

Chemostratigraphy at the Brunswick No. 6 Volcanic-Sediment-Hosted Massive Sulfide Deposit, New Brunswick: Resolving Geometry from Drill Core in Deformed Felsic Volcanic Rocks

A.O. WILLS¹, D.R. LENTZ¹, AND G. ROY²

(Received March 31, 2003; accepted December 2, 2006)

Abstract — Diamond-drill hole DDH-B357, located 1.5 km north of the Brunswick No. 6 Zn-Pb-Cu-Ag volcanic-sediment-hosted massive sulfide (VSHMS) deposit, intersects three exhalative horizons within variably altered felsic volcanic rocks of the Nepisiguit Falls and Flat Landing Brook formations. These three petrographically indistinguishable iron formation intervals ($\text{Fe}_2\text{O}_3^T \geq 21.4$ wt.%) likely represent cogenetic hydrothermal sedimentary units because they display a common geochemical signature: $\text{Fe}_2\text{O}_3^T = 42.9 \pm 10.5$ wt.%, $\text{MnO} = 5.4 \pm 3.1$ wt.%, elevated base metal values ($\text{Zn}+\text{Pb} = 1999 \pm 1091$ ppm), strong enrichment in additional exhalative components ($\text{CaO} = 5.3 \pm 3.9$ wt.%; $\text{P}_2\text{O}_5 = 1.43 \pm 1.00$ wt.%), oxidized signature ($\text{Fe}/\text{Mn} = 10 \pm 6$), as well as a common immobile element signature ($\text{Zr}/\text{TiO}_2 = 0.025 \pm 0.007$) representative of a pelagic source. The calc-alkaline to transitional host volcanic rocks can be discriminated by Zr/TiO_2 , and to a lesser extent by Th/Nb : Nepisiguit Falls Formation: $\text{Zr}/\text{TiO}_2 = 0.053 \pm 0.004$, $\text{Th}/\text{Nb} = 1.08 \pm 0.37$; Flat Landing Brook Formation: $\text{Zr}/\text{TiO}_2 = 0.107 \pm 0.043$, $\text{Th}/\text{Nb} = 0.86 \pm 0.17$. A symmetrical repetition of the footwall–iron formation–hanging wall stratigraphic sequence is observed in DDH-B357, with distinct felsic volcanic rock domains separated by the three iron formations. This is best explained by parasitic F_2 folds on the west flank of the south-plunging Brunswick antiform, similar to the fold closures known to host massive sulfide accumulations in the Brunswick No. 6 and No. 12 mines. Iron formation geochemistry and felsic volcanic rock chemostratigraphy from drill core sampling can provide an effective mineral exploration tool for the structurally complex rocks of the Bathurst Mining Camp. © 2007 Canadian Institute of Mining, Metallurgy and Petroleum. All rights reserved.

Key Words: Massive sulfide deposit, Iron formation, Felsic volcanic rocks, Geochemistry, Chemostratigraphy, Deformation, Brunswick No. 6, Bathurst Mining Camp.

Sommaire — Le forage au diamant DDH-B357, situé à 1.5 km au nord du gisement de Sulfures Massifs à Encaissant Volcanique et Sédimentaire (SMEVS) de Zn-Pb-Cu-Ag Brunswick No. 6 recoupe trois horizons exhalatifs au sein des roches volcaniques felsiques diversement altérées des formations de Nepisiguit Falls et de Flat Landing Brook. Ces trois intervalles de formation de fer, impossibles à distinguer pétrographiquement les uns des autres, représentent vraisemblablement des unités sédimentaires hydrothermales cogénétiques sur la base de leur signature géochimique commune: $\text{Fe}_2\text{O}_3^T = 42.9 \pm 10.5$ % poids, $\text{MnO} = 5.4 \pm 3.1$ % poids, des teneurs élevées en métaux usuels ($\text{Zn}+\text{Pb} = 1999 \pm 1091$ ppm), un fort enrichissement en composantes exhalatives additionnelles ($\text{CaO} = 5.3 \pm 3.9$ % poids; $\text{P}_2\text{O}_5 = 1.43 \pm 1.00$ % poids), une signature oxydée ($\text{Fe}/\text{Mn} = 10 \pm 6$), ainsi qu'une signature d'éléments immobiles communs ($\text{Zr}/\text{TiO}_2 = 0.025 \pm 0.007$) indicative d'une source pélagique. Les roches volcaniques encaissantes calco-alkalines à transitionnelles peuvent être reconnues par leur rapport Zr/TiO_2 , et à un moindre degré par leur rapport Th/Nb : Formation de Nepisiguit Falls: $\text{Zr}/\text{TiO}_2 = 0.053 \pm 0.004$, $\text{Th}/\text{Nb} = 1.08 \pm 0.37$; Formation de Flat Landing Brook: $\text{Zr}/\text{TiO}_2 = 0.107 \pm 0.043$, $\text{Th}/\text{Nb} = 0.86 \pm 0.17$. Une répétition symétrique de la séquence stratigraphique Mur–Formation de Fer–Toit a été observée dans le forage DDH-B357, avec des domaines distincts constitués de roches volcaniques felsiques séparés par les trois formations de fer. La meilleure explication est que le flanc ouest de l'anticlinal Brunswick à plongée sud est affecté par des plis parasites F_2 , similaires aux zones de charnière contenant les sulfures massifs des mines Brunswick No. 6 et No. 12. La géochimie des formations de fer et la chemostratigraphie des roches volcaniques felsiques en forage peuvent fournir un outil d'exploration minérale efficace dans les roches structuralement complexes du Camp Minier de Bathurst. © 2007 Canadian Institute of Mining, Metallurgy and Petroleum. All rights reserved.

¹Department of Geology, University of New Brunswick, P.O. Box 4400, Fredericton, New Brunswick, E3B 5A3.

²Xstrata Zinc plc., Exploration, Box 899 Matagami, Quebec J0Y 2A0.

Introduction

The polydeformed Bathurst Mining Camp (BMC) in northeastern New Brunswick contains many volcanic-sediment-hosted massive sulfide (VSHMS) deposits, including the “super-giant” Brunswick No. 12 Zn-Pb-Ag-Cu mine that originally contained over 229 Mt of sulfide ore (7.66 wt.% Zn, 3.01 wt.% Pb, 0.46 wt.% Cu, and 91 g/t Ag; McCutcheon et al., 2003). The smaller and slightly lower-grade Brunswick No. 6 deposit comprised 12.2 Mt of 5.43 wt.% Zn, 2.15 wt.% Pb, 0.40 wt.% Cu, and 67 g/t Ag (Luff, 1995). These deposits and many others in the BMC are associated with an Algoma-type iron formation (Gross and McLeod, 1980), the so-called Brunswick horizon, which lies stratigraphically between the Lower to Middle Ordovician Nepisiguit Falls and Flat Landing Brook formations of the Tetagouche Group. Iron formations within the Brunswick horizon have been studied extensively (Saif, 1983; Troop, 1984; Peter and Goodfellow, 1996; Peter, 2003) and can be readily identified both geochemically and petrographically.

Chemostratigraphic analysis has been successfully used to distinguish between felsic volcanic rocks of the Nepisiguit Falls and Flat Landing Brook formations in the BMC (Lentz, 1996a, 1996b; Lentz et al., 1997), where the distribution of units has been complicated by five phases of deformation (van Staal, 1992a, 1994; van Staal and de Roo, 1995). Primary petrographic textures are partially obscured by regional biotite-grade greenschist metamorphism (van Staal and Williams, 1984) with varying degrees of deformation and resultant mobile-element mass change (Lentz and van Staal, 1995; Lentz, 1999a). Ratios of elements that are relatively immobile during hydrothermal alteration can be used geochemically to constrain the origins of felsic volcanic rocks (see Jenner, 1996). These ratios include Zr/Y (Leshner et al., 1986; MacLean and Barrett, 1993), Th/Nb (Gorton and Schandl, 2000; Schandl and Gorton, 2002), and Zr/TiO₂ (Winchester and Floyd, 1977; Petersen, 1983; Lavery, 1985; MacLean and Barrett, 1993). Although the felsic volcanic rocks of the Nepisiguit Falls and Flat Landing Brook formations are quite similar in terms of bulk composition, Zr/TiO₂ serves as a reliable chemostratigraphic discriminator (Lentz et al., 1997; Lentz, 1999b).

Diamond-drill hole (DDH) B357, collared in felsic volcanic rocks of the Flat Landing Brook Formation approximately 1.5 km northwest of the Brunswick No. 6 deposit (Fig. 1), intersects three intervals of iron formation within variably altered felsic volcanic and volcanosedimentary rocks. There has been debate as to whether these iron formations represent separate depositional events or structural repetitions of one horizon. This study was undertaken to: (1) characterize geochemically the iron formation intervals in DDH-B357; (2) evaluate their position within the context of the felsic-volcanic rock stratigraphy using known geochemical signatures for the Nepisiguit Falls and Flat Landing Brook formations; (3) demonstrate whether the exhalative units belong to a single stratigraphic horizon

(i.e., the Brunswick horizon); and (4) validate the structural interpretation of the area north of Brunswick No. 6.

Geological Setting

The Brunswick No. 6 mine is located in the eastern part of the BMC, approximately 9 km to the south of the Brunswick No. 12 deposit along the Brunswick Belt (Fig. 1). These deposits are hosted within the Tetagouche Group, a Late Ordovician bimodal volcanic complex that formed within the Tetagouche-Exploits back arc basin (Okinawa-type) along the Gander margin of Avalon (van Staal, 1987, 1994; Rogers and van Staal, 1997; Whalen et al., 1997; van Staal et al., 2003). The Tetagouche Group bimodal volcanic rocks were deposited on Patrick Brook Formation pelagic and siliciclastic sedimentary rocks of the Mirimachi Group flysch apron (Goodfellow and Peter, 1996). The volcanic stratigraphy of the Tetagouche Group consists mostly of rhyodacitic volcanic and volcanoclastic rocks of the Nepisiguit Falls Formation, and younger rhyolite flows and rhyolitic volcanoclastic/hyaloclastic rocks of the Flat Landing Brook Formation. Subsequent rifting of this sequence resulted in the eruption of alkali basalt flows of the Little River Formation (Rogers et al., 2003).

The Nepisiguit Falls Formation (469 ± 2 Ma, U-Pb zircon; Sullivan and van Staal, 1995) consists predominantly of variably altered quartz- and feldspar-phyric crystal tuffs (Fig. 2a) and felsic volcanosedimentary rocks, locally graded and reworked into beds of varying thickness (van Staal et al., 1992; Goodfellow and McCutcheon, 2003). The coarse-grained quartz-feldspar-phyric tuffs represent explosively erupted deep-water pyroclastic rocks (Downey and Lentz, 2006), whereas fine-grained ash tuff and associated sedimentary rocks are more likely water-settled deposits (see Stix, 1991; Cas, 1992; Gibson et al., 1999). Fine-grained sedimentary rocks (Fig. 2b) are locally present in the upper part of the Nepisiguit Falls Formation, notably in the immediate vicinity of both the Brunswick No. 12 and No. 6 deposits. These rocks underlie, and are laterally equivalent to the massive sulfides and associated iron formation of the Brunswick Horizon, and are interpreted to be deposited in fault-bounded grabens and half grabens (Lentz, 1999b). Syn-sedimentary normal faults likely served as conduits for evolved hydrothermal brines in the formation of the BMC deposits (McCutcheon, 1992; Goodfellow and McCutcheon, 2003), akin to the Miocene Kuroko deposits, which occur within subsidence-related marginal depressions near volcanic centers (Scott, 1978; Franklin et al., 1981). The spatial relationship between fine-grained Nepisiguit Falls sedimentary rocks and massive sulfide accumulations, where the geometry can be resolved, has mineral exploration relevance for the BMC.

