felsic syenite (i.e., ML10006-46.15). Indeed, the ferropargasite in this sample has the lowest F content of the ferropargasite in all the samples analyzed (Table 3). As F is an incompatible volatile that should accumulate in the residual liquid, F would be expected to be most concentrated in the ferropargasite in the most evolved felsic syenite (the ferrosyenite would represent

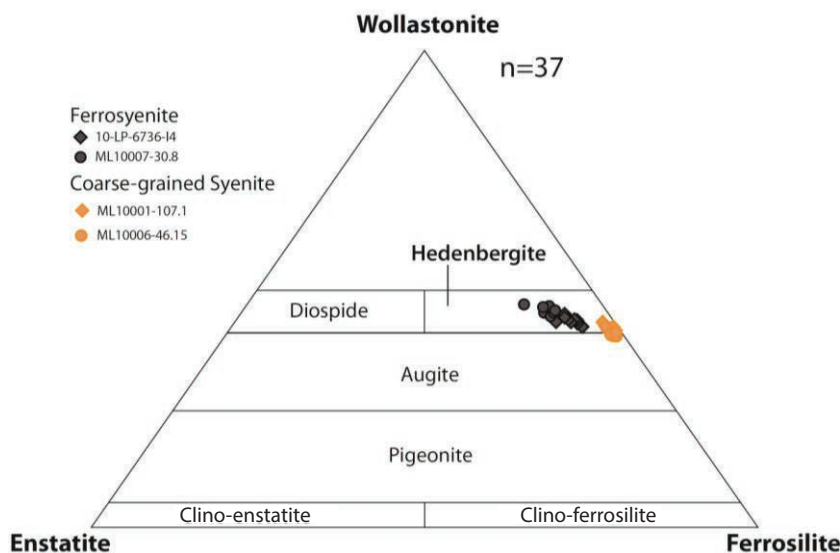


FIG. 13. The composition of clinopyroxene in the ferrosyenite and felsic syenite in terms of the components: enstatite, wollastonite, and ferrosilite. The fields of the different clinopyroxenes were taken from Morimoto (1988).

the crystallized fraction of the parent melt). We attribute this incongruity to the fact that apatite has a strong affinity for fluorine (the Misery apatite contains nearly 3 wt % F; see below) and this mineral fractionated relatively early in the evolution of the syenite to form apatite cumulates. This depleted the residual magma in fluorine. The amphibole in the sodically metasomatized coarse-grained syenite is arfvedsonite. It contains significantly less Fe^{2+} , Mg, Al, and Ti than ferropargasite but is much more enriched in Na, F, and Mn.

Finally, the mica in the Misery syenites corresponds to a member of the phlogopite-annite series, with a composition ranging from approximately 70 to 95% of the annite component (Fig. 15). As is the case for ferropargasite, its Mg and F contents are

significantly higher in the ferrosyenite than in the felsic syenite and the Mn content is similar in the two rock types.

High field strength element (HFSE) minerals

REEs are present in appreciable concentrations in fluorapatite, britholite-(Ce), fergusonite-(Y), and REE fluorocarbonate minerals. Niobium is concentrated mainly in fergusonite-(Y) and to a minor extent in columbite-(Fe), pyrochlore, and inferred normandite (EDS spectra); the last three minerals are observed as trace components in all units of the Misery intrusion, except for the quartz-fayalite dikes, in which fergusonite-(Y) is a major component (see above). Zirconium occurs as zircon, which is an important component

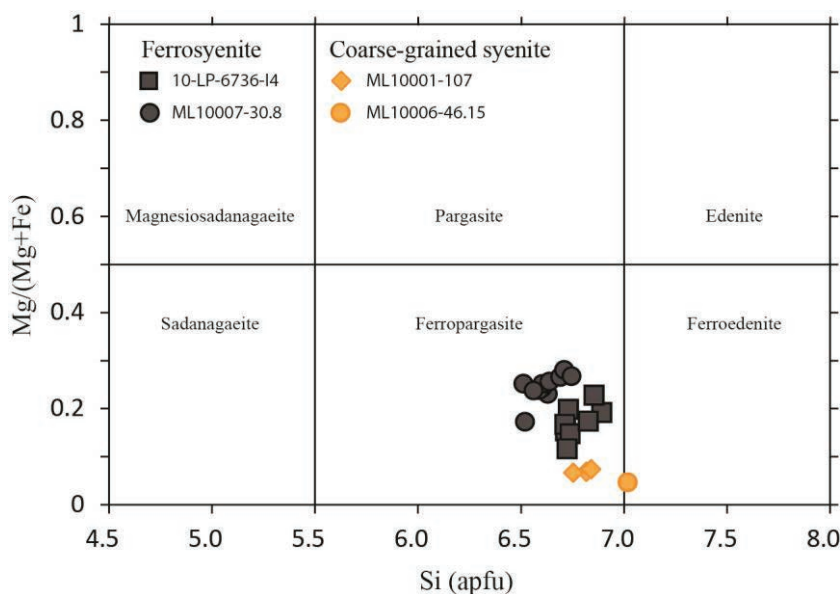


FIG. 14. The composition of amphibole in the ferrosyenite and felsic syenite represented by the $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio and Si content. The fields of the different amphiboles were taken from Hawthorne et al. (2012).

