The Canadian Mineralogist
Vol. 39, pp. 1597-1616 (2001)

MINERALOGY AND GEOCHEMISTRY OF SUSPENDED SEDIMENTS FROM GROUNDWATERS ASSOCIATED WITH UNDISTURBED Zn–Pb MASSIVE SULFIDE DEPOSITS, BATHURST MINING CAMP, NEW BRUNSWICK, CANADA

MATTHEW I. LEYBOURNE[§]

Department of Geosciences, University of Texas at Dallas, Richardson, Texas 75083-0688, U.S.A.

ABSTRACT

Suspended sediments from groundwaters were recovered from two undisturbed massive sulfide deposits (Halfmile Lake and Restigouche) in the Bathurst Mining Camp, New Brunswick, Canada. Suspended sediments in most groundwaters are dominated by quartz and aluminum silicate minerals. Fe oxyhydroxides are probably present as surface coatings in addition to amorphous phases. Suspended sediments from groundwaters recovered from boreholes that intersect the Restigouche orebody near its surface expression consist primarily of Fe, Pb, and Zn sulfate and Fe sulfide minerals. In general, suspended sediments are depleted in the mobile elements K, Rb and Cs compared to host rock-types from both deposits. Suspended sediments show generally flat element-enrichment patterns normalized to respective felsic host-rocks for most other elements, but exhibit strong enrichments in Pb, Fe, Co, Zn, Ag, and Eu. Iron-oxide-rich suspended sediments from a borehole that penetrates massive sulfide gossan at the Halfmile Lake deposit are more strongly depleted in most elements relative to other sediments. At the Restigouche deposit, the degree of enrichment in Pb, Zn, Cu, and Ag in the suspended sediment is greater than for the deeper Halfmile Lake deposit. Compared to coexisting groundwaters, suspended sediments are relatively enriched in Al, Fe, Pb, and relatively depleted in Ca, Sr, and Mg. Potassium and Rb are generally more strongly fractionated into the suspended sediment phase than other mobile elements, suggesting that their abundance in the groundwaters is controlled by secondary phases (illite – white mica), consistent with SEM and XRD data. Comparisons of groundwaters, suspended material and host rocks yield important information regarding relative fractionation of major and trace elements among these reservoirs. Suspended sediments proximal to massive sulfide ore have elevated Fe/Ti and base-metal contents; with increasing distance away from mineralization, Al/(Al + Fe + Mn) values increase, base-metal contents decrease, and Zn/Pb values increase. The elevated base-metal content of suspended sediments associated with massive sulfides is important, as mining activities in the Bathurst mining camp can result in changes in groundwater Eh–pH conditions, potentially resulting in greater dispersion of metals that are presently strongly sorbed onto sediments.

Keywords: suspended sediment, massive sulfide, adsorption, groundwater, mineralogy, geochemistry, Bathurst mining camp, New Brunswick, Canada.

SOMMAIRE

Les sédiments en suspension dans les nappes d'eau souterraines ont été échantillonnés près de deux gisements du sulfures massifs intacts, Halfmile Lake et Restigouche, dans le camp minier de Bathurst, au Nouveau-Brunswick, Canada. Dans la plupart des cas, de tels sédiments contiennent surtout du quartz et des silicates d'aluminium. Les oxyhydroxides de fer sont probablement présents sous forme de recouvrements de surface, en partie amorphes. Les sédiments en suspension prélevés des trous de forage qui croisent le gisement de Restigouche près de son expression à la surface contiennent surtout des sulfates, de Fe, Pb, et de Zn, ainsi que des particules de sulfure de fer. En général, ces sédiments sont appauvris en éléments mobiles, tels K, Rb et Cs, par rapport aux roches-hôtes des deux gisements. Ils ne montrent aucun enrichissement dans les autres éléments, comme on le constate dans les tracés normalisés par rapport aux roches felsiques, sauf pour Pb, Fe, Co, Zn, Ag, et Eu. Les sédiments en suspension prélevés dans un trou de forage qui traverse un chapeau de fer contenant sulfures massifs au gisement de Halfmile Lake sont plus fortement appauvris dans la plupart des éléments par rapport aux autres sédiments. Au gisement de Restigouche, l'enrichissement relatif en Pb, Zn, Cu, et Ag dans la charge en suspension est plus marqué que pour le gisement de Halfmile Lake, plus profond. En comparaison des eaux coexistantes, les sédiments en suspension sont relativement enrichis en Al, Fe, et Pb, et appauvris en Ca, Sr, et Mg. Le K et le Rb sont généralement plus fortement enrichis dans la fraction sédiment que les autres éléments mobiles, faisant penser que leur abondance dans les nappes d'eau est régie par des minéraux secondaires (illite – mica blanc), comme semblent l'indiquer les analyses au MEB et par diffraction X. Les comparaisons de la composition de l'eau, du matériau en suspension, et des roches hôtes révèlent des faits importants à propos du fractionnement relatif des éléments majeurs et à l'état de traces parmi ces réservoirs. Les sédiments en suspension dans l'eau près des gisements possèdent un rapport Fe/Ti et des teneurs en métaux de base élevés; en s'éloignant des gisements, les valeurs Al/(Al + Fe + Mn) augmentent, les teneurs en