The Flat Landing Brook Formation (466 ± 2 Ma, U-Pb zircon; Sullivan and van Staal, 1990) is composed of massive, aphyric to sparsely quartz-feldspar-phyric rhyolite flows, domes, fragmental rhyolite, hyalotuffs, and reworked

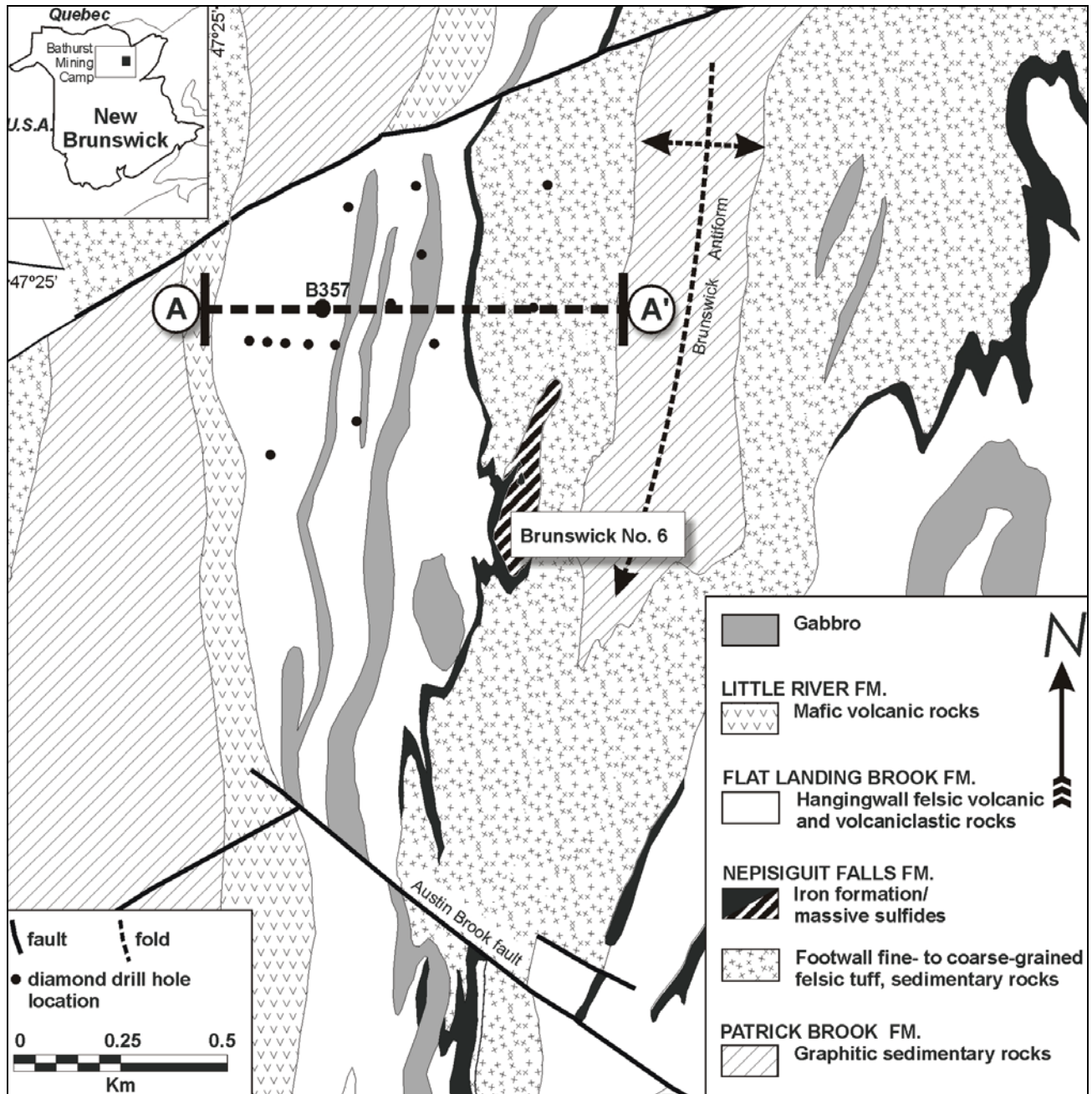


Fig. 1. Geology of the Brunswick No. 6 mine area, Bathurst Camp, New Brunswick (after van Staal, 1992a). The study area northwest of the deposit shows collar positions for several drillholes, including DDH-B357. The vertical cross section shown in Fig. 8 is labeled A–A'.

volcanoclastic debris (see Cas, 1992; McCutcheon, 1992). Fine-grained, schistose, sedimentary and tuffaceous rocks, ascribed to the Flat Landing Brook Formation, form the hanging-wall sequence at the Brunswick No. 12 deposit, where rhyolite flows are absent. It can be difficult to distinguish petrographically between fine-grained sedimentary rocks of the Nepisiguit Falls (Fig. 2b) and Flat Landing Brook (Fig. 2c) formations, which makes their geochemical discrimination particularly important. Mafic

volcanic and associated sedimentary rocks (457 ± 1 Ma; Sullivan and van Staal, 1995) of the Little River Formation overlie the Flat Landing Brook volcanic pile, and constitute the upper portion of the Tetagouche Group.

Iron formation in the Brunswick Horizon has been differentiated into sulfide, carbonate, oxide, and silicate facies (see Gross and McLeod, 1980) based on the predominant exhalative sediment mineralogy (Bhatia, 1970; Saif, 1983; Peter and Goodfellow, 1996; Peter, 2003). The

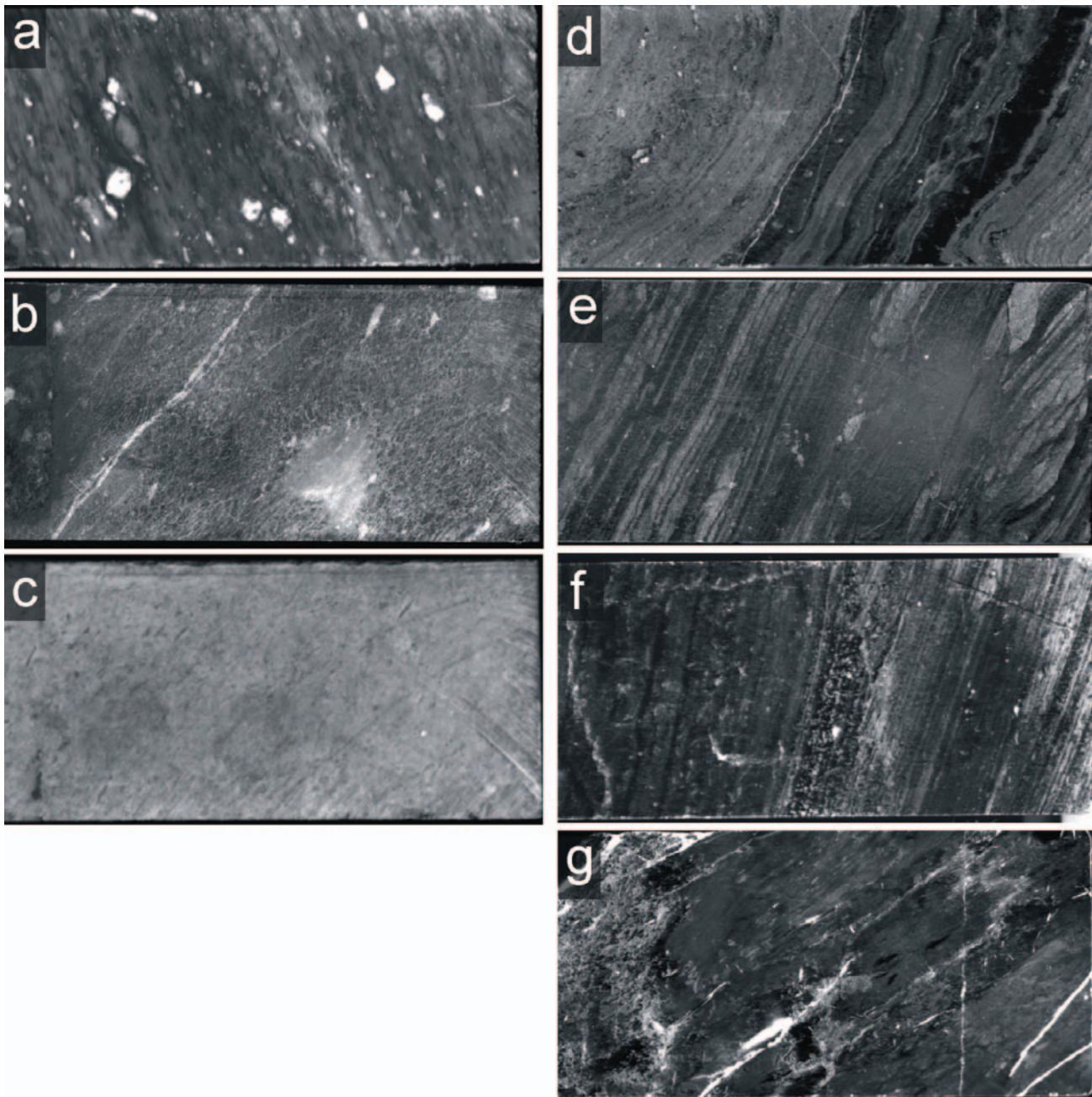


Fig. 2. Photographs of DDH-B357 core samples: *a.* Nepisiguit Falls Formation quartz-feldspar crystal tuff (downhole depth = 474.0 m); *b.* Nepisiguit Falls Formation felsic volcanosedimentary rock with quartz crystal fragments (downhole depth = 235.3 m); *c.* Flat Landing Brook altered aphyric rhyolite (downhole depth = 285.0 m); *d.* Iron formation IF-A (downhole depth = 435.9 m); *e.* IF-B (downhole depth = 312.4 m); *f.* IF-C (downhole depth = 245.5 m); *g.* Strongly chlorite-altered Flat Landing Brook rock associated with gabbro intrusion (downhole depth = 147.5 m). Each photograph measures 9.3 cm across.

close relationship between iron formation and massive sulfide deposits in the Brunswick horizon was first noted by McAllister (1960). It remains the most relied on geochemical, geophysical, and structural marker horizon for the exploration of massive sulfides in the BMC. This Algoma-type sulfide-carbonate-oxide-silicate iron formation is considered to be a time-stratigraphic, distal-facies equivalent to massive sulfide horizons in the Brunswick horizon (Peter and Goodfellow, 1996; Peter, 2003), and marks a hiatus in volcanism between the deposition of the distinct Nepisiguit Falls (footwall) and Flat Landing Brook (hanging wall) formations.

Multiple iron formation units were identified in several diamond-drill holes, including DDH-B357 (Fig. 1), situated immediately north of the Brunswick No. 6 mine. These were initially logged as separate exhalative units at discrete stratigraphic levels within the Flat Landing Brook felsic volcanic pile, possibly representing multiple periods of volcanic quiescence. Alternatively, fold or thrust repetitions of a single Brunswick horizon may account for these multiple iron formation intervals.

Samples and Analytical Methods

A total of 56 samples were collected from DDH-B357 to characterize geochemically the felsic volcanic and volcanosedimentary host rocks, and the multiple iron-rich protoliths identified in drill core. Samples from the felsic volcanic units separating iron formations were selected with the objective of establishing a chemostratigraphic footwall–iron formation–hanging wall sequence based on geochemical rather than petrographical criteria.

Samples of drill core from DDH-B357 were collected to avoid quartz veining, gouge, and severe chlorite/sericite alteration. A 20-cm split section was retained for the preparation of polished slabs, and the remaining material was crushed and pulverized in a soft-steel swingmill. Samples were analyzed for SiO₂, TiO₂, Al₂O₃, Fe₂O₃^T, MnO, Na₂O, Ba, Ga, Nb, Rb, Sr, Y, and Zr by X-ray fluorescence spectrometry (XRF) at Memorial University of Newfoundland, using a pressed-pellet technique (see Longerich, 1995). Additional trace element data were obtained from Activation Laboratories in Ancaster, Ontario, using a combination of inductively coupled plasma-emission spectrometry (ICP-ES) and instrumental neutron activation analysis (INAA) methods, together providing sensitive detection for elements with very low concentrations, such as the high field strength elements used in this study. MgO, CaO, K₂O, P₂O₅, S, Cd, Cu, Ni, Pb, V, and Zn were obtained from ICP-ES, and As, Co, Cr, Cs, Sb, Sc, Th, U, La, Ce, Nd, Sm, Eu, Yb, and Lu were analyzed by INAA. An in-house standard, IF-1 (Lentz, 1995), was submitted in multiple to monitor analytical accuracy and precision. The standard deviations of analytical results compared to the IF-1 composition indicate that major element values have less than 6% relative error, except for MgO, which has 18%. Trace elements tend to have higher error values than major

elements, particularly those of low abundance. However, most deviate less than 20% from the IF-1 standard. Geochemical data for the rock units intersected by DDH-B357 are given in Table 1.

Nepisiguit Falls rocks occur as coarse-grained quartz-alkali feldspar crystal tuffs (Fig. 2a) in the lower core section. However, aphyric Nepisiguit Falls rocks (Fig. 2b) can be petrographically very similar to the fine-grained Flat Landing Brook rhyolitic tuffs (Fig. 2c), with variable proportions of sericite and chlorite alteration both having endured pervasive upper greenschist-grade metamorphism (Lentz, 1999b). Such visually indistinguishable medium-gray, non-magnetic, aphyric volcanosedimentary rock units are situated immediately downhole, between, and above the iron formation intersections in DDH-B357, and were sampled where quartz veining, faulting, and chlorite/sericite alteration is minimal.