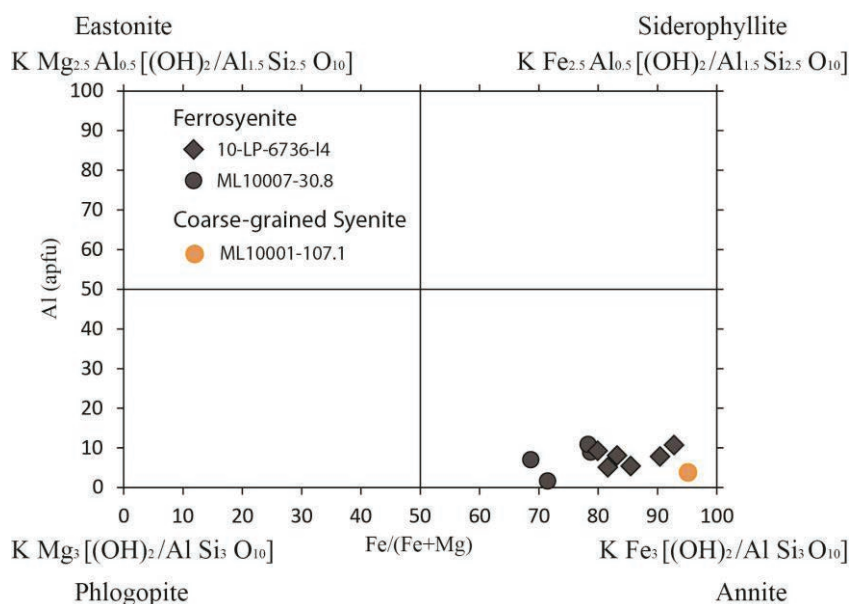


FIG. 15. The composition of mica in the ferrosyenite and felsic syenite in terms of the components: eastonite, siderophyllite, phlogopite, and annite.

of the Misery rock units. However, in contrast to many REE deposits, the zircon is generally not enriched in the REEs (in some deposits zircon is a major carrier of the REEs, e.g., Sheard et al., 2012).

The REE minerals in greatest abundance in the Misery intrusion are the apatite-group minerals, namely fluorapatite and britholite-(Ce). As discussed earlier, each mineral has been subdivided into two subtypes. Fluorapatite 1 refers to idiomorphic, non-zoned, rarely altered fluorapatite crystals, whereas fluorapatite 2 corresponds to idiomorphic to subhedral, commonly altered, compositionally zoned crystals with cores similar in composition to fluorapatite 1. Britholite-(Ce) 1, which was described earlier, replaced fluorapatite 2. Britholite-(Ce) 2 replaced an unknown apatite-group mineral.

Fluorapatite 1 is the most common apatite group mineral in the Misery syenites, and is also the least enriched in REEs, with an average content of 2.28 wt % TREO (Table 8). Its chondrite-normalized REE profile is relatively flat with a slight LREE enrichment, and it does not appear to have a negative Eu anomaly (Fig. 16A). However, it should be cautioned that in some crystals the contents of several REEs, including Eu, are below the limit of detection and thus the presence or absence of an anomaly has not been confirmed.

Fluorapatite 2 crystals, which typically are zoned compositionally, have REE contents that range from the REE content of fluorapatite 1 to contents approximately 1.5 orders of magnitude higher. Even in the same sample and within individual crystals, this variation in composition is appreciable, as are the variations in the concentrations of Ca and Si (Table 8). Their chondrite-normalized REE profiles are considerably steeper (negative) than the fluorapatite 1 profiles and they are generally characterized by a negative Eu anomaly (Fig. 16B). Most fluorapatite 2 crystals display enrichment in Si and REEs, and depletion in Ca and P from the core to the rim of the crystals (Fig. 17). This distribution is readily explained by a coupled substitution of $\text{REE}^{3+} + \text{Si}^{4+} \rightleftharpoons \text{Ca}^{2+} + \text{P}^{5+}$, which is evident

from the relative proportions of P + Ca and Si + REEs; concentrations of these component pairs are linearly distributed when represented as a binary plot (Fig. 18).

The REE content of britholite-(Ce) 1 is commonly very similar to that of the outer zones of the fluorapatite 2 that it replaced, although in general, the REE content of britholite-(Ce) 1 is considerably higher than that of fluorapatite 2. Britholite-(Ce) 1 contains up to 40 wt % TREO and on average 32.2 wt % TREO, whereas the average TREO content of fluorapatite 2 is 10.74 wt % (Table 8). Moreover, the chondrite-normalized REE profile of britholite-(Ce) 1 is very similar to that of fluorapatite 2 (Fig. 16B, C). In Figure 17, we compare the composition of britholite-(Ce) 1 with fluorapatite 2 which it replaced. From this figure, it is evident that the britholite-(Ce) 1 is strongly depleted in Ca and P, relative to fluorapatite 2, and strongly enriched in REEs and Si. However, the Fe content of britholite-(Ce) 1 is significantly lower than that of fluorapatite 2 or for that matter fluorapatite 1.

In contrast to britholite-(Ce) 1, the composition of britholite-(Ce) 2 is very homogeneous. Britholite-(Ce) 2 also contains significantly more REEs than britholite-(Ce) 1, with an average concentration of 42.32 wt % TREO (Table 8). However, the shape of its chondrite-normalized REE profile is similar to that of britholite-(Ce) 1 (Fig. 16D). As is the case for britholite-(Ce) 1 and fluorapatite 2, the chondrite-normalized REE profile for britholite-(Ce) 2 has a pronounced Eu anomaly.