---

[§] *E-mail address*: mleybo@utdallas.edu

métaux de base diminuent, et les valeurs Zn/Pb augmentent. Le fait que les teneurs en métaux de base des sédiments en suspension associés aux sulfures massifs sont élevées est important, parce qu'un accroissement des activités minières dans le camp minier de Bathurst pourrait causer un changement des conditions Eh–pH dans les nappes d'eau, et donc une plus grande dispersion des métaux qui sont présentement fortement sorbés sur les sédiments.

(Traduit par la Rédaction)

Mots-clés: sédiment en suspension, sulfures massifs, adsorption, eau souterraine, minéralogie, géochimie, camp minier de Bathurst, Nouveau-Brunswick, Canada.

INTRODUCTION

The processes of adsorption onto clay and oxide surfaces have been the focus of intense research over the last few decades because of their importance in sewage sludge disposal, leaching of solutes from landfills, pesticide and fertilizer applications to soils and runoff to water systems, mine tailings and acid mine drainage, and soil and groundwater quality in general (Anderson & Christensen 1988, Lasaga 1990). At a more fundamental level, interactions of mineral surfaces and aqueous fluid greatly influence or control most water–rock processes, including the movement of solutes through rock, soil and groundwater systems, weathering reactions and diagenesis, and redox reactions such as sulfide precipitation (Eggleston & Stumm 1993). The fate of trace metals (*e.g.*, As, Sb, Se, Cr, Co, Ni, Cd, Cu, Zn, Pb) in the natural aquatic environment depends critically on adsorption–desorption reactions at particle surfaces (Müller & Sigg 1992). This study is concerned with the complexation and transport of the products of sulfide oxidation. This kind of information has important implications for both exploration and environmental geochemistry of waters associated with massive sulfide deposits and their tailings in the Bathurst Mining Camp (BMC), New Brunswick, Canada, and elsewhere.

BACKGROUND INFORMATION

The colloidal and suspended fractions of particulate material in ground and surface waters have received increased attention in recent years, as it has been recognized that particulate matter may be important in the transport of contaminants and radionuclides (Swartz *et al.* 1997). It has also been increasingly recognized that suspended sediments and colloids complicate the simplistic view that metal distribution can be described in terms of water–rock partitioning (Miekeley *et al.* 1992). Surface reactions between metals in solution and suspended material, and between suspended material and the aquifer, are fundamental in regulating the transport of trace metals. In addition, recent studies have shown that there is a strong relationship between adsorption onto fine colloids and coagulation of the colloid into larger particles in the case of some metals (Wen *et al.* 1997).

Particles and colloids have the potential to concentrate pollutants by sorption. In some cases, such sorption can lead to greater stability of particles and potentially enhance metal mobility if the particles are sufficiently small to migrate with groundwater (Miekeley *et al.* 1992). In the case of groundwaters intimately associated with massive sulfide deposits in the BMC, it is important to assess the possibility of enhanced mobility of certain elements associated with sulfide mineralization that are not normally very mobile in aqueous systems (*e.g.*, Pb).