Samples from the iron formation units in DDH-B357 (Fig. 2d–f) are generally dark green to black, strongly magnetic, very dense, and composed of laminated cryptocrystalline quartz, magnetite, sulfides, chlorite, and subsidiary siderite. The three iron formation intersections are made up of millimeter- to meter-scale bands, commonly in sharp contact with their adjacent felsic volcanic host rocks, although there are also chlorite-altered transition zones extending both uphole and downhole into the felsic rocks. Petrographical and mineralogical differentiation of the three iron formation intervals in DDH-B357 is not possible because they are texturally very similar. A chloritite unit (Fig. 2g), which is non-magnetic, massive (not laminated), and composed mostly of dark green to black chlorite, was sampled to determine whether it was a chloritic exhalative horizon or altered Flat Landing Brook rock. It was deemed to be non-exhalative based on geochemistry (see below).

The iron formation samples were re-examined after their geochemical compositions were obtained, selectively considering only samples meeting the compositional criterion of Gross and McLeod (1980; Fe^T ≥ 15.0 wt.%, equivalent to Fe₂O₃^T ≥ 21.4 wt.%, where Fe₂O₃^T indicates total iron calculated as Fe₂O₃). The most iron-rich samples (Fe₂O₃^T up to 61.6 wt.%), taken from the three iron formation intersections, consist of massive to banded magnetite and chert with subordinate carbonate (siderite) laminae. Slightly less iron-rich samples (Fe₂O₃^T = 30.1 to 35.8 wt.%) are dominated by chlorite and/or siderite with substantial magnetite, and are locally weakly to moderately magnetic. The least iron-rich of the iron formation samples (Fe₂O₃^T = 21.4 to 25.8 wt.%) tend to be combinations of laminated dark green and black chlorite, buff siderite, and chert, and are non-magnetic to weakly magnetic. The less well-developed chemical sedimentary rocks, which occur as transition zones or as felsic detritus-bearing layers within the iron formation intervals, are dominated by laminated siderite or chert-chlorite, but fall below the iron formation compositional cut-off of Fe₂O₃^T ≥ 21.4 wt.%.

Geochemistry

Felsic Volcanic Host Rocks

The Nepisiguit Falls and Flat Landing Brook felsic volcanic rocks encountered in DDH-B357 are at first glance compositionally similar based on whole-rock major and trace element geochemistry (Table 1). Caution must therefore be employed in differentiating the samples into two groups based on geochemical differences. For example, the range of SiO₂ abundances among the Nepisiguit Falls and Flat Landing Brook samples cannot distinguish the Flat Landing Brook (72.6 ± 5.8 wt.% SiO₂; Lentz, 1999b) and Nepisiguit Falls rocks (68.8 ± 5.3 wt.% SiO₂; Lentz, 1999b). The mass addition or removal of a mobile component during hydrothermal alteration, such as SiO₂, obscures original rock composition. Other elements that are mobile during low- to high-temperature sub-seafloor hydrothermal alteration (Fe, Mn, Mg, Ca, Na, K, P) may have had their abundances significantly shifted from original compositions. However, high field strength elements (HFSE), such as Ti, Nb, Th, Zr, and Y, are considered immobile under most hydrothermal alteration conditions, and subtle differences in their abundances can be reliably used to identify and differentiate felsic volcanic units (MacLean and Barrett, 1993; Jenner, 1996).

Data listed in Table 1 show that, relative to Nepisiguit Falls, Flat Landing Brook samples tend to have higher abundances of Zr (Nepisiguit Falls = 312 ± 74 ppm, Flat Landing Brook = 440 ± 74 ppm), Nb (Nepisiguit Falls = 16 ± 3 ppm, Flat Landing Brook = 23 ± 6 ppm), Y (Nepisiguit Falls = 43 ± 3 ppm, Flat Landing Brook = 55 ± 14 ppm), and Th (Nepisiguit Falls = 16.3 ± 4.6 ppm, Flat Landing Brook = 19.6 ± 3.2 ppm); whereas Flat Landing Brook samples have lower TiO₂ contents (Nepisiguit Falls = 0.57 ± 0.12 wt.%, Flat Landing Brook = 0.46 ± 0.15 wt.%). However, more diagnostic and statistically more reliable comparative trace element abundances are expressed in the ratios Zr/TiO₂ (Nepisiguit Falls = 0.053 ± 0.004, Flat Landing Brook = 0.107 ± 0.043) and Th/Nb (Nepisiguit Falls = 1.08 ± 0.37, Flat Landing Brook = 0.86 ± 0.17 ppm).

The schematic Zr/TiO₂ versus Y/TiO₂ diagram (Fig. 3a) is used to determine the magmatic affinity of the felsic volcanic Nepisiguit Falls and Flat Landing Brook formations intersected in DDH-B357. Although both plot within a comparable calc-alkaline to transitional range, the Flat Landing Brook Formation (Y/TiO₂ = 0.014 ± 0.010 ppm) is slightly more calc-alkaline than Nepisiguit Falls (Y/TiO₂ = 0.009 ± 0.003 ppm). Mildly calc-alkaline felsic magmas fractionate immobile elements (Ti and Zr) in a predictable way to provide an idealized fractionation curve (Fig. 3b), the intersection with which indicates that Nepisiguit Falls rocks are rhyodacitic (Zr/TiO₂ = 0.053 ± 0.004) and Flat Landing Brook rocks are rhyolitic (Zr/TiO₂ = 0.107 ± 0.043) in composition (MacLean and Barrett, 1993). This is generally consistent with the rhyodacite-rhyolite (total alkali–silica) nomenclature of the least-altered samples. Samples from the

three intervals of iron formation share Zr/TiO₂ signatures (IF-A = 0.025 ± 0.005; IF-B = 0.026 ± 0.011; IF-C = 0.027 ± 0.008), differentiating them from either Nepisiguit Falls or Flat Landing Brook rocks. Chloritite samples exhibit an affinity (Zr/TiO₂ = 0.061 ± 0.030) with the Flat Landing Brook rocks (Fig. 3b). Zr/TiO₂ is very effective in discriminating between the felsic volcanic rocks of the Nepisiguit Falls and Flat Landing Brook formations (Fig. 3c), whereas Th/Nb is somewhat less successful in revealing subtle compositional differences between them (Fig. 3d).

Iron Formations

Bhatia (1970), Saif (1983), Troop (1984), Peter and Goodfellow (1996), and Peter (2003) have geochemically and spatially related iron formation to the large VSHMS deposits along the Brunswick horizon. These results provide a basis for the characterization of iron formation in this study. Apart from petrographic differences, the three units of iron formation intersected in DDH-B357 (IF-A, IF-B, and IF-C; see Table 1) are easily distinguished from their felsic volcanic host rocks most notably by their higher abundances of Fe₂O₃^T (IF-A = 45.0 ± 10.9 wt.%; IF-B = 43.7 ± 7.7 wt.%; IF-C = 34.8 ± 11.6 wt.%), as well as elevated abundances of MnO, P₂O₅, S, As, Co, Cu, Ni, Pb, Sb, Sr, V, and Zn (see Table 1). The iron formation intervals are characterized by low abundances of TiO₂, Al₂O₃, Nb, Sc, Th, and Zr. A fourth iron-rich interval (Fe₂O₃^T = 28.8 ± 4.7 wt.%), classified as a chloritite (altered version of Flat Landing Brook Formation), is notably low in MnO, P₂O₅, As, Co, Pb, Sr, and Zn, as well as being petrographically distinct (Fig. 2). Although the chloritite is located within the Flat Landing Brook Formation, it is spatially associated with a gabbro intersection in DDH-B357. The gabbro is geochemically distinct with particularly elevated TiO₂ (1.02 ± 0.23 wt.%) and Al₂O₃ (15.8 ± 2.9 wt.%), but low SiO₂ (51.2 ± 8.8 wt.%) and Fe₂O₃^T (3.6 ± 1.0 wt.%) contents.

An interelement cluster dendrogram (Fig. 4) for the iron formation samples (*n* = 23), demonstrates the relationship between components introduced from hydrothermal, terrigenous, and mixed-input sources (see Troop, 1984; Peter, 2003). The iron formation compositions display strongest correlation among the hydrothermally enriched components (Fe₂O₃^T, MnO, CaO, As, Ba, Cd, Cu, Pb, S, Sb, Sr, V, and Zn) relative to their felsic host rocks. Detrital oxide and aluminosilicate fragments and clay minerals, attributed to terrigenous material, contribute TiO₂, Al₂O₃, Hf, Nb, Sc, Th, and Zr, which are not easily transported by hydrothermal processes. Uranium and MgO exhibit strong Pearson Product correlation with Zr due to the presence of detrital ferromagnesian minerals (Peter and Goodfellow, 1996), whereas Y, La, Ce, Nd, Sm, Yb, and Lu are introduced predominantly from terrigenous material, but may partially be related to the skeletal remains of marine organisms (Troop, 1984; Peter and Goodfellow, 1996). The contents of SiO₂, Na₂O, K₂O, Co, Cs, Eu, Ni, and Rb are highly variable in the iron formation samples, and were likely introduced from

Table 1. Whole-Rock Major and Selected Trace Element Geochemical Data for Rock Units Identified in DDH-B357*