An interesting feature of the compositional data for fluorapatite and britholite-(Ce) is that the La/Ce, La/Nd, and La/Gd ratios of fluorapatite 2 and britholite-(Ce) 1 are very similar, as are these ratios for fluorapatite 1 and britholite-(Ce) 2. By contrast, the ratios for fluorapatite 1 and 2 differ considerably and the same is true for britholite-(Ce) 1 and britholite-(Ce) 2. Although the similarity of these ratios for fluorapatite 2 and britholite-(Ce) 1 was expected, given that britholite-(Ce) 1 replaced fluorapatite 2, it was unexpected for fluorapatite 1

TABLE 8. Average Compositions of Apatite-Group Minerals in the Misery Syenitic Intrusion

	Fluorapatite 1 n = 32	Fluorapatite 2 n = 56	Britholite-(Ce) 1 n = 33	Britholite-(Ce) 2 n = 13
F	2.73 ± 0.25	2.81 ± 0.67	1.28 ± 0.89	0.62 ± 0.04
SiO ₂	0.44 ± 0.22	3.37 ± 2.51	11.82 ± 6.13	16.09 ± 0.39
Pr ₂ O ₃	0.11 ± 0.07	0.53 ± 0.38	1.56 ± 0.81	2.36 ± 0.10
P ₂ O ₅	41.29 ± 0.47	34.42 ± 4.90	19.75 ± 11.47	12.08 ± 0.55
La ₂ O ₃	0.34 ± 0.10	2.04 ± 1.44	6.24 ± 3.15	6.77 ± 0.17
Nd ₂ O ₃	0.45 ± 0.14	1.86 ± 1.30	5.42 ± 2.67	8.69 ± 0.18
Cl	0.01 ± 0.01	0.01 ± 0.01	0.04 ± 0.04	0.02 ± 0.01
Ce ₂ O ₃	0.93 ± 0.21	4.62 ± 3.27	14.10 ± 7.24	18.22 ± 0.35
CaO	53.22 ± 0.54	46.29 ± 5.81	31.37 ± 11.81	25.21 ± 0.62
Gd ₂ O ₃	0.08 ± 0.07	0.25 ± 0.20	0.74 ± 0.36	1.14 ± 0.04
Y ₂ O ₃	0.24 ± 0.16	0.98 ± 0.68	2.66 ± 1.19	3.09 ± 0.10
Eu ₂ O ₃	b.l.	0.04 ± 0.04	0.10 ± 0.06	0.11 ± 0.08
ThO ₂	b.l.	0.14 ± 0.16	0.81 ± 0.50	1.49 ± 0.08
Dy ₂ O ₃	0.07 ± 0.03	0.18 ± 0.14	0.50 ± 0.24	0.68 ± 0.04
Sm ₂ O ₃	0.07 ± 0.05	0.25 ± 0.19	0.71 ± 0.39	1.25 ± 0.04
FeO	n.a.	b.l.	0.46 ± 0.51	b.l.
Na ₂ O	n.a.	b.l.	b.l.	b.l.
MnO	n.a.	b.l.	b.l.	b.l.
As ₂ O ₅	n.a.	b.l.	b.l.	b.l.
BaO	n.a.	b.l.	b.l.	b.l.
TiO ₂	n.a.	b.l.	b.l.	b.l.
SrO	n.a.	b.l.	b.l.	b.l.
Total	98.85	96.99	96.99	97.76
REE ₂ O ₃	2.28	10.74	32.02	42.32
La/Ce	0.37	0.44	0.44	0.37
La/Nd	0.76	1.10	1.15	0.78
La/Gd	4.33	8.29	8.47	5.93

Fluorapatite 1: (Ca_{9.50}, La_{0.02}, Ce_{0.06}, Nd_{0.03})Σ_{9.61}(P_{5.82}, Si_{0.07})Σ_{5.89}O_{23.56}(OH_{0.39}, F_{1.20})Σ_{1.59}

Fluorapatite 2: (Ca_{8.95}, La_{0.14}, Ce_{0.35}, Pr_{0.04}, Nd_{0.12})Σ_{9.60}(P_{5.82}, Si_{0.07})Σ_{5.89}O_{23.56}(OH_{0.39}, F_{1.60})Σ_{1.99}

Britholite-(Ce) 1: (La_{0.50}, Ce_{1.11}, Pr_{0.12}, Nd_{0.42}, Ca_{7.24})Σ_{9.39}(Si_{2.55}, P_{3.60})Σ_{6.15}O_{24.60}(F_{0.87}, OH_{0.11}, Cl_{0.02})Σ_{1.00}

Britholite-(Ce) 2: (La_{0.59}, Ce_{1.58}, Pr_{0.20}, Nd_{0.74}, Ca_{6.40})Σ_{9.51}(Si_{3.82}, P_{2.43})Σ_{6.25}O₂₅(OH_{0.53}, F_{0.47}, Cl_{0.01})Σ_{1.01}

Note: n.a. = non analyzed; b.l. = below detection limit, which is as follows for oxides (wt.%): Pr, 0.13; La, 0.04; Nd, 0.11; Ce, 0.04; Gd, 0.07; Y, 0.07; Eu, 0.02; Th, 0.06; Dy, 0.08; Sm, 0.07; Sr, 0.06; Ti, 0.04; Ba, 0.14; As, 0.19; Mn, 0.4; Na, 0.04; Fe, 0.04; Ca, 0.03; Cl, 0.02; P, 0.04; Si, 0.06; F, 0.03.

and britholite-(Ce) 2. This suggests that the unknown mineral replaced by britholite-(Ce) 2 was fluorapatite 1, despite the fact that this mineral was never observed to have been replaced.

The bastnäsite-(Ce), parisite-(Ce), and synchysite-(Ce) are preferentially enriched in the LREEs (Table 7) and have a convex chondrite-normalized profile from La to Sm (Fig. 16E). Although these minerals have very similar overall REE profiles, the La/Nd and La/Gd ratios decrease progressively from bastnäsite-(Ce) to synchysite-(Ce).

Fergusonite-(Y), which occurs in significant proportions only in the quartz-fayalite dikes, contains up to 31.30 wt % TREO, up to 49.45 wt % Nb₂O₅, and up to 22.9 wt % Y₂O₃ (Table 7). As expected, its REE profile normalized to chondrite confirms its preferential enrichment in HREEs (Fig. 16F). Although the columbite-(Fe) does not contain detectable REEs, it is an important host for Nb, containing 75.66 wt % Nb₂O₅. The Nb/Ta ratios for fergusonite-(Y) and columbite-(Fe) differ somewhat (41.31 and 38.22).