The Halfmile Lake and Restigouche massive sulfide deposits are located in the Bathurst Mining Camp, part of the Miramichi terrane of northern New Brunswick (Fig. 1). Rocks of the Tetagouche Group host numerous massive sulfide deposits that are interpreted to have formed within an Ordovician (465–471 Ma) ensialic rift basin (van Staal *et al.* 2001). The detailed geology of the Halfmile Lake and Restigouche deposits has been described elsewhere (Adair 1992, Barrie 1982, Gower 1996, McCutcheon 1997). Briefly, the stratigraphy at the Halfmile Lake deposit consists of felsic units of quartz porphyry, felsic pyroclastic rocks and minor felsic flows, fine-grained volcaniclastic sediments, stringer-zone sulfides, massive sulfides with associated argillite and chert, and younger mafic to intermediate flows and pyroclastic rocks. The deposit is overturned and dips steeply to the north and northwest. The massive sulfides locally crop out, with a well-developed gossan (Fig. 2A), although the bulk of the massive sulfides occur at greater depth. The Restigouche deposit is dominated by metasedimentary (sandstones, argillites, graphitic and mafic tuff, and ferruginous and graphitic argillites) and felsic metavolcanic rocks (Barrie 1982, McCutcheon 1997). There is a northeast-trending swarm of mafic dykes that cross-cuts the deposit and in places appears to infill fault zones (Barrie 1982). Quartz and carbonate veins are common in both the footwall and hanging-wall units, with local development of feldspar veins. The massive sulfides at the Restigouche deposit crop out on the south side of Charlotte Brook as a small body of gossan (Fig. 2B).

Accumulations of massive sulfides at the Halfmile Lake and Restigouche deposits are lens-shaped, stratiform bodies with well-developed stockwork zones. These bodies are dominated by pyrrhotite (Halfmile

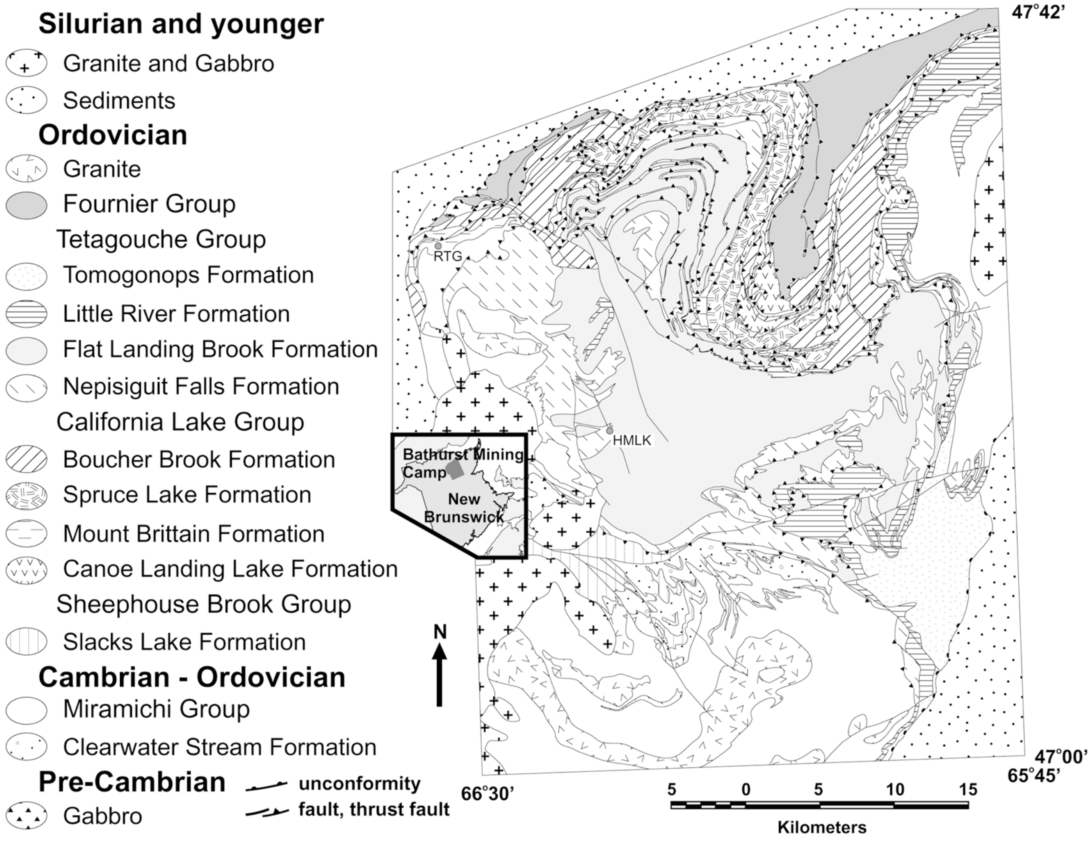

FIG. 1. Location and general geology of the Bathurst Mining Camp, showing the locations of the Halfmile Lake (HMLK) and Restigouche (RTG) deposits. Geology modified after van Staal *et al.* (2001).