	NF			FLB			IF-A			IF-B			IF-C			Gabbro			Chloritite		
	\bar{x}	1s	n	\bar{x}	1s	n	\bar{x}	1s	n	\bar{x}	1s	n	\bar{x}	1s	n	\bar{x}	1s	n	\bar{x}	1s	n
wt. %:																					
SiO ₂	69.44	3.63	10	67.84	6.21	15	32.53	7.70	13	35.67	5.03	6	38.41	9.30	4	51.20	8.83	4	61.97	5.01	4
TiO ₂	0.57	0.12	10	0.46	0.15	15	0.26	0.20	13	0.22	0.11	6	0.25	0.14	4	1.02	0.23	4	0.09	0.03	4
Al ₂ O ₃	14.49	1.55	10	16.55	3.18	15	4.70	3.74	13	3.92	2.86	6	4.51	2.84	4	15.79	2.88	4	3.65	1.04	4
Fe ₂ O ₃ ^T	4.23	1.62	10	4.84	2.75	15	44.99	10.86	13	43.67	7.67	6	34.83	11.57	4	10.82	3.01	4	28.80	4.75	4
MnO	0.14	0.08	10	0.12	0.07	15	5.59	3.31	13	5.83	3.16	6	4.11	2.68	4	0.36	0.43	4	0.25	0.09	4
MgO	1.82	0.82	10	2.13	1.94	15	2.14	1.67	13	1.71	0.82	6	2.66	1.58	4	3.29	1.29	4	1.25	0.44	4
CaO	1.34	1.29	10	1.02	0.79	15	4.70	2.82	13	5.17	3.66	6	7.40	6.92	4	7.62	5.16	4	1.19	1.50	4
Na ₂ O	3.01	0.65	10	2.31	1.11	15	0.39	0.23	13	0.52	0.12	6	0.47	0.14	4	2.06	1.48	4	0.72	0.13	4
K ₂ O	4.43	1.39	10	5.38	1.67	15	0.43	0.35	13	0.80	0.27	6	1.45	1.28	4	3.43	1.30	4	1.10	0.26	4
P ₂ O ₅	0.13	0.06	10	0.11	0.05	15	1.69	1.22	13	1.35	0.42	6	0.71	0.34	4	0.16	0.09	4	0.06	0.04	4
S	0.04	0.03	5	0.15	0.34	10	0.20	0.18	13	0.29	0.46	6	0.43	0.78	4	0.01	0.01	4	0.43	0.53	4
ppm:																					
Ag (ppm)	0.7	0.4	5	1.0	0.5	10	0.2	0.1	13	0.2	0.1	6	0.2	0.0	4	0.2	0.0	4	0.2	0.0	4
As	8.8	8.5	5	21.1	46.3	10	97.2	149.6	13	70.2	84.8	6	477.1	855.7	4	20.7	39.4	4	8.3	14.8	4
Ba	635	138	10	687	287	15	454	363	13	118	35	6	131	53	4	383	178	4	149	58	4
Cd	0.2	0.0	5	0.2	0.2	10	1.6	1.1	13	1.4	1.0	6	1.2	1.0	4	0.7	0.5	4	0.3	0.2	4
Co	9	3	10	10	21	15	22	12	13	19	6	6	33	24	4	29	14	4	6	5	4
Cr	53	24	10	25	25	15	36	21	13	24	5	6	25	11	4	171	279	4	9	6	4
Cs	5	2	5	7	6	10	15	16	13	23	7	6	31	11	4	14	7	4	36	12	4
Cu	11	6	5	11	7	10	36	20	13	62	93	6	38	62	4	16	24	4	53	57	4
Ga	17	3	10	22	8	15	11	4	13	8	9	6	13	7	4	18	2	4	1	2	4
Nb	16	3	10	23	6	15	8	5	13	7	3	6	6	2	4	10	6	4	4	2	4
Ni	13	11	10	14	25	15	45	18	13	47	15	6	45	18	4	47	27	4	32	30	4
Pb	54	99	10	54	67	15	1774	1278	13	1739	511	6	1216	1050	4	37	20	4	10	12	4
Rb	107	30	10	165	74	15	30	28	13	69	18	6	101	50	4	176	73	4	110	29	4
Sb	1.6	0.5	5	1.9	1.2	10	4.3	2.6	13	8.6	4.6	6	8.9	7.7	4	1.8	1.1	4	3.6	3.0	4
Sc	13.0	4.1	5	15.1	5.1	10	5.3	4.2	13	4.6	2.6	6	6.1	3.5	4	38.1	1.1	4	3.3	1.5	4
Sr	52	26	10	55	51	15	139	85	13	165	89	6	103	74	4	143	70	4	14	4	4
Th	16.3	4.6	10	19.6	3.2	15	4.4	4.7	13	3.6	2.6	6	4.2	2.4	4	4.9	3.5	4	3.3	2.3	4
U	5.4	2.2	10	6.9	2.9	15	2.1	1.7	13	1.3	0.6	6	1.6	0.9	4	7.6	7.8	4	3.0	2.3	4
V	51	13	10	32	18	15	134	72	13	81	18	6	62	23	4	248	45	4	35	19	4
Y	43	3	10	55	14	15	43	29	13	31	9	6	27	5	4	33	6	4	23	12	4
Zn	69	17	10	97	42	15	371	122	13	302	83	6	242	26	4	78	19	4	48	12	4
Zr	312	74	10	440	74	15	64	52	13	66	65	6	66	35	4	130	70	4	55	35	4
La (ppm)	39.9	8.7	10	56.3	17.8	15	31.7	26.4	13	21.4	8.1	6	19.3	6.1	4	21.6	12.4	4	8.2	2.2	4
Ce	89	18	10	122	35	15	47	41	13	29	17	6	31	12	4	47	26	4	19	5	4
Nd	36	7	10	54	19	15	23	21	13	14	6	6	13	5	4	18	7	4	7	4	4
Sm	7.4	0.9	5	11.4	3.3	10	5.6	4.9	13	3.6	1.7	6	3.8	1.1	4	5.0	1.7	4	1.7	0.5	4
Eu	1.3	0.3	5	1.9	0.5	10	2.7	1.1	13	2.2	0.5	6	1.9	0.5	4	1.4	0.3	4	0.2	0.1	4
Yb	4.9	0.3	5	6.4	1.7	10	3.5	2.0	13	2.6	0.8	6	2.5	0.8	4	3.2	0.7	4	4.3	1.8	4
Lu	0.7	0.1	5	1.0	0.3	10	0.5	0.3	13	0.4	0.1	6	0.4	0.1	4	0.5	0.1	4	0.7	0.3	4
Hf	8	1	5	11	1	10	1	1	13	1	1	6	1	1	4	3	1	4	1	1	4
Rb	130	21	5	186	60	10	28	26	13	66	19	6	87	37	4	162	71	4	104	55	4
Zr/TiO ₂	0.053	0.004	5	0.107	0.043	15	0.025	0.005	13	0.026	0.011	6	0.027	0.008	4	0.013	0.007	4	0.061	0.030	4
Th/Nb	1.08	0.37	5	0.86	0.17	15	0.44	0.31	13	0.52	0.16	6	0.67	0.18	4	0.45	0.12	4	0.84	0.36	4
Y/TiO ₂	0.009	0.003	5	0.014	0.010	15	0.022	0.012	13	0.016	0.007	6	0.013	0.006	4	0.003	0.001	4	0.027	0.012	4
Zn+Pb	99	28	5	152	78	15	2145	1287	13	2041	542	6	1459	1062	4	115	31	4	59	23	4
Fe/Mn	34	17	5	38	15	15	10	5	13	11	9	6	11	6	4	55	34	4	118	53	4

Notes

* North of the Brunswick No. 6 Zn-Pb-Ag deposit.
 NF = Nepesiguit Falls Formation; FLB = Flat Landing Brook Formation; IF = Iron Formation; \bar{x} = average.

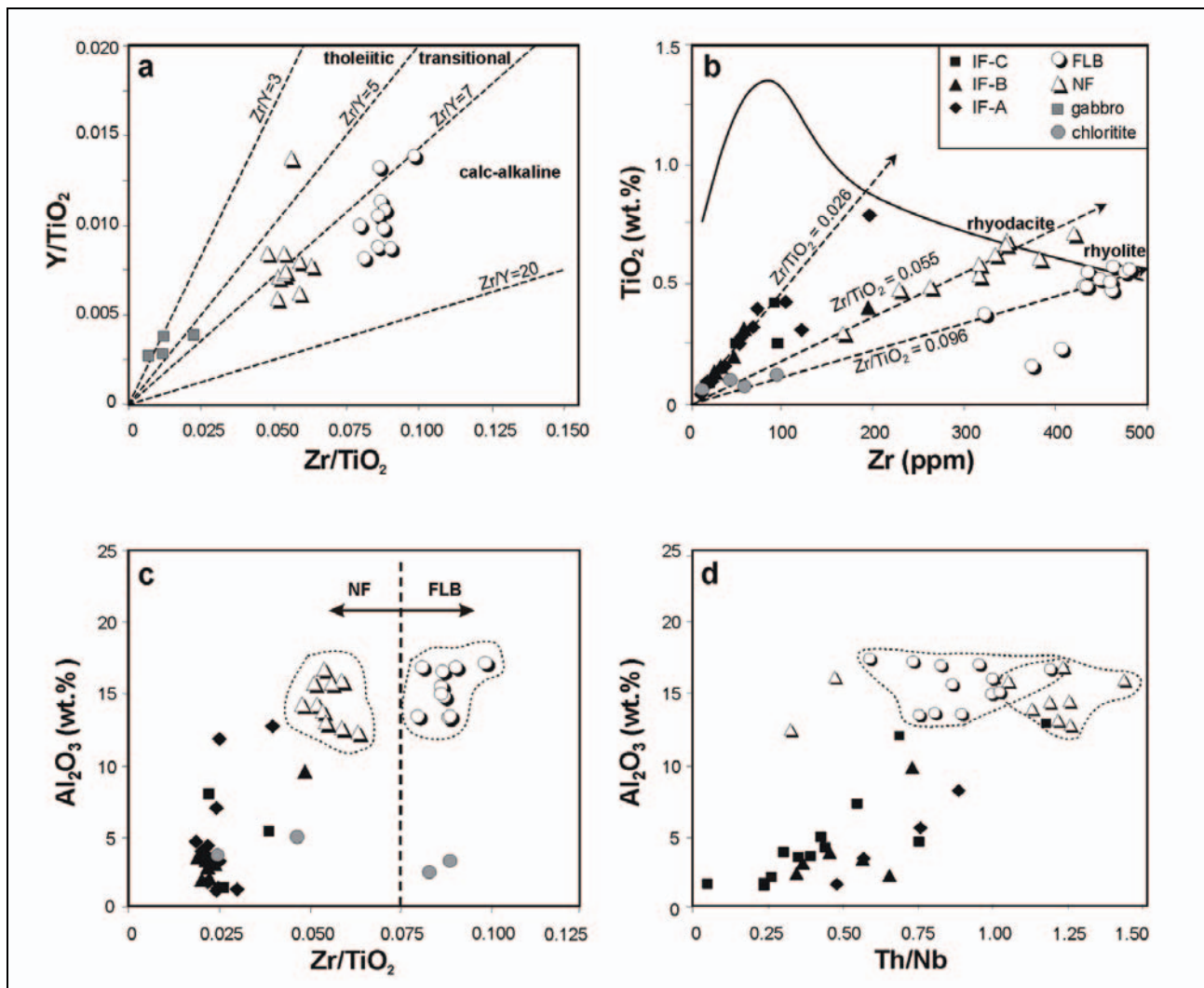


Fig. 3. Immobile element diagrams for samples from DDH-B357: *a*. Magmatic affinity based on Y/TiO_2 vs. Zr/TiO_2 with the distribution of Nepisiguit Falls (NF), Flat Landing Brook (FLB), and gabbro rocks; *b*. Iron formations (IF-A, IF-B, and IF-C) have different compositions in TiO_2 vs. Zr, with calc-alkaline to transitional magmatic fractionation curve (after MacLean and Barrett, 1993). *c*. Al_2O_3 vs. Zr/TiO_2 and *d*. Al_2O_3 vs. Th/Nb, with separate Nepisiguit Falls and Flat Landing Brook sample populations, both distinct from iron formation.

mixed terrigenous and hydrothermal sources (Fig. 4). Apatite is common in iron formation rocks, and accumulated primarily by precipitation from hydrothermal fluids; therefore, P_2O_5 is particularly useful in determining relative proximity to vent source (Peter and Goodfellow, 1996).

Discussion

Zr and TiO_2 Behavior

Two distinct calc-alkaline to transitional magmas, such as those that formed the felsic volcanic rocks of the Nepisiguit Falls and Flat Landing Brook formations, may be distinguished using incompatible versus compatible element ratios (for example, Zr/TiO_2 and Th/Nb). Various studies provide precedent for the general application of this

technique (e.g., Floyd and Winchester, 1975; Winchester and Floyd, 1977; Gorton and Schandl, 2000; Schandl and Gorton, 2002), as well as studies specific to Nepisiguit Falls and Flat Landing Brook rocks (Langton and McCutcheon, 1993; Lentz, 1996a, 1996b, 1999b). In order to understand why Zr/TiO_2 is the most effective method of distinguishing between Nepisiguit Falls and Flat Landing Brook rocks, trace element partition coefficients have been examined in evolving partial melting regimes governed by: (1) mineral phase partial fusion and/or fractionation of Zr- and Ti-bearing phases; (2) variably siliceous liquid composition and melt polymerization (SiO_2 content); and (3) temperature and pressure (Hellman and Green, 1979; Watson, 1979; Watson and Harrison, 1983; Nash and Crecraft, 1985; Green and Pearson, 1986). Zr^{4+} and Ti^{4+} have similar high ratios of ionic charge to ionic radius

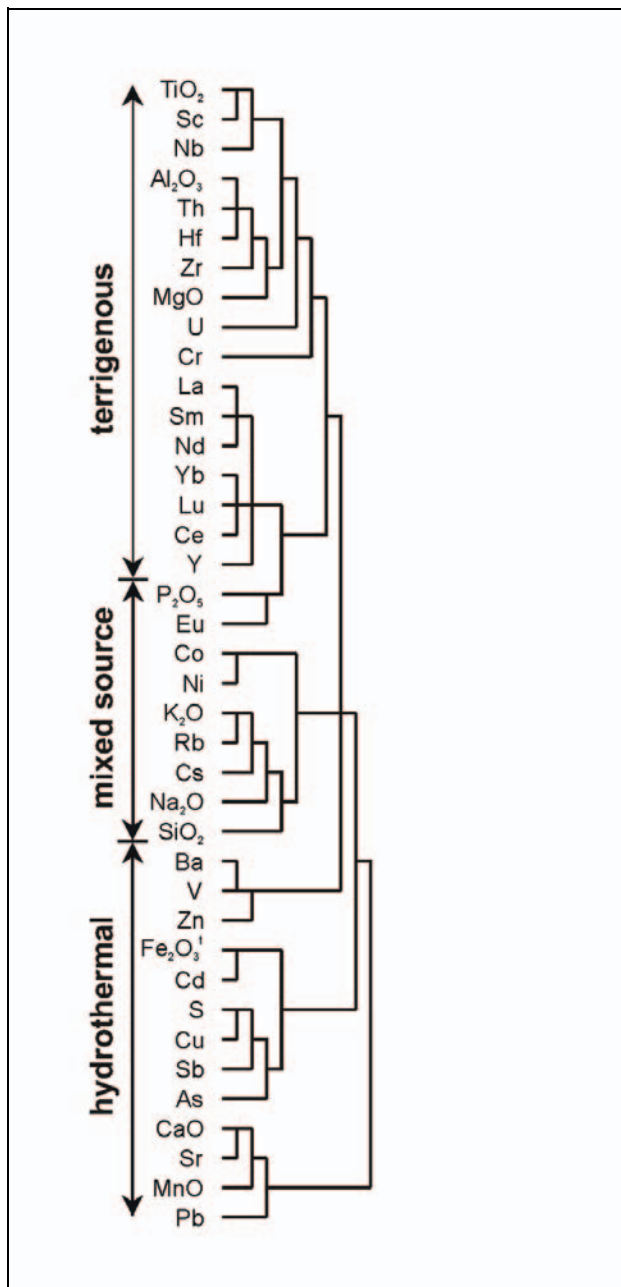


Fig. 4. Interelement cluster dendrogram using between-group Pearson Product correlation for the iron formation rock samples in DDH-B357 ($n = 23$), with groupings of components indicating relative influence of hydrothermal, terrigenous, and mixed-input sources.