Ti in quartz

Five quartz grains from a sample of quartz-fayalite dike and five quartz grains from a sample of Mistastin rapakivi granite were analyzed for titanium concentrations in order to estimate

the temperature of crystallization. This was done using the TitaniQ thermometer of Wark and Watson (2006) with the more recent calibration of Thomas et al. (2010) that considers the effect of pressure.

The trace-element analysis of quartz was performed in the Department of Earth Sciences at the University of New Brunswick, Canada. The LA-ICP-MS system used was a Resonetics M-50 193nm excimer laser system connected, via Nylon tubing, to an Agilent 7700x quadrupole ICP-MS equipped with dual external rotary pumps. Quartz samples were ablated to produce 64 μm craters using a 5Hz repetition with the laser energy regulated at ~14 J/cm². The ICP-MS was operated at 1450W and a torch depth of 5.0 mm. Ion lens settings were tuned while rastering on NIST610 glass to achieve maximum sensitivity on ⁴⁷Ti and maintain oxide production (²⁴⁸ThO/²³²Th) to <0.4% and ²³⁸U/²³²Th ~1.05. An analysis comprised 60 s of background gas collection followed by 30 s of ablation. Dwell times for ²³Na (10 ms), ²⁷Al (10 ms), ³¹P (10 ms), ²⁹Si (10 ms), ⁴⁷Ti (100 ms), ⁴⁹Ti (100 ms), ⁹⁰Zr (10ms), and ⁹⁸Mo (10 ms) were set to achieve a total quadrupole sweep time of ~0.35 s yielding ~85 individual measurements in 30 s of ablation. Unknown samples were calibrated against silicate glass reference material, NIST610, with internal standardization using Si. The reference glass, NIST612, was used as

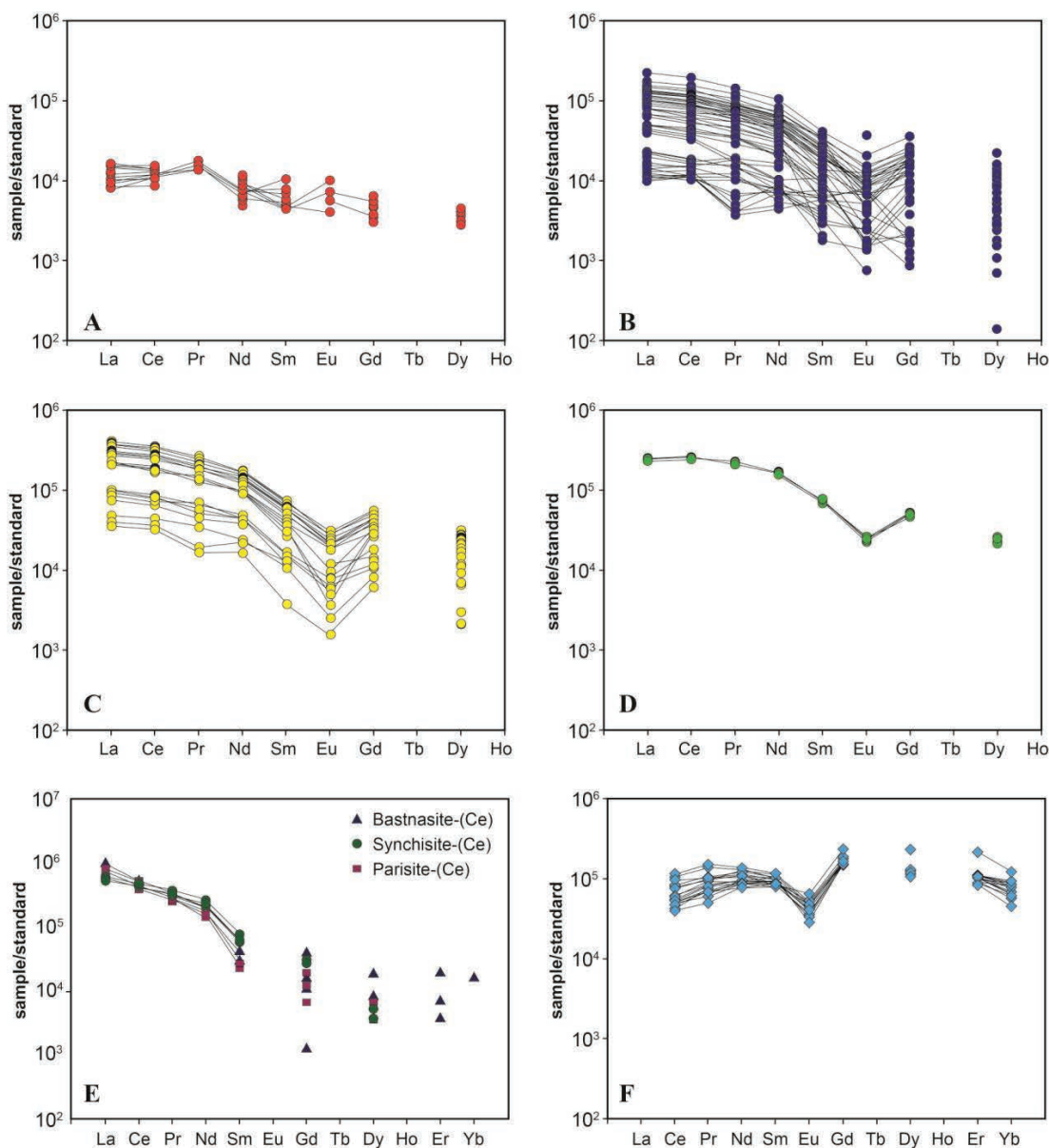


FIG. 16. Chondrite-normalized REE profiles for (A) Fluorapatite 1, (B) Fluorapatite 2, (C) Britholite-(Ce) 1, (D) Britholite-(Ce) 2, (E) REE fluorocarbonate minerals and (F) Fergusonite-(Y). The chondrite data are from (McDonough and Sun, 1995).

a quality control standard. The sequence of 35 spot analyses consisted of six analyses of NIST610 and five analyses of NIST612 evenly distributed among the unknown quartz samples. All data were reduced offline using Iolite v. 2.2 (Paton et al., 2011) under Wavemetrics IgorPro v. 6.22.