Lake), pyrite, sphalerite, galena, and chalcopyrite. Both deposits have gossans, which formed by weathering of the sulfides during the late Tertiary (1–4 Ma) (Symons *et al.* 1996). Gossans produced by weathering of massive sulfide in the BMC are dominated by goethite, which displays relict sulfide textures, along with secondary minerals, dominated by silica, jarosite minerals and other Fe sulfate and Fe oxide phases (Boyle 2001). The gossan at the Restigouche deposit is interpreted to have been subsequently reworked, as shown by the destruction of primary sulfide textures and the replacement of plumbojarosite [$PbFe_6(SO_4)_4(OH)_{12}$] with anglesite ($PbSO_4$) (Boyle 2001).

At both deposits, relief varies from 100 to 400 meters. Soils are thinly developed, and till cover is thin, commonly less than one or two meters in thickness. Groundwater flow at both deposits is fracture-controlled, with more steeply dipping structures at the Halfmile Lake deposit.

METHODS

Groundwaters and associated suspended sediments were collected during the summers of 1994 to 1996 from exploration diamond drill-holes using both flow-through bailer and straddle-packer systems. Boreholes were drilled from 2 to 40 years prior to sampling, sufficient time for equilibrium with natural conditions of groundwater flow to have been attained. Drilling typically utilized local surface waters as drilling fluid. Groundwaters were recovered from 13 boreholes (91 samples) from the Halfmile Lake deposit and 15 boreholes (108 samples) at the Restigouche deposit (Fig. 2). Of these, three boreholes (11 samples) and six boreholes (20 samples) from the two deposits, respectively, had sufficient suspended sediment for geochemical, SEM (scanning electron microscopy) and XRD (X-ray diffraction) analysis.