(high field strength). Furthermore, both Zr⁴⁺ and Ti⁴⁺ have contrasting compatibilities in silicic magmas (Floyd and Winchester, 1975; MacLean and Barrett, 1993), and partition into silicate melt structures given sufficient alkali-cation and nonbridging oxygen contents, which serve as silicate-melt network modifiers (Mysen et al., 1980; Watson and Harrison, 1983). The abundances of Zr and Ti may also be controlled by solubility of respective refractory mineral phases like

zircon, pyroxenes, titanite, and rutile during partial melting and subsequent saturation in the evolving magma (Woodhead et al., 1993; Vannucci et al., 1998).

Melt temperature and, to a lesser degree, SiO₂ content control the contrasting Zr contents (zircon saturation) in the Nepisiguit Falls and Flat Landing Brook felsic volcanic rocks from DDH-B357 (Fig. 5a). The occurrence of primary euhedral zircon phenocrysts in Nepisiguit Falls rocks (Sullivan and van Staal, 1995) indicates that zircon reached saturation during Nepisiguit Falls magma evolution. In contrast, zircon phenocrysts are rare in Flat Landing Brook rhyolites, except for sparse, irregular, rounded, and acicular crystals suggestive of magmatic resorption followed by rapid quenching (Sullivan and van Staal, 1990). The work of Watson and Harrison (1983) explains that Zr is incompatible in melts up to at least 67 wt.% SiO₂. Whole-rock SiO₂ contents for Nepisiguit Falls (69.4 ± 3.6 wt.%) and Flat Landing Brook (67.8 ± 6.2 wt.%) rocks in DDH-B357 (see Table 1) may not exactly reflect primary compositions, but the higher precursor SiO₂ content of Flat Landing Brook (~72.0 wt.%; Lentz, 1999b) relative to Nepisiguit Falls (~68.0 wt.%; Lentz, 1999b) means that Flat Landing Brook rocks should be accompanied by lower Zr values, all other factors being equal. In fact, Flat Landing Brook rocks are enriched in Zr relative to Nepisiguit Falls rocks (Fig. 5a). Lentz (1999b) considered Nepisiguit Falls/Flat Landing Brook chemostratigraphy using the Zr-saturation equation of Watson and Harrison (1983), and proposed that the Nepisiguit Falls volcanic rocks represent an initial melt (840°C) from amphibolite-grade lower crust, followed by a second-stage of higher temperature Flat Landing Brook partial melts (890°C) containing more incompatible HFSE. The amount of H₂O in a melt has two key effects: (1) depression of liquidus temperatures, such that a lower-temperature melt can be generated with lower Zr and Ti solubilities; and (2) depolymerization of the silicate melt structure allowing for higher Zr and Ti solubilities. Watson and Harrison (1983) noted that a high-temperature (1200°–1500°C) isothermal rhyolite (granitic) melt containing 0.2 wt.% H₂O will dissolve 30% to 40% less zircon than the same melt with 2 wt.% H₂O. Considering the explosive pyroclastic textures in Nepisiguit Falls rocks compared to the Flat Landing Brook lavas, the former is assumed to be more volatile rich. Therefore, despite the effects of volatile content on melt depolymerization, melt temperature must be the principal control on higher Zr content in Flat Landing Brook rocks, with SiO₂ and volatile content playing subordinate roles.

The TiO₂ contents in Nepisiguit Falls and Flat Landing Brook melts (Ti-phase saturation) are governed predominantly by the SiO₂ content of melt and less significantly by temperature (Fig. 5b). Ti, as compared to Zr, is compatible through a much wider range of SiO₂ contents and is also more compatible with intermediate to high SiO₂ contents like Nepisiguit Falls and Flat Landing Brook felsic volcanic rocks (Mysen et al., 1980). As with Zr, there is a

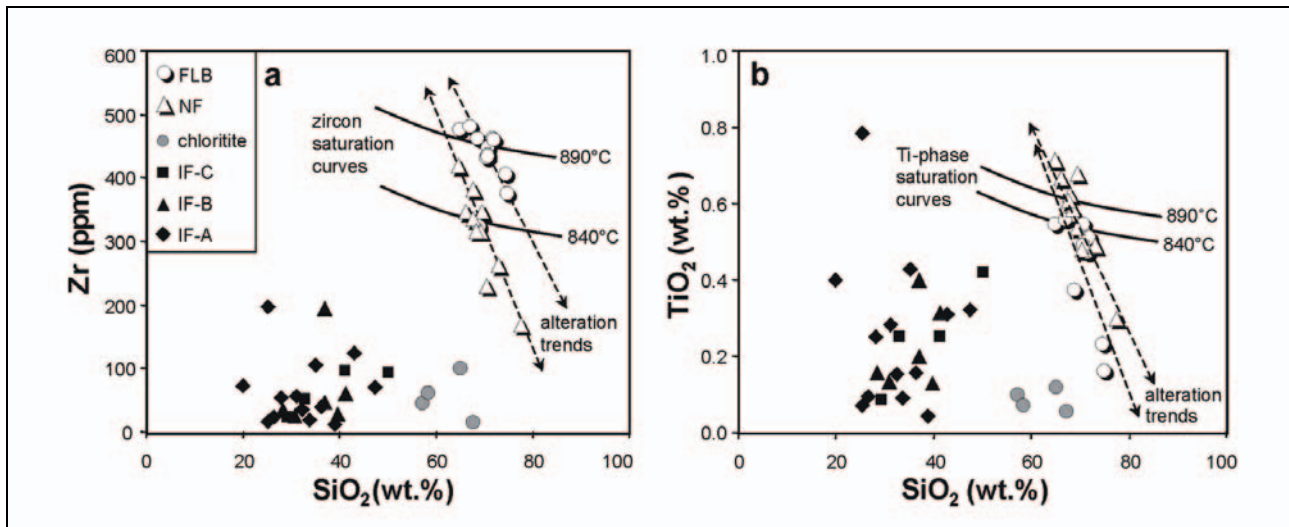


Fig. 5. *a.* TiO_2 vs. SiO_2 for Nepisiguit Falls and Flat Landing Brook rocks, with Ti-saturation curves inferred from experimental work by Green and Pearson (1986). *b.* Zr vs. SiO_2 for Nepisiguit Falls and Flat Landing Brook rocks, with Zr-saturation curves inferred from experimental work by Watson and Harrison (1983). Melt (fusion) temperatures calculated for Nepisiguit Falls (840°C) and Flat Landing Brook (890°C) are from Lentz (1999b).

consistently antithetic relationship between whole-rock TiO_2 and SiO_2 contents over a range of pressure and temperature (Green and Pearson, 1986). At the lower temperatures for Nepisiguit Falls compared to Flat Landing Brook melts under isobaric conditions, the TiO_2 versus SiO_2 saturation curves become relatively flattened and TiO_2 contents are somewhat lower, but a subtle difference in SiO_2 content, for these highly silicic magmas is accompanied by a significant change in TiO_2 abundance (Fig. 5b). The modestly lower TiO_2 content of Flat Landing Brook relative to Nepisiguit Falls samples (Fig. 5b) is a function of Ti-phase solubility during the respective melt evolution at subtly different bulk SiO_2 contents, where contrasting magma temperatures have only a slight counteracting effect.

The Zr/TiO_2 differences between Nepisiguit Falls and Flat Landing Brook volcanic rocks reflect the divergent behavior of Zr and Ti during magma evolution with subtly different partial melting temperatures and SiO_2 contents. Therefore, the Zr/TiO_2 ratio serves as a reliable chemostratigraphic discriminator of the otherwise very similar Nepisiguit Falls and Flat Landing Brook rocks as shown in Figure 3c. The Th/Nb ratio is also a rather effective geochemical discriminator of Nepisiguit Falls and Flat Landing Brook rocks. Th is a lithophile element concentrated in association with Zr (zircon) and rare earth elements (monazite), whereas Nb (and Ta) is associated with TiO_2 , because it is concentrated into Ti-phases such as titanite and rutile.

Iron Formations

The Zr/TiO_2 ratio (Table 1; Fig. 3b,c) is used to identify the provenance of detrital material in the iron formation

samples, assuming that neither Zr nor TiO_2 are carried by hydrothermal fluids, and their ratio is constant and characteristic for each of the possible detrital sources (Nepisiguit Falls, Flat Landing Brook, etc.). Neither Zr nor TiO_2 correlate with hydrothermal components in iron formations (Fig. 4), because both are considered immobile under most hydrothermal alteration processes, low-grade metamorphism, and weathering (Floyd and Winchester, 1975; Finlow-Bates and Stumpfl, 1981). The iron formation samples from DDH-B357 exhibit a linear immobile element signature (Fig. 3b,c) indicative of a common detrital source, but have Zr/TiO_2 values (average for all IF $n = 23$; $\text{Zr}/\text{TiO}_2 = 0.025 \pm 0.007$), not typical of either Nepisiguit Falls ($\text{Zr}/\text{TiO}_2 = 0.053 \pm 0.004$) or Flat Landing Brook ($\text{Zr}/\text{TiO}_2 = 0.107 \pm 0.043$) rocks (Table 1). The statistically-linked detrital “terrigenous” components (Fig. 4) inherent to the iron formation intervals are consistent with sedimentary rocks of the Patrick Brook Formation ($\text{Zr}/\text{TiO}_2 = 0.021 \pm 0.007$; Lentz et al., 1995), suggesting that the iron formations have material input similar to the older Patrick Brook rocks, possibly derived from continental detritus. Their closely similar Zr/TiO_2 ratios suggest that the three iron formation intersections in DDH-B357 represent the same exhalative horizon (i.e., Brunswick horizon) with similar terrigenous inputs.

Apart from absolute abundances, element ratios provide insight into the genesis of iron formations. A plot of MnO versus Fe/Mn (Fig. 6a) reflects the redox conditions and subsequent precipitation of mineral phases during exhalative activity in a stratified basin: a high Fe/Mn ratio indicates anoxic conditions, but low Fe/Mn reflects an oxidizing setting (Whitehead, 1973). The three iron formation