The titanium concentration of the quartz in the Mistastin granite ranges from 28.5 to 53.2 ppm, and averages 32 ppm, and in the quartz-fayalite dikes ranges from 23.0 to 27.6 ppm and averages 26 ppm (Table 9). As rutile is not present in either the Mistastin granite (there is trace of ilmenite) or the quartz-fayalite dikes (there is a trace of secondary magnetite with less than 1 wt % of Ti), we can assume that the Ti activity was <1. We therefore calculated temperature for values of Ti activity of 0.5 and 0.1 and for comparison also calculated it for unit Ti activity (Table 10). Temperatures were calculated

assuming a pressure of 3.5 kbar, which is the value estimated for the emplacement of the granitoids in the Nain plutonic suite (Emslie and Stirling, 1993). The use of this pressure is justified by our earlier observation that the Misery syenites pass gradually into the host rapakivi granites and monzonites of the Mistastin batholith. The average temperatures so calculated for the Mistastin rapakivi granite are 629° and 845°C for a_{Ti} values of 0.5 and 0.1, and for the quartz-fayalite dike sample are 591° and 787°C, respectively (Table 10). For comparison, the late-stage crystallization temperatures of granitoid rocks in the Nain Plutonic Suite are estimated to have been 750° to 850°C. Minimum temperatures for the Mistastin rapakivi granite and the quartz-fayalite dike, corresponding to the values for unit activity of Ti, are 560° and 528°C, respectively.

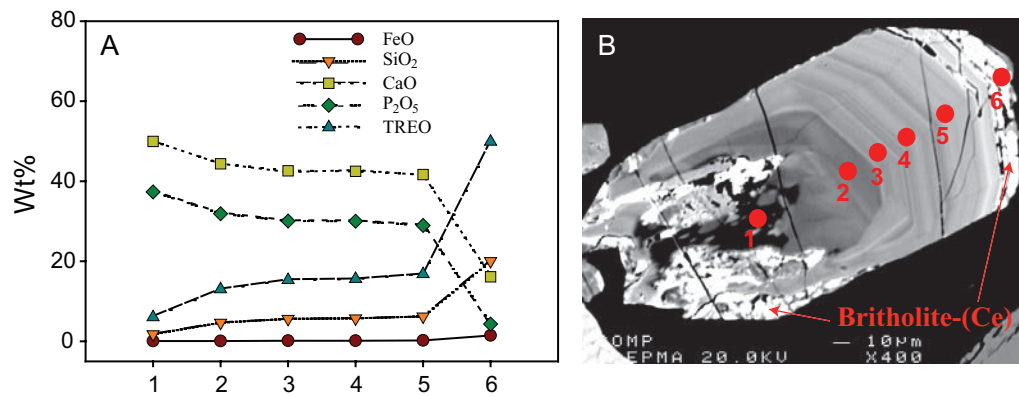


FIG. 17. Transect from core to rim across a fluorapatite 2 crystal that was replaced locally by britholite-(Ce) 1 in sample 205447. (A) shows the distribution of Ca, Si, P, REEs, and Fe (point 6 corresponds to britholite-(Ce) 1); (B) shows the location of the analyzed points on the fluorapatite 2 crystal.

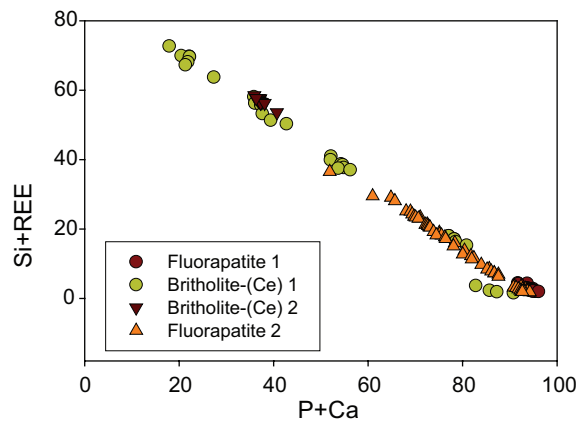


FIG. 18. A plot of P + Ca vs Si + REEs for the four types of apatite-group minerals from five different samples.

TABLE 9. Titanium Concentration in Quartz from Mistastin Granite and Quartz-Fayalite Dikes					
Rock type	Sample ID	Concentration		Error (2σ)	
		Si (CPS)	Ti (ppm)	Si	Ti
Granite (10-Lp-6717B)	Gran-G-5-r	14160000	41.9	760000	1.0
	Gran-G-5C	14750000	28.5	830000	0.6
	Gran-G-5r2	14990000	17.5	920000	0.7
	Gran-G-4-C	14790000	37.3	780000	1.0
	Gran-G-4-R	14780000	45.4	820000	1.4
	Gran-G-3-C	14580000	41.2	830000	0.9
	Gran-G-2-C	15630000	47.8	830000	1.0
	Gran-G-2-R	15770000	53.2	860000	1.1
Quartz-fayalite dikes (205494)	Gran-G-1-C	15180000	31.0	790000	1.7
	Dyke-G-5C	14560000	24.9	780000	1.5
	Dyke-G-5R_1	15230000	25.0	860000	0.8
	Dyke-G-4-C	15340000	27.0	770000	0.8
	Dyke-G-4R	13640000	24.1	650000	0.5
	Dyke-G-3-c	15990000	26.5	920000	0.5
	Dyke-G-3-r	15770000	25.2	840000	1.0
	Dyke-G-2C	16330000	25.2	740000	1.4
	Dyke-G-2r	15100000	23.0	840000	0.6
	Dyke-G-1	17250000	26.8	960000	0.6
	Dyke-G-1-r	16600000	27.6	1000000	0.7