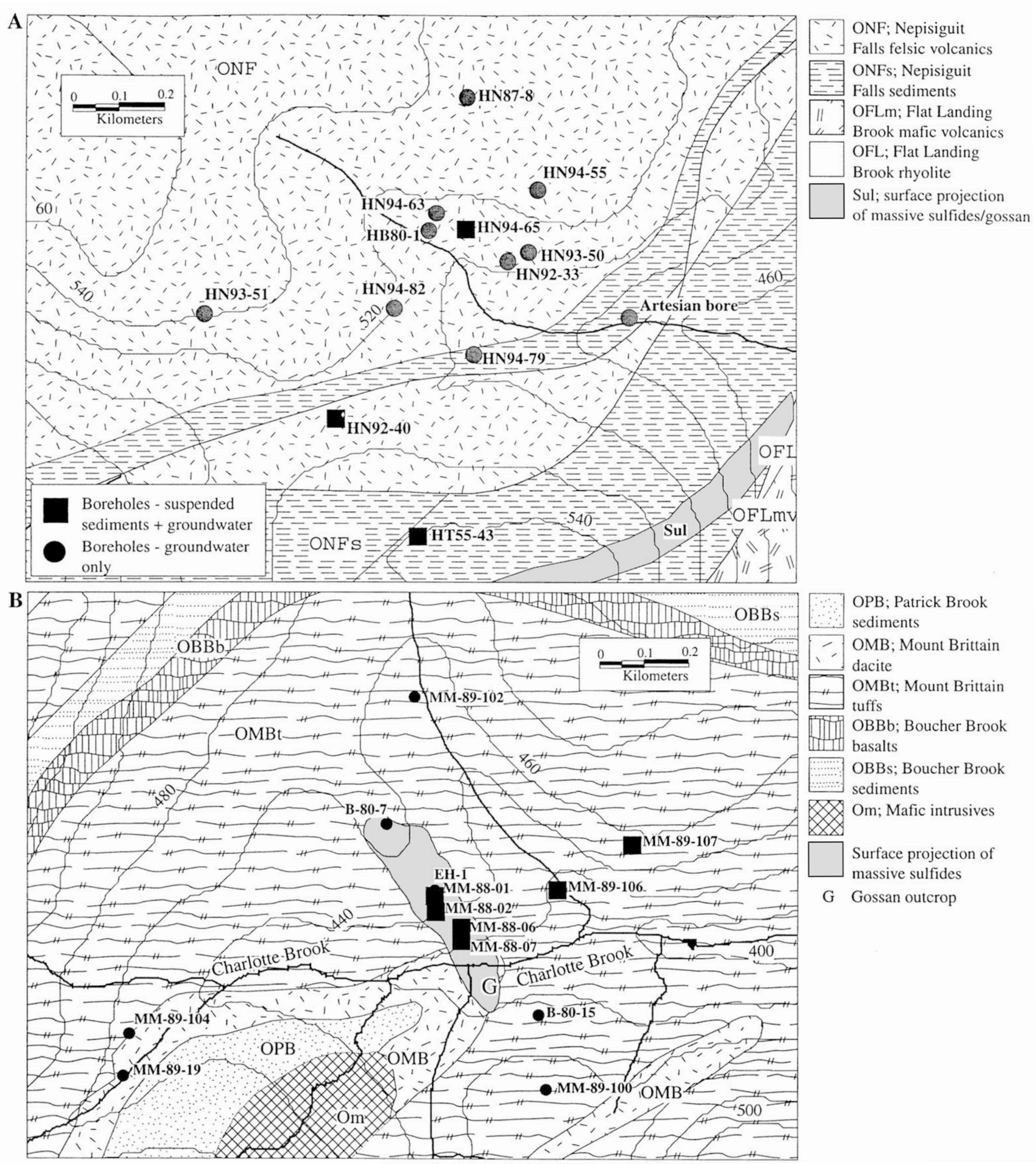

FIG. 2. A) Geology of the Halfmile Lake deposit, showing the location of boreholes sampled for groundwater. Contours are in 20 m intervals. B) Geology of the Restigouche deposit and location of sampled boreholes. Contour interval is 20 m.

The bailer sampler consists of a 1-L PVC tube with two stop-valves through which water flows as the bailer is lowered down-hole owing to the neutral buoyancy of the stop-valves. As the bailer is retrieved, the valves are closed, trapping the groundwater sample. The bailer system is useful in that it allows rapid sampling of borehole waters. However, the degree to which a bailer sample approximates the groundwaters flowing through bedrock at the depth recovered is highly dependent on the flow regime and distribution of hydraulic heads. The straddle-packer system consists of two packers, spaced 1.5 m apart, and the packers are inflated using N_2 gas. Samples were collected after different development time-intervals depending on the hydraulic conductivity of the zone being developed, until the electrical conductivity of the recovered water reached a steady state, which is assumed to represent the conductivity of groundwater at that depth. Parameters measured in the field were pH, Eh, conductivity, temperature, and dissolved oxygen (DO; measured by KCl probe). All samples were filtered *in situ* through 0.45 μm filters.

The suspended sediments discussed here represent the residue collected on 0.45 μm filters during groundwater sampling. Samples were filtered to dryness and sediment-laden filters transferred to individual sealed plastic bags. Sediments were air dried within the plastic bags. Samples of suspended sediment are identified as MLF with the corresponding water sample labeled MLW. Most of the samples described here represent groundwaters collected using the flow-through bailer. Bailer waters typically had a greater amount of suspended material compared to packer samples. The packer apparatus included an in-line 45 μm filter to prevent clogging of the cracking valve in the sample head. In addition, suspended sediment on filters collected during packer sampling tended to decrease with time during development of a zone. Although many recent studies have focussed on the suspended sediment contents of surface waters, streams at the Halfmile Lake and Restigouche deposits typically have insufficient loads of suspended sediment for routine sampling. A detailed discussion of groundwater compositions has been presented elsewhere (Leybourne 1998, Leybourne & Goodfellow 2001, Leybourne *et al.* 1998).

The suspended sediments were analyzed for major elements by inductively coupled plasma – emission spectrometry (ICP–ES) and trace elements by ICP–MS [mass spectrometry; Ag, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Hf, In, Mo, Nb, Ni, Pb, Rb, Sc, Sn, Sr, Ta, Th, Tl, U, V, Y, Zn, Zr, and rare-earth elements (*REE*)] at the Geological Survey of Canada. Full details of the analytical procedures are given in Leybourne (1998). Suspended sediments were analyzed with a scanning electron microscope (SEM) and by X-ray diffraction (XRD) (Table 1) at the Geological Survey of Canada and the University of Ottawa, respectively. Filters con-

TABLE 1. MINERALOGY OF SUSPENDED SEDIMENTS IN GROUNDWATER ASSOCIATED WITH UNDISTURBED Zn–Pb MASSIVE SULFIDE DEPOSITS, BATHURST MINING CAMP, NEW BRUNSWICK