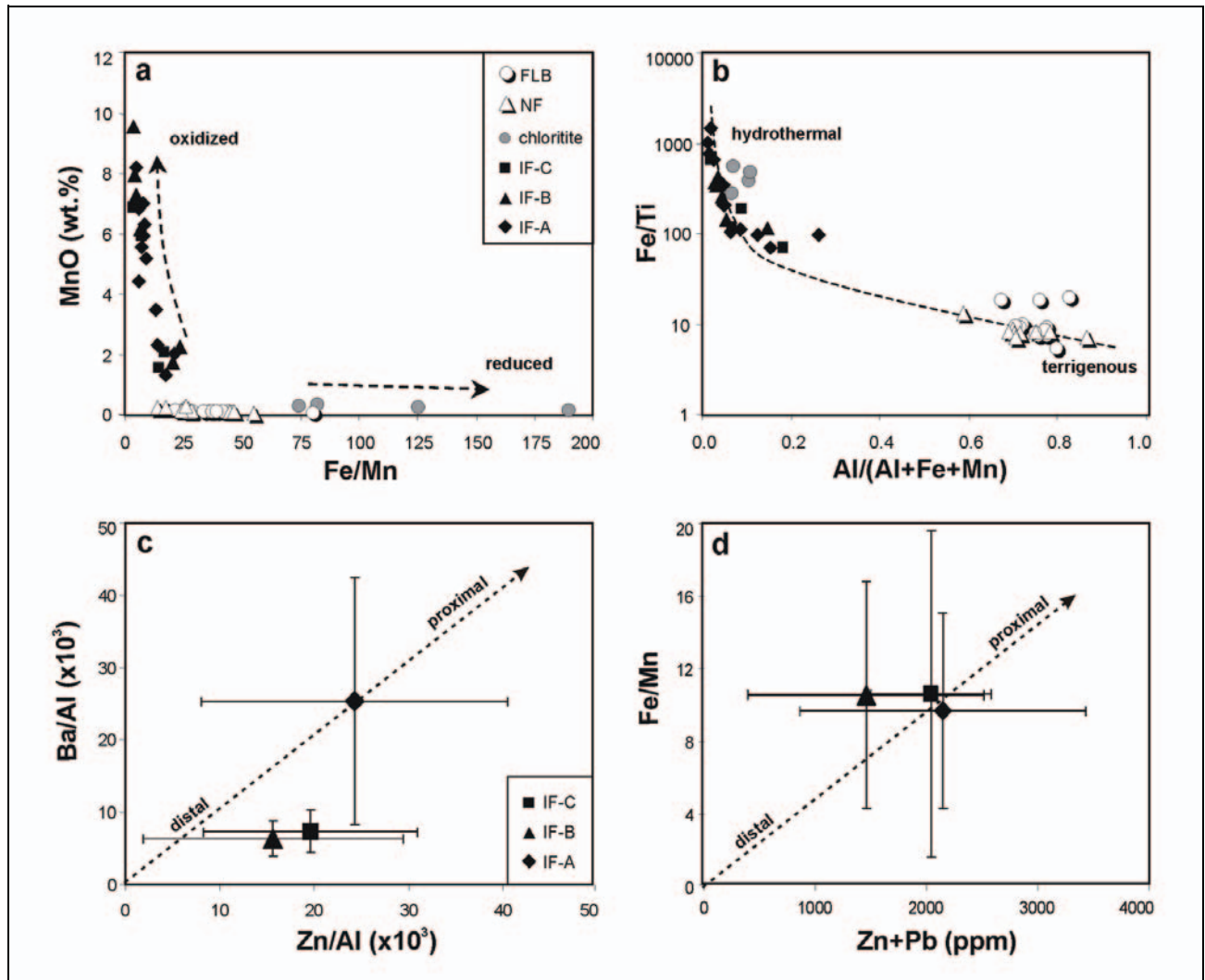


Fig. 6. *a.* MnO vs. Fe/Mn for iron formation (IF-A, IF-B, and IF-C), Nepisiguit Falls (NF), and Flat Landing Brook (FLB) samples from DDH-B357; *b.* Fe/Ti vs. Al/(Al+Fe+Mn) plot (after Boström, 1973). Mineral exploration vectors: *c.* Ba/Al vs. Zn/Al plot and *d.* Fe/Mn vs. Zn+Pb plot with mean compositions ± 1 standard deviation, illustrating relative proximity to hydrothermal sediment source.

intersections have relatively low Fe/Mn (IF-A = 10 ± 5 , IF-B = 11 ± 9 , IF-C = 11 ± 6) due to high MnO contents (IF-A = 5.6 ± 3.3 wt.%, IF-B = 5.8 ± 3.2 wt.%, IF-C = 4.1 ± 2.7 wt.%). The Boström plot (Fig. 6b) illustrates the variable hydrothermal (Fe and Mn) and terrigenous (Ti and Al) input to these sedimentary rocks, supported by their respective clustering in the inter-element cluster dendrogram (Fig. 4). The samples from the three iron formation intersections along with the chloritite samples plot as hydrothermal-dominated in the Boström diagram (Fig. 6b), although mostly because of their elevated Fe contents.

Mineral exploration vectors indicating proximity to a paleohydrothermal vent source can be established using components carried by, and precipitated from, hydrothermal fluids, as indicated by co-variation clustering in Figure 4

(Peter, 2003). For example, Ba/Al versus Zn/Al (Fig. 6c) and Fe/Mn versus Zn+Pb (Fig. 6d) indicate that IF-A formed closer to a source of hydrothermal fluids than did IF-B or IF-C due to the relative enrichment in hydrothermal components (Fig. 6c,d).

The three iron formation intersections are enriched in components known to be carried predominantly by hydrothermal fluids (i.e., Fe_2O_3^T , MnO, CaO, Zn+Pb), and exhibit similar bulk HFSE abundances (TiO_2 , Al_2O_3 , Nb, Sc, Th, and Zr) with consistent Zr/ TiO_2 ratios. This implies that IF-A, IF-B, and IF-C either: (1) formed as distinct exhalative strata under comparable submarine conditions, and precipitated from very similar hydrothermal fluids with the similar detrital material inputs; or (2) are structural repetitions of the same horizon. Chemostratigraphic analysis of rocks

encountered in DDH-B357 support a model of these iron formations being folded repetitions of a single exhalative horizon: the Brunswick horizon.

Chemostratigraphic Reconstruction

The downhole geochemical profiles (Fig. 7) use immobile element ratios (Zr/TiO_2 and Th/Nb) and hydrothermal element abundances ($Fe_2O_3^T$, MnO , and $Pb+Zn$) to ascribe each rock sample to one of six rock types: iron formation, Nepisiguit Falls Formation rhyodacite, Flat Landing Brook Formation rhyolite, gabbro, and chloritite associated with the gabbro. The three iron formations (IF-A, IF-B, IF-C) are immediately recognizable based on their very high concentrations of $Fe_2O_3^T$ (up to 61.6 wt.%), MnO (up to 14.1 wt.%), and $Pb+Zn$ (up to 4592 ppm). The felsic volcanic and volcanosedimentary rocks that separate the iron formations can be identified as either Nepisiguit Falls or Flat Landing Brook formations based on Zr/TiO_2 (Nepisiguit Falls < 0.075 ; Flat Landing Brook > 0.075) and Th/Nb (Nepisiguit Falls > 1.05 ; Flat Landing Brook < 1.05). The gabbro has

high TiO_2 concentrations (> 1.0 wt.%) and its associated chloritite has high $Fe_2O_3^T$ values (up to 33.3 wt.%), but very low MnO and $Pb+Zn$ concentrations. The downhole geochemical profiles (Fig. 7) reveal a repetition of Nepisiguit Falls and Flat Landing Brook rocks between multiple iron formations with a symmetry that can be explained by folding (Figs. 8, 9).

Structural Implications

In consideration of the structural interpretations that provide our understanding of the Brunswick No. 6 deposit (Skinner, 1974; van Staal and Williams, 1984; van Staal, 1987, 1992a; van Staal and Fyffe, 1991), the repetition of iron formation in DDH-B357 could be explained by two isoclinal F_2 folds parasitic to the west-dipping limb of the larger Brunswick antiform (Figs. 8, 9). However, this view implies there to be two additional iron formation intersections in DDH-B357 at about 160 m and 400 m (Figs. 7, 8, 9). The drill core section from 155 m to 165 m is altered and fractured, and marks a transition from Nepisiguit Falls to Flat Landing

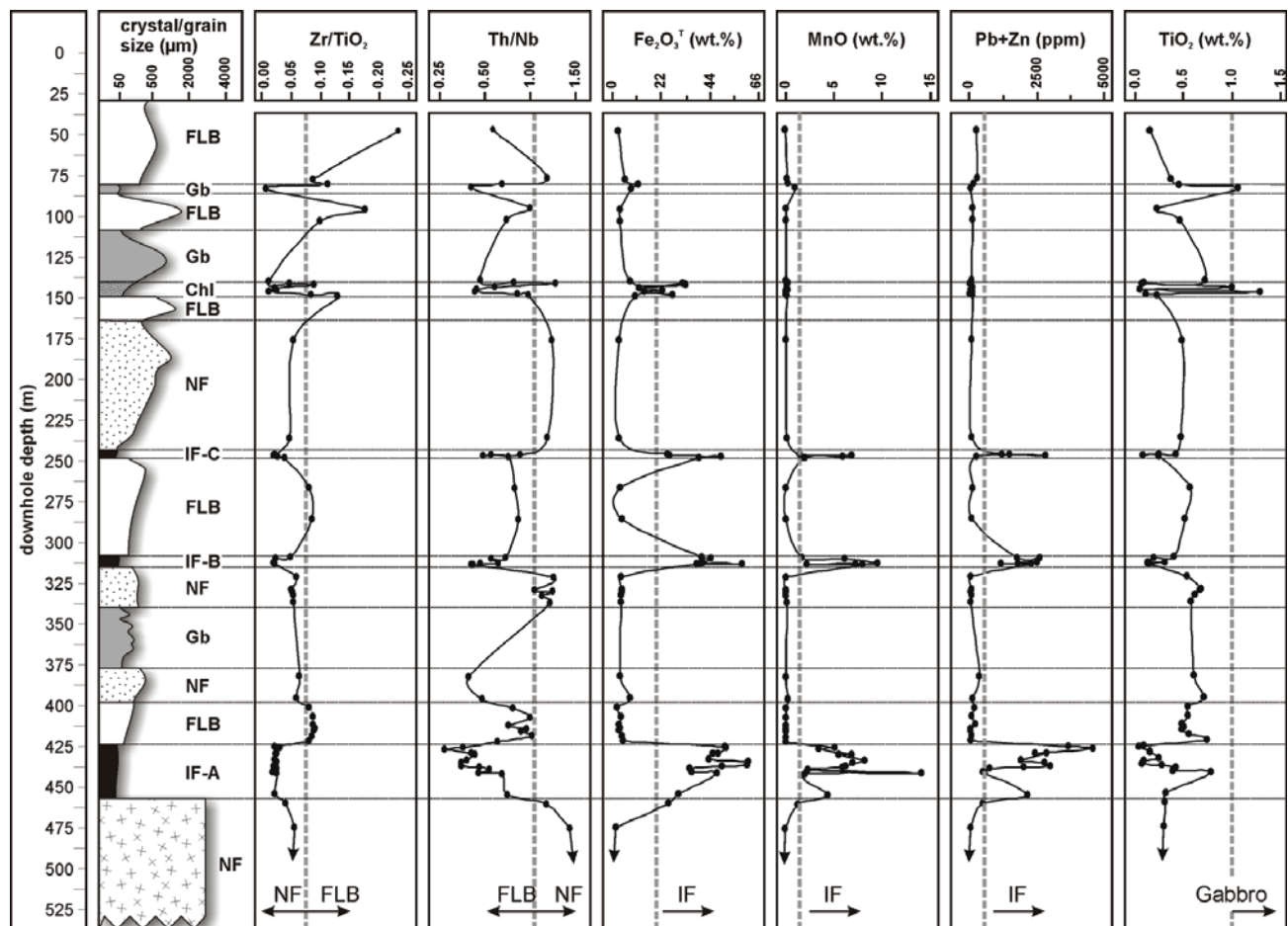


Fig. 7. DDH-B357 Downhole geochemical profiles for chemostratigraphic and metallogenic indicators: Zr/TiO_2 , Th/Nb , $Fe_2O_3^T$, MnO , $Pb+Zn$, and TiO_2 . Rock units are assigned based on geochemical signature for (NF) Nepisiguit Falls Formation, (FLB) Flat Landing Brook Formation, (IF) iron formation, (Gb) gabbro, and (Chl) chloritite.