Discussion

Parental magma to the Misery syenitic intrusion

As reported above, the Misery syenitic intrusion and the Mistastin granitoid rocks (rapakivi granite and monzonite) are characterized by extremely high FeO/FeO + MgO ratios (~0.92–0.98), high alkali and low CaO contents, and by high proportions of large-ion lithophile elements (LILE) and HFSE. Their compositions are thus consistent with A-type magmatism (Frost et al., 2001). Formation of these magmas has been attributed to three processes: (1) extreme differentiation of a mantle-derived tholeiitic magma, underplated beneath the crust, with or without crustal contamination (Barker et al., 1975; Frost et al., 2002; Kumar et al., 2007; Shellnutt and Zhou, 2008); (2) fractional crystallization of ferrodioritic magma residual to anorthosite crystallization (Scoates et al., 1996; Frost et al., 2002; Anderson et al., 2003); and (3) remelting of deep crustal material with or without mantle contamination (Emslie et al., 1994; Lubala et al., 1994; Magaji et al., 2011).

Based on the similarity of their Nd and Sr isotope compositions to those of the basement in the Churchill and Nain Provinces, the Nain Plutonic Suite granitoids have been interpreted to be the products of melting of the lower crust (Emslie et al., 1994). As the syenites of the Misery intrusion (ferrosyenite and the more felsic, fine-, medium-, and coarse-grained syenites) have similar trace element compositions to the granitoids of the Mistastin batholith, it is reasonable to propose that they had a similar origin (Fig. 12A). Both units are enriched in Nd and Th and depleted in Sr, Pb, Ba, and Eu, consistent with a crustal origin for the magma. A significant difference between the Mistastin granitoids and the Misery syenites is the higher HFSE and REE concentration of the syenites (Fig. 12B). This could indicate that the Misery syenites are a differentiated product of the Mistastin granitoids. Indeed, on a TAS diagram (Fig. 10), the Mistastin granitoid compositions lie along a line that trends toward the field of alkali-rich syenites. Furthermore, the group 3 syenites lie on this line, suggesting, as proposed earlier, that they represent hybridization of the Misery and Mistastin magmas. This line intersects the line defining the Misery fractional crystallization trend that produced the ferrosyenites and the fine-, medium-, and coarse-grained felsic syenites, supporting the

TABLE 10. Temperatures Obtained Using the TitaniQ Geothermometer (Thomas et al., 2010)

Titania activity		$\ln X^{\text{quartz-TiO}_2}$	$a\text{TiO}_2 = 1$ T(°C)	$a\text{TiO}_2 = 0,5$ T(°C)	$a\text{TiO}_2 = 0,1$ T(°C)
Rock type	Sample ID				
Granite (sample 10-Lp-6717B)	Gran-G-5-r	-8.7387	572	643	866
	Gran-G-5C	-9.1226	537	602	804
	Gran-G-5r2	-9.6121	497	555	733
	Gran-G-4-C	-8.8556	561	630	846
	Gran-G-4-R	-8.6577	580	652	880
	Gran-G-3-C	-8.7538	571	642	863
	Gran-G-2-C	-8.6062	585	658	889
	Gran-G-2-R	-8.4992	595	671	909
	Gran-G-1-C	-9.0392	544	611	817
	Average	-8.8305	560	629	845
Quartz-fayalite dikes (sample 205494)	Dyke-G-5C	-9.2583	526	589	783
	Dyke-G-5R_1	-9.2535	526	589	784
	Dyke-G-4-C	-9.1766	532	597	795
	Dyke-G-4R	-9.2918	523	586	778
	Dyke-G-3-c	-9.1968	531	595	792
	Dyke-G-3-r	-9.2463	527	590	785
	Dyke-G-2C	-9.2463	527	590	785
	Dyke-G-2r	-9.3372	519	581	772
	Dyke-G-1	-9.1863	532	596	794
	Dyke-G-1-r	-9.1546	534	599	799
	Average	-9.2334	528	591	787

suggestion that the Misery syenites were the products of differentiation of the Mistastin granitoid magma. The point of intersection of the two trends is interpreted to record the composition of the original Misery magma, which differentiated by fractional crystallization to produce ferrosyenites with low silica and alkali contents, and alkali-rich syenites, which crystallized from the residual liquid and have compositions corresponding to the alkali- and silica-rich end of the trend.

It follows from the above analysis that if the Mistastin granitoids were produced by melting of the lower crust, then the magma crystallizing the Misery syenites very likely was crustal in origin. This does not, however, explain the very high concentrations of incompatible elements such as Zr, Nb, REEs, and F in the syenites. We therefore propose, as did Martin (2006) to explain the origin of A-type granitoids, that the lower crust was metasomatised by mantle fluids prior to melting, and that this led to its enrichment in REEs, Zr, Nb, and F.

Magmatic evolution

The Misery syenites can be subdivided into three groups of rock: the ferrosyenite, the felsic syenites—including the fine-, medium- and coarse-grained syenites, which form much of the exposed intrusion—and late quartz-fayalite dikes. As the ferrosyenite displays cumulate textures with normal grading of fayalite, it is interpreted to have formed through the accumulation of ferromagnesian minerals as the result of gravitational settling. In the felsic syenites, the crystallization sequence was markedly different, as shown by the observation that the ferromagnesian minerals are interstitial to perthitic K-feldspar. This indicates that the ferromagnesian minerals must have crystallized from a residual, iron-rich melt phase.

As noted above, ferromagnesian minerals in both the ferrosyenite and the felsic syenites crystallized in the sequence: fayalite followed by hedenbergite and, in turn, by ferropargasite

or ferroedenite. The hedenbergite is a calcic clinopyroxene, whereas the ferropargasite and ferroedenite contain appreciable sodium. This reflects the evolution of the magma from more calcic to more sodic compositions during crystallization. We propose that the fractionation of ferromagnesian minerals to form the ferrosyenites depleted the residual magma in Fe. Consequently, the magmas that produced the felsic syenites were progressively enriched in alkalis and silica, and only became saturated in ferromagnesian minerals at a very late stage of crystallization, thereby explaining the interstitial crystallization of the ferromagnesian minerals.

Continued evolution through crystallization of perthite would have depleted the residual magma in alkalis and alumina and enriched it in iron and silica. In principle, this could have led to the magma that formed the quartz-fayalite dikes, although direct evidence for this has not been reported previously in the literature. Alternatively, as suggested by experimental studies of the system MgO-FeO-SiO_2 (Bowen and Schairer, 1935), the system $\text{SiO}_2\text{-KAlSi}_2\text{O}_6\text{-Fe}_2\text{SiO}_4$ (Roedder, 1951; Roedder, 1978; Visser and Koster Van Groos, 1979; Freestone and Powell, 1983), and more recently of the system $\text{SiO}_2\text{-KAlSi}_3\text{O}_8\text{-Fe}_2\text{SiO}_4\text{-CaO-MgO-TiO}_2\text{-P}_2\text{O}_5$ (Bogaerts and Schmidt, 2006), the magma may have exsolved an immiscible liquid highly enriched in Fe_2SiO_4 and silica and relatively impoverished in MgO and KAlSi_3O_8 . According to these studies, such a liquid would crystallize at very high temperature, well above that inferred for the Misery intrusion. However, high concentrations of fluxing agents such as fluorine and phosphorous would lower the solidus temperature considerably (Manning, 1981; London et al., 1993; Dolejs and Baker, 2007; Filiberto et al., 2012), possibly to that of the Misery intrusion. We therefore propose that the quartz-fayalite dikes crystallized from an FeO-SiO_2 -rich liquid that separated from a highly fractionated syenite magma enriched in iron and

silica and that this liquid preferentially sequestered rare metals such as Zr, Nb, and REEs (note that quartz and fayalite will react to form ferrosilite, but only at pressures above 10 kbar; Bohlen et al., 1980). If, however, this was not the case and the quartz-fayalite dikes were hydrothermal in origin, which seems unlikely as fluid inclusions were not observed in either the quartz or fayalite, then the temperature of their formation of $>528^{\circ}\text{C}$ (Table 10) makes it clear that these dikes formed at near-magmatic conditions.

The above interpretation of a magmatic origin for the quartz-fayalite dikes is supported by the composition of the ferromagnesian minerals, i.e., fayalite, hedenbergite, and the amphiboles. These minerals evolved from higher Mg number and Ti content in the ferrosyenite to lower contents of these elements and a correspondingly higher Fe content in the felsic syenites. Although fayalite is the only one of these ferromagnesian minerals in the quartz-fayalite dikes, it is significant that this fayalite has the highest Fe and lowest Mg content of any fayalite analyzed in the Misery intrusion (Table 2). The evolution of ferromagnesian minerals to higher Fe content is also observed within the felsic syenite rock group; the greater the enrichment in silica and alkalis, the greater the Fe enrichment of the ferromagnesian minerals (samples ML10001-107 and ML10006-46.15). The residual melt was therefore depleted in Mg but enriched in iron, silica, and alkalis consistent with the predictions of an experimental study by Bowen and Schairer (1935) that a magma of this type will evolve toward enrichment in iron and silica.

Hydrothermal activity

Hydrothermal alteration of the main rock-forming minerals (silicates) of the Misery syenites was limited to sodic metasomatism, which resulted in local replacement of K-feldspar by fine-grained albite, and ferroedenite or ferropargasite by arfvedsonite in the coarse-grained syenites. This was accompanied by the formation of secondary REE fluorocarbonates and a REE-, Ca-P-bearing phase with a composition close to that of britholite-(Ce), and is interpreted to have occurred as a result of the interaction of the rock with externally derived fluids, which equilibrated with the Mistastin granitoids. Such fluids initially would have been in equilibrium with K-feldspar and albite, but since they were heated by the Misery magma, they entered the field of stability of albite (Lagache and Weisbrod, 1977).

In contrast to the silicate minerals, fluorapatite was altered extensively to britholite-(Ce), thereby enriching the rocks in the REEs, as well as in Si and Fe (Table 8; Fig. 17). As the La/Ce, La/Nd, and La/Gd ratios are very similar for both minerals, we propose that the REEs added to form britholite-(Ce) were derived locally from the decomposition of fluorapatite. Considering that there appears to have been no hydrothermal alteration of the associated silicate minerals, it seems likely that the fluorapatite was more reactive than the silicate minerals, and that britholite-(Ce) formation occurred early, due to exsolution of small quantities of magmatic fluid during or immediately after crystallization of the magma. In the Pilansberg complex (South Africa) and the Eden Lake complex (Manitoba, Canada), britholite-(Ce) is also interpreted to have crystallized in an early postmagmatic stage, in those cases from a more evolved magma that reacted with existing

minerals (Arden and Halden, 1999; Liferovich and Mitchell, 2006).