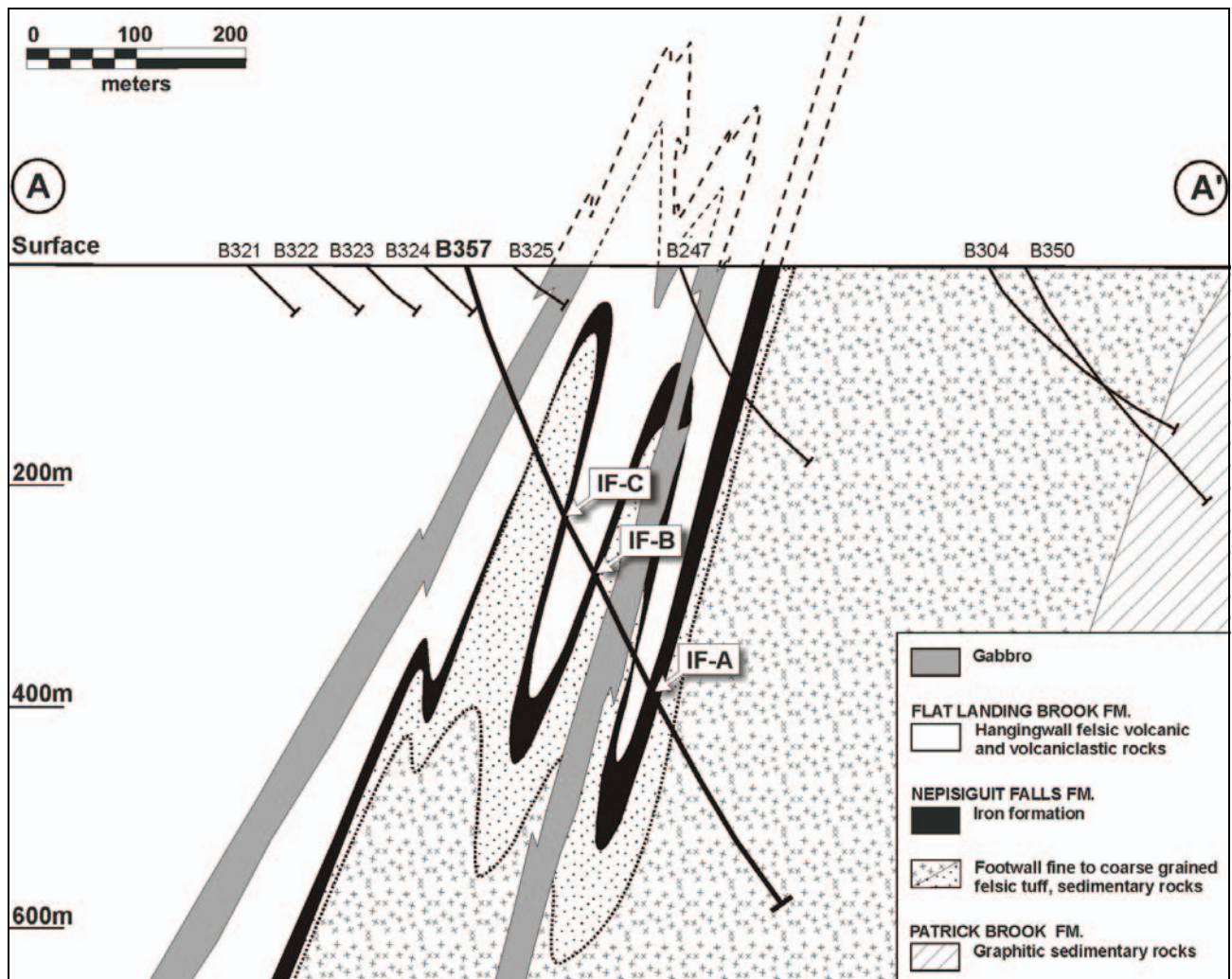


Fig. 8. East-west cross section through DDH-B357 showing several nearby drillholes (surface trace of section indicated in Fig. 1). The iron formation intersections in DDH-B357 are explained by two sets of isoclinal F_2 folds parasitic to the west-dipping limb of the Brunswick antiform.

Brook rocks. The section from 394.5 m to 396.2 m is also altered and fractured, but contains laminated chert that may be the remnants of a weak exhalite. Thus, paleodepositional heterogeneities in iron formation thickness and/or subsequent structural pinching-out may explain the absence of well-developed iron formation in the two downhole intervals where they would otherwise be expected. Goodfellow and Peter (1996) discuss the depositional conditions for the massive sulfide deposits along the Brunswick Belt, where metalliferous brines (and base-metal sulfides) accumulate in isolated paleotopographic lows of the submarine volcanic terrain. These depressions would be related to normal faulting during caldera collapse, accumulating reworked and weathered felsic material prior to, and during, the most intense stages of hydrothermal discharge and massive sulfide accumulation (Goodfellow and McCutcheon, 2003). The fine-grained Nepisiguit Falls sedimentary rocks in DDH-

B357 (Fig. 2b) could be a facies related to caldera-collapse (re)sedimentation in paleo-topographic lows proximal to massive sulfide accumulation.

The subsurface structural reconstruction (Figs. 8, 9) is based on the detailed structural and surface geology studies of the area north of the Brunswick No. 6 deposit, relogging and correlating existing drill core from DDH-B357 and other nearby holes, and from the downhole geochemical logs (Fig. 7). Assuming that the iron formation intersections are in fact isoclinal fold repetitions of the same time-stratigraphic horizon (i.e., the Brunswick horizon), mobile element vectoring using Ba/Al versus Zn/Al, and Fe/Mn versus Zn+Pb (Fig. 6c,d) suggests increasing distance from a hydrothermal vent source going from IF-A to IF-B to IF-C. van Staal and Williams (1984) presented evidence that the Brunswick No. 6 and No. 12 orebodies are a combination of enrichment in palaeotopographic lows, further concentrated

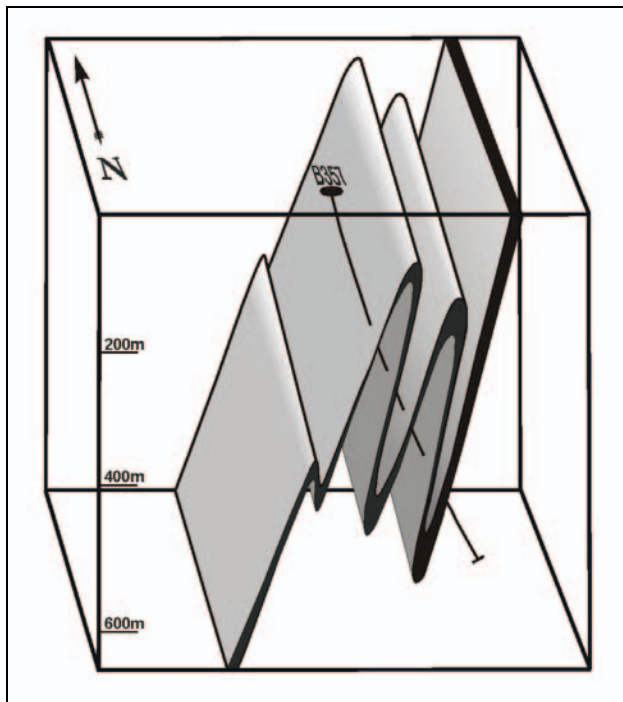


Fig. 9. Schematic block diagram of folded Brunswick horizon iron formation through DDH-B357, based on the downhole geochemical profiles (Fig. 7) and cross section (Fig. 8).

by diagenetic processes, and later tectonically thickened into sheath-like F_1/F_2 interference folds. In the area surrounding the Brunswick No. 6 mine, F_1 folds are recumbent, asymmetrical to isoclinal, and originally overturned to the north, whereas the tighter F_2 folds are also asymmetrical to isoclinal, but overturned to the east, with steep, west-dipping axial planes and shallow southerly plunges (van Staal and Williams, 1984). The parasitic F_2 folding, confirmed by this reconstruction of DDH-B357 north of Brunswick No. 6 using chemostratigraphy, may provide prospective downdip fold closures favorable to exploration for base-metal massive sulfides.

Conclusions

Based on 56 whole-rock geochemical samples and relogging of DDH-B357, situated approximately 1.5 km northwest of the Brunswick No. 6 deposit, three intervals of exhalative iron formation ($n = 23$) have been identified within variably altered felsic volcanic and volcanosedimentary rocks of the Nepisiguit Falls Formation ($n = 10$) and Flat Landing Brook Formation ($n = 15$). The objective was to resolve the geometry of the volcanic succession using chemostratigraphy because alteration and deformation have made petrographic identification of the Nepisiguit Falls and Flat Landing Brook felsic rocks ambiguous. From the geochemical data, several key suppositions can be made:

1. Three iron formation intersections ($\text{Fe}_2\text{O}_3^T \geq 24.1 \text{ wt.}\%$) identified in DDH-B357 represent the same stratigraphic

horizon. They exhibit virtually indistinguishable mobile element composition, with low Fe/Mn (oxidized signature), elevated base metal (Zn+Pb) values, and strong enrichment in other exhalative components. Furthermore, the three iron formation intersections possess a common immobile element, nonhydrothermal signature (i.e., Zr/TiO₂), which reflects the same pelagic source as the underlying Patrick Brook Formation.

2. Zr/TiO₂ is the most reliable chemostratigraphic index in distinguishing the footwall Nepisiguit Falls from the hanging wall Flat Landing Brook rocks, despite strong alteration and fine-grained textures found in the felsic samples from DDH-B357. The Th/Nb ratio serves as a less precise discriminator of Nepisiguit Falls and Flat Landing Brook rocks, although it helps confirm other rock-identification methods. As shown in downhole geochemical profiles, DDH-B357 starts in the Flat Landing Brook formation, which is followed by a symmetric repetition of the distinct felsic volcanic domains separated by three iron formations.
3. The three iron formation intersections in DDH-B357, separated by felsic units with Nepisiguit Falls and Flat Landing Brook chemostratigraphic signatures, are interpreted to be the result of a folded footwall–iron formation–hanging wall stratigraphic succession. Two overturned F_2 parasitic anticlines are inferred on the west-dipping limb of the Brunswick antiform. Iron formation is absent in two downhole intervals where it would be expected to occur based on the structural model, which may reflect variable iron formation paleo-thickness, subsequent structural thinning along fold limbs, or poor drill core recovery through a fault intersection. Geochemical vectoring, using hydrothermal components ratioed against Al (Ba/Al vs. Zn/Al, and Fe/Mn vs. Zn+Pb) indicates that IF-A formed in a more vent proximal location than IF-B and IF-C.
4. The identification of cogenetic iron formation intersections in DDH-B357 with hydrothermal-chemical enrichment, particularly in base metals (Zn+Pb exceeding 4500 ppm), in fold-repeated footwall–iron formation–hangingwall stratigraphy, suggests the area northwest (up-plunge and downdip) of the Brunswick No. 6 VMS deposit may be a favorable location for structurally controlled massive sulfide deposits as yet undiscovered.

Acknowledgments

We express appreciation for the support and feedback from G. Woods and the entire Noranda (now Xstrata) exploration (Bathurst) team: C. Collins, R. Banville, B. Drolet, G. Graves, R. Kempster, C. Moreton, and L. Petrie. Many thanks go to S. McCutcheon (DNR, Bathurst) and S. McClenaghan (UNB) for constructive discussions, advice, and review of an early version of this paper. We are also grateful for the constructive journal reviews from J. Langton and S. Piercey. This study was financed by Noranda Inc.

(now Xstrata plc) and a grant to DL from the Natural Sciences and Engineering Research Council of Canada (NSERC).