HFSE mineralization

Magmatic concentration: Apatite is a common accessory phase in igneous rocks, and is one of the major accessory minerals in the Misery rock units. Locally, apatite-group minerals are concentrated in thin layers or pods of varying size, which most likely formed by gravity settling. These cumulates are composed mainly of fluorapatite 2 and britholite-(Ce) 1 and 2, and are very REE rich, containing up to 5.24 wt % TREO. Apatite-group minerals are able to incorporate appreciable proportions of a wide variety of cations and anions into their structures, including the REEs, preferentially the LREEs (Watson and Green, 1981; Roeder et al., 1987; Ronsbo, 1989; Pan and Fleet, 2002; Liferovich and Mitchell, 2006). Two types of magmatic apatite-group minerals have been observed in the Misery syenites: fluorapatite 1 and fluorapatite 2. The latter fluorapatite is much more enriched in REEs than fluorapatite 1 (an average of 10.74 wt % vs. 2.28 wt %) and its REE concentration increases from the cores to the rims of crystals. As the cores of fluorapatite 2, have the same composition as the unzoned fluorapatite 1 crystals, we conclude that fluorapatite 2 postdated fluorapatite 1. The progressive enrichment in the REEs (and silica) toward the margins of fluorapatite 2 crystals is interpreted to reflect a coupled substitution in which phosphorus and calcium were replaced by LREEs and Si according to the reaction $\text{LREE}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^5$ (Figs. 17, 18). This proposed substitution is supported by the interpreted evolution of the magma toward enrichment in silica and REEs. Substitutions of this type are observed widely in apatite-group minerals (Pan and Fleet, 2002), and have been documented for peralkaline intrusions, notably Ilímaussaq and Pilansberg (Ronsbo, 1989; Liferovich and Mitchell, 2006; Ronsbo, 2008). The significance of this substitution for the Misery intrusion is that it permitted fluorapatite 2 crystals to incorporate appreciable quantities of LREEs.

Although the crystallization of apatite-group minerals satisfactorily explains the magmatic enrichment of the Misery syenites in LREEs, it is the crystallization of the quartz-fayalite dikes that was responsible for the concentration of the HREEs, Zr, and Nb. These narrow dikes contain several vol % of fergusonite-(Y) and zircon or up to 2.27 wt % of TREO, 2.56 wt % ZrO_2 , and 1.48 wt % of Nb_2O_5 . As discussed above, they are interpreted to have crystallized from a rare metal-rich FeO-SiO_2 liquid that exsolved from a highly evolved syenite magma. The fergusonite-(Y) formed with zircon just prior to and during the crystallization of fayalite and quartz. Although this rock unit has only been observed as very narrow dikes, a major thrust of the ongoing exploration is to identify the larger magma bodies that seem likely to have fed these dikes.

Hydrothermal concentration: It was demonstrated above that fluorapatite crystals were partly or completely replaced by britholite-(Ce). Their crystallization occurred as a result of interaction of the fluorapatites with a syn- or postmagmatic hydrothermal fluid enriched in REEs, silica, and minor iron. This hydrothermal replacement was important for REE concentration at Misery Lake as britholite-(Ce) 1 and britholite-(Ce) 2 carry an average of 32.02 and 42.32 wt % of TREO, respectively. The enrichment led to the presence of 14 or 4

times more REEs in the crystal structure of britholite-(Ce) than in the precursor fluorapatite, respectively.

The other hydrothermal REE concentration at Misery Lake occurred in the sodically altered, coarse-grained syenite, which contains aggregates of britholite-(Ce) and REE fluorocarbonates, such as parisite-(Ce), synchysite-(Ce), and bastnäsite-(Ce). The crystallization of the latter (the REE fluorocarbonates) was due most likely to the presence of abundant REEs and F in the rock and magmatic fluids respectively, and the high concentrations of CO₂ in the external fluid responsible for the sodic metasomatization. The presence of these components in the fluid helped precipitate the REE fluorocarbonates. We propose that the REEs were mobilized as chloride complexes and precipitated REE fluorocarbonates during the decrease in pH and temperature that accompanied fluid-rock interaction (Williams-Jones et al., 2012).

Genetic Model

The Misery syenitic intrusion is part of an anorogenic complex, namely the Nain Plutonic Suite, and was emplaced contemporaneously with the Mistastin batholith, which, like many other members of the Nain Plutonic Suite, is composed of A-type granitoids. These intrusions represent magmas produced by melting of deep crustal rocks that had been enriched in incompatible elements, notably REEs, Zr, Nb, and volatiles like F, as a result of their interaction with mantle fluids. Evolution of the Misery magma proceeded through the concentration of early crystallizing ferromagnesian minerals that settled under gravity to form ferrosyenite. Accumulation of the ferromagnesian minerals caused depletion of the residual magma in iron and a relative enrichment in alkalis and silica. This magma crystallized coarse-, medium-, and fine-grained felsic syenites. In contrast to the ferrosyenite, in which ferromagnesian minerals were the early phases on the liquidus and perthite was an interstitial phase, the main liquidus mineral in the felsic syenites was perthite and the ferromagnesian minerals crystallized from a residual iron-enriched liquid. With continued crystallization of perthite, the magma eventually became highly depleted in both alkalis and alumina and evolved to a composition dominated by silica and iron and incompatible elements such as Zr, Nb, REEs, and F, and exsolved an immiscible silica- and iron-rich liquid into which Zr, Nb, REEs, and F partitioned preferentially. This last liquid represents the most evolved liquid at Misery Lake and crystallized to form quartz-fayalite dikes with elevated contents of zircon and fergusonite-(Y).

During magmatic crystallization, fluorapatite containing high concentrations of REEs accumulated by settling under gravity in ferrosyenite and also in felsic syenite. This mineral was partly or completely replaced by britholite-(Ce), which further concentrated the REEs during interaction of the rocks with magmatic hydrothermal fluids. Locally, the coarse-grained syenites were altered by external fluids that had previously equilibrated with the host granitoids. Owing to the higher temperature of the syenites, these fluids albited the perthite, forming microcrystalline albite, and remobilized the REEs in the rocks, crystallizing britholite-(Ce), monazite-(Ce) and REE fluorocarbonate minerals.

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