References

- Bhatia, D.M.S., 1970, Facies change in iron formation at Brunswick No. 12 mine, Bathurst: Unpublished M.Sc. Thesis, Fredericton, University of New Brunswick, 179 p.
- Boström, K., 1973, The origin and fate of ferromagnesian active ridge sediments: *Stockholm Contributions to Geology*, v. 27, p. 147–243.
- Cas, R.A.F., 1992, Submarine volcanism: Eruption styles, products, and relevance to understanding the host-rock successions to volcanic-hosted massive sulfide deposits: *Economic Geology*, v. 87, p. 511–541.
- Downey, W., and Lentz, D.R., 2006, A review of deep submarine silicic pyroclastic volcanism: *Geoscience Canada*, v. 33, p. 5–24.
- Finlow-Bates, T., and Stumpfl, E.F., 1981, The behavior of so-called immobile elements in hydrothermally altered rocks associated with volcanogenic submarine-exhalative ore deposits: *Mineralium Deposita*, v. 16, p. 319–328.
- Floyd, P.A., and Winchester, J.A., 1975, Magma type and tectonic setting discrimination using immobile elements: *Earth and Planetary Science Letters*, v. 27, p. 211–218.
- Franklin, J.M., Sangster, D.M., and Lydon, J.W., 1981, Volcanic-associated massive sulfide deposits: *Economic Geology*, 75th Anniversary Volume, p. 485–627.
- Gibson, H.L., Morton, R.L., and Hudak, G.J., 1999, Submarine volcanic processes, deposits, and environments favorable for the location of volcanic-associated massive sulfide deposits: *Reviews in Economic Geology*, v. 8, p. 13–51.
- Goodfellow, W.D., and McCutcheon, S.R., 2003, Geological and genetic attributes of volcanic sediment-hosted massive sulfide deposits of the Bathurst Mining Camp, northern New Brunswick—A synthesis: *Economic Geology*, Monograph 11, p. 245–301.
- Goodfellow, W.D., and Peter, J.M., 1996, Sulphur isotope composition of the Brunswick No. 12 Massive sulphide deposit, Bathurst Mining Camp, New Brunswick: Implications for ambient environment, sulphur source, and ore genesis: *Canadian Journal of Earth Sciences*, v. 33, p. 231–251.
- Gorton, M.P., and Schandl, E.S., 2000, From continents to island arcs: A geochemical index of tectonic setting for arc-related and within-plate felsic to intermediate volcanic rocks: *Canadian Mineralogist*, v. 38, p. 1065–1073.
- Green, T.H., and Pearson, N.J., 1987, An experimental study of Nb and Ta partitioning between Ti-rich minerals and silicate liquids at high pressure and temperature: *Geochimica and Cosmochimica Acta*, v. 51, p. 55–62.
- Gross, G.A., and McLeod, C.R., 1980, A preliminary assessment of the chemical composition of iron formations in Canada: *Canadian Mineralogist*, v. 18, p. 223–229.
- Hellman, P.L., and Green, T.H., 1979, The role of sphene as an accessory phase in the high-pressure partial melting of hydrous mafic compositions: *Earth and Planetary Science Letters*, v. 42, p. 191–201.
- Jenner, G.A., 1996, Trace element geochemistry of igneous rocks: Geochemical nomenclature and analytical geochemistry, *in* Wyman, D.A., ed., *Trace element geochemistry of volcanic rocks: Applications for massive sulphide exploration*: Geological Association of Canada, Short Course Notes 12, p. 51–77.
- Langton, J.P., and McCutcheon, S.R., 1993, Brunswick project, NTS 21 P/5 west, 21 P/4 west, Gloucester County, New Brunswick: New Brunswick Department of Natural Resources, Minerals, Policy and Planning Division, Information Circular 93-1, p. 31–51.
- Lavery, N.G., 1985, Quantifying chemical changes in hydrothermally altered volcanic sequences—Silica enrichment as a guide to the Crandon massive sulfide deposit, Wisconsin, U.S.A.: *Journal of Geochemical Exploration*, v. 24, p. 1–27.
- Lentz, D.R., 1995, Preliminary evaluation of six in-house rock geochemical standards from the Bathurst Camp, New Brunswick: New Brunswick Department of Natural Resources and Energy, Miscellaneous Report 18, p. 81–89.
- Lentz, D.R., 1996a, Trace element systematics of felsic volcanic rocks associated with massive sulphide deposits in the Bathurst Mining Camp: Petrogenetic, tectonic, and chemostratigraphic implications for VMS exploration, *in* Wyman, D.A., ed., *Trace element geochemistry of volcanic rocks: Applications for massive sulphide exploration*: Geological Association of Canada, Short Course Notes 12, p. 359–402.
- Lentz, D.R., 1996b, Recent advances in litho-geochemical exploration for massive sulphide deposits in volcano-sedimentary environments: Petrogenetic, chemostratigraphic, and alteration aspects with examples from the Bathurst Camp, New Brunswick: New Brunswick Department of Natural Resources, Minerals, Policy and Planning Division, Mineral Resource Report 96-1, p. 73–119.
- Lentz, D.R., 1999a, Deformation-induced mass transfer in felsic volcanic rocks hosting the Brunswick No. 6 massive sulfide deposit, New Brunswick: Geochemical effects and petrogenetic implications: *Canadian Mineralogist*, v. 37, p. 489–512.
- Lentz, D.R., 1999b, Petrology, geochemistry, and oxygen isotope interpretation of felsic volcanic rocks and related rocks hosting the Brunswick No. 6 and No. 12 massive

- sulfide deposits, Bathurst Mining Camp, New Brunswick, Canada: *Economic Geology*, v. 94, p. 57–86.
- Lentz, D.R., and van Staal, C.R., 1995, Predeformational origin of massive sulfide mineralization and associated footwall alteration at the Brunswick No. 12 Pb-Zn-Cu deposit, Bathurst, New Brunswick: Evidence from the porphyry dike: *Economic Geology*, v. 90, p. 453–463.
- Lentz, D.R., Hall, D.C., and Hoy, L.D., 1997, Chemostratigraphic, alteration, and oxygen isotopic trends in a profile through the stratigraphic sequence hosting the Heath Steele B zone massive sulfide deposit, New Brunswick: *Canadian Mineralogist*, v. 35, p. 841–874.
- Leshner, C.M., Goodwin, A.M., Campbell, I.H., and Gorton, M.P., 1986, Trace element geochemistry of ore-associated and barren felsic metavolcanic rocks in the Superior Province, Canada: *Canadian Journal of Earth Sciences*, v. 23, p. 222–237.
- Longerich, H.P., 1995, Analysis of pressed pellets of geological samples using wavelength-dispersive X-ray fluorescence spectrometry: *X-Ray Spectrometry*, v. 24, p. 123–136.
- Luff, W.M., 1995, A history of mining in the Bathurst area, northern New Brunswick, Canada: *CIM Bulletin*, v. 88, no. 994, p. 63–68.
- MacLean, W.H., and Barrett, T.J., 1993, Lithogeochemical techniques using immobile elements: *Journal of Geochemical Exploration*, v. 48, p. 109–133.
- McAllister, A.L., 1960, Massive sulfide deposits in New Brunswick: *CIM Bulletin*, v. 53, p. 88–98.
- McCutcheon, S.R., 1992, Base-metal deposits of the Bathurst-Newcastle district: Characteristics and depositional models: *Exploration and Mining Geology*, v. 1, p. 105–119.
- McCutcheon, S.R., Luff, W.M., and Boyle, R.W., 2003, The Bathurst Mining Camp, New Brunswick, Canada: History of discovery and evolution of geologic models: *Economic Geology*, Monograph 11, p. 17–35.
- Mysen, B.O., Ryerson, F.J., and Virgo, D., 1980, The influence of TiO₂ on the structure and derivative properties of silicate melts: *American Mineralogist*, v. 65, p. 1150–1165.
- Nash, W.P., and Crecraft, H.R., 1985, Partition coefficients for trace elements in silicic magmas: *Geochimica et Cosmochimica Acta*, v. 49, p. 2309–2322.
- Peter, J.M., 2003, Ancient iron formations: Their genesis and use in exploration for stratiform base metal sulphide deposits, with examples from the Bathurst Mining Camp: *Geological Association of Canada, GeoText 4*, p. 145–176.
- Peter, J.M., and Goodfellow, W.D., 1996, Mineralogy, bulk and rare earth element geochemistry of massive sulfide-associated hydrothermal sediments of the Brunswick Horizon, Bathurst Mining Camp, New Brunswick: *Canadian Journal of Earth Sciences*, v. 33, p. 252–283.
- Petersen, M.D., 1983, The use of the “immobile” elements Zr and Ti in lithogeochemical exploration for massive sulphide deposits in the Precambrian Pecos Greenstone belt of northern Mexico: *Journal of Geochemical Exploration*, v. 19, p. 615–617.
- Rogers, N., and van Staal, C.R., 1997, Comparing the Bathurst Mining Camp to the Japan Sea and Okinawa Trough: Ancient, recent, and active back-arcs [abs.]: *Geological Association of Canada-Mineralogical Association of Canada Annual Meeting, Abstract Volume 22*, p. A-127.
- Rogers, N., van Staal, C.R., Winchester, J.A., and Fyffe, L.R., 2003, Provenance and chemical stratigraphy of the sedimentary rocks of the Miramichi, Tetagouche, California Lake and Fournier groups, northern New Brunswick: *Economic Geology, Monograph 11*, p. 111–128.
- Saif, S.I., 1983, Petrographic and geochemical characteristics of iron-rich rocks and their significance in exploration for massive sulfide deposits, Bathurst, New Brunswick, Canada: *Journal of Geochemical Exploration*, v. 19, p. 705–721.
- Schandl, E.S., and Gorton, M.P., 2002, Application of high field strength elements to discriminate tectonic settings in VMS environments: *Economic Geology*, v. 97, p. 629–642.
- Scott, S.D., 1978, Structural control of the Kuroko deposits of the Hokuroku district, Japan: *Mining Geology*, v. 28, p. 301–311.
- Skinner, R. 1974, Geology of Tetagouche Lakes, Bathurst, and Nepisiguit Falls map areas, New Brunswick with emphasis on the Tetagouche Group: *Geological Survey of Canada, Memoir 371*, 133 p.
- Stix, J., 1991, Subaqueous, intermediate silicic-composition explosive volcanism: A review: *Earth Science Reviews*, v. 31, p. 21–53.
- Sullivan, R.W., and van Staal, C.R., 1990, Age of a metarhyolite from the Tetagouche Group, Bathurst, New Brunswick, from U-Pb isochron analyses of zircons enriched in common Pb: *Geological Association of Canada, Report 3, Paper 89-2, Radiogenic Age and Isotopic Studies*, p. 109–117.
- Sullivan, R.W., and van Staal, C.R., 1995, Preliminary chronostratigraphy of the Tetagouche and Fournier groups in northern New Brunswick: *Geological Association of Canada, Report 9, Current Research 1995-F, Radiogenic Age and Isotopic Studies*, p. 43–56.
- Troop, D.G., 1984, The petrology and geochemistry of Ordovician banded iron formations and associated rocks at the Flat Landing Brook massive sulphide deposit, northern New Brunswick: Unpublished M.Sc. thesis, Toronto, University of Toronto, 218 p.

- Vannucci, R., Bottazzi, E., Wulff-Pedersen, E., and Neumann, E.R., 1998, Partitioning of REE, Y, Sr, Zr, and Ti between clinopyroxene and silicate melts in the mantle under La Palma (Canary Islands): Implications for the nature of the metasomatic agents: *Earth and Planetary Science Letters*, v. 158, p. 39–51.
- van Staal, C.R., 1987, Tectonic setting of the Tetagouche group in northern New Brunswick: Implications for plate tectonic models of the northern Appalachians: *Canadian Journal of Earth Sciences*, v. 24, p. 1329–1351.
- van Staal, C.R., 1992a, The Ordovician Tetagouche group, Bathurst Camp, northern New Brunswick, Canada: History, tectonic setting, and distribution of massive sulfide deposits: *Exploration and Mining Geology*, v. 2, p. 93–103.
- van Staal, C.R., 1992b, Geology and structure of the Brunswick Mines area: New Brunswick Department of Natural Resources and Energy, Mineral Resources, Open File Map 91-40f (21-P5 e,f).
- van Staal, C.R., 1994, Brunswick subduction complex in the Canadian Appalachians: Record of the Late Ordovician to Late Silurian collision between Laurentia and the Gander margin of Avalon: *Tectonics*, v. 13, p. 946–962.
- van Staal, C.R., and de Roo, J.A., 1995, Mid-Paleozoic tectonic evolution of the Appalachian Central Mobile belt in northern New Brunswick, Canada: Collision, extensional collapse, and dextral transpression: *Geological Association of Canada, Special Paper 41*, p. 367–389.
- van Staal, C.R., and Williams, P.F., 1984, Structure, origin, and concentration of the Brunswick 6 and 12 orebodies: *Economic Geology*, v. 79, p. 1669–1692.
- van Staal, C.R., Fyffe, L.R., McCutcheon, S.R., and Langton, J.P., 1992, The Ordovician Tetagouche Group, Bathurst Camp, northern New Brunswick, Canada: History tectonic setting, and distribution of massive-sulfide deposits: *Exploration and Mining Geology*, v. 1, p. 93–103.
- van Staal, C.R., Wilson, R.A., Rogers, N., Fyffe, L.R., Langton, J.P., McCutcheon, S.R., McNicoll, V., and Ravenhurst, C.E., 2003, Geology and tectonic history of the Bathurst Supergroup, Bathurst Mining Camp and its relationships to coeval rocks in southwestern New Brunswick and adjacent Maine—A synthesis: *Economic Geology Monograph 11*, p. 37–60.
- Watson, E.B., 1979, Zircon saturation in felsic liquids: Experimental results and applications to trace element geochemistry: *Contributions to Mineralogy and Petrology*, v. 70, p. 407–419.
- Watson, E.B., and Harrison, T.M., 1983, Zircon saturation revisited: temperature and compositional effects in a variety of crustal magma types: *Earth and Planetary Science Letters*, v. 64, p. 295–304.
- Whalen, J.B., Rogers, N., van Staal, C.R., Longstaffe, F.J., Jenner, G.A., and Winchester, J.A., 1998, Geochemical and isotopic (Nd, O) data from the Ordovician felsic plutonic and volcanic rocks of the Miramichi Highlands: Petrogenetic and metallogenic implications for the Bathurst Mining Camp: *Canadian Journal of Earth Sciences*, v. 35, p. 237–252.
- Whitehead, R.E., 1973, Environment of stratiform sulphide deposition: Variation in Mn:Fe ratio in host rocks at Heath Steele mine, New Brunswick, Canada: *Mineralium Deposita*, v. 8, p. 148–160.
- Winchester, J.A., and Floyd, P.A., 1977, Geochemical discrimination of different magma series and their differentiation products using immobile elements: *Chemical Geology*, v. 20, p. 325–343.
- Woodhead, J., Eggins, S., and Gamble, J., 1993, High field strength and transition element systematics in island arc and back-arc basin basalts: Evidence for multi-phase melt extraction and a depleted mantle wedge: *Earth and Planetary Science Letters*, v. 114, p. 491–504.