Sample#	Borehole	Type	Anal.	Qtz	Silicates	Fe oxides	Other
					Halfmile Lake deposit		
MLF94-209	HN94-55	bailer	SEM	✓	White mica, Chm	coatings?	
MLF94-237	HN94-65	bailer	XRD	✓	White mica, Chm, Ab		pyrite
MLF94-238	HN94-65	bailer	XRD	✓	White mica, Chm, Ab		pyrite
MLF94-244	HN94-65	bailer	SEM	✓	White mica, Chm, Kln	✓	pyrite
MLF94-250	HN94-65	bailer	SEM	✓	White mica, Chm, Kln	coatings?	pyrite
MLF94-257	HT55-43	bailer	XRD	✓	Chm, white mica	Lepidocrocite	
MLF96-698	HN96-40	packer	SEM	✓	Chm, white mica, Kln	Fe–Mn coatings	pyrite
					Restigouche deposit		
MLF95-312	MM-88-01	bailer	XRD	✓	White mica, Chm, Kln		pyrite
MLF96-671	MM-88-01	packer	SEM	tr.	White mica, Kln		Fe sulfate, Zn sulfate, S
MLF95-331	MM-88-02	bailer	SEM	✓	White mica, Chm?		Minor barite, rare Ti oxide
MLF95-326	MM-88-02	bailer	SEM		White mica, rare Chm		NaCl, barite, Fe sulfate, pyrite
MLF95-358	MM-88-06	bailer	SEM		White mica, Kln, Ab?	Fe, Pb, Zn oxides?	Pb, S, Fe, Zn with small O peaks, *i.e.*, pyrite, galena, sphalerite + sulfates
MLF95-364	MM-88-06	bailer	XRD	✓	White mica, Kln, feldspar		pyrite
MLF95-315	MM-88-07	bailer	SEM				Fe, Pb sulfates or sulfides
MLF95-317	MM-88-07	bailer	XRD	✓	Kln, feldspar, white mica		pyrite, anglesite?
MLF95-332	MM-89-106	bailer	XRD	✓	White mica, Chm, Kln, Ab, Ksp		
MLF95-341	MM-89-106	bailer	XRD	✓	White mica, Chm, Kln, Ab		
MLF95-504	MM-89-106	packer	SEM	✓	Kln? Typically with trace K and Fe	coatings?	NaCl, S common, *REE* phosphates
MLF95-592	MM-89-107	packer	XRD	✓	White mica, Kln, Chm, Ab, Ksp		

Some white mica is likely illite. Mineral symbols: Ab albite, Chm chamosite, Kln kaolinite, Ksp K-feldspar, Qtz quartz. ✓: present; tr.: trace.

taining suspended sediment were carbon-coated and mounted directly in an SEM. Owing to the small size of samples, XRD analyses were performed by grinding the sediment in a mortar and pestle and mounting on a zero-background silica disc as a slurry of sediment and acetone. As a result, counts are generally quite low (generally <2000 counts/peak).

MINERALOGY OF SUSPENDED SEDIMENTS IN GROUNDWATER

Suspended sediment from the Halfmile Lake deposit is dominated by quartz and aluminum silicate minerals (Table 1, Fig. 3). XRD analyses suggest that quartz is the dominant silicate, although SEM data indicate that K-bearing silicates (illite and white mica) also are common. Chamosite is a common phase in some samples, and kaolinite also is present, although typically in lesser abundance. Accessory phases include albite, pyrite, and Fe oxides (Table 1). Oxides of Fe and Al were only rarely positively identified, but most phases analyzed by SEM indicate a Fe peak, consistent with surface coatings of Fe oxides on other mineral phases. Standard SEM is poor at resolving Fe and Al oxides where they have thicknesses less than 5 μm (Coston *et al.* 1995). XRD results for Fe-rich sediments from the borehole in the gossan suggest that there may be only minor lepidocrocite present, suggesting that the oxides are dominantly amorphous and so were not detected by XRD. Suspended particles of sediment from all Halfmile Lake deposit samples are dominantly <10 μm in size (*e.g.*, Fig. 3).

Suspended sediments from Restigouche deposit groundwaters are also dominated by quartz and aluminum silicates (mainly illite – white mica, chamosite and lesser kaolinite; Table 1). However, there is greater variety than is the case for the Halfmile Lake deposit. Suspended sediments from shallow boreholes within the massive sulfide zone are dominated by Fe, Pb, and Zn sulfides or sulfates. XRD data suggest that pyrite is the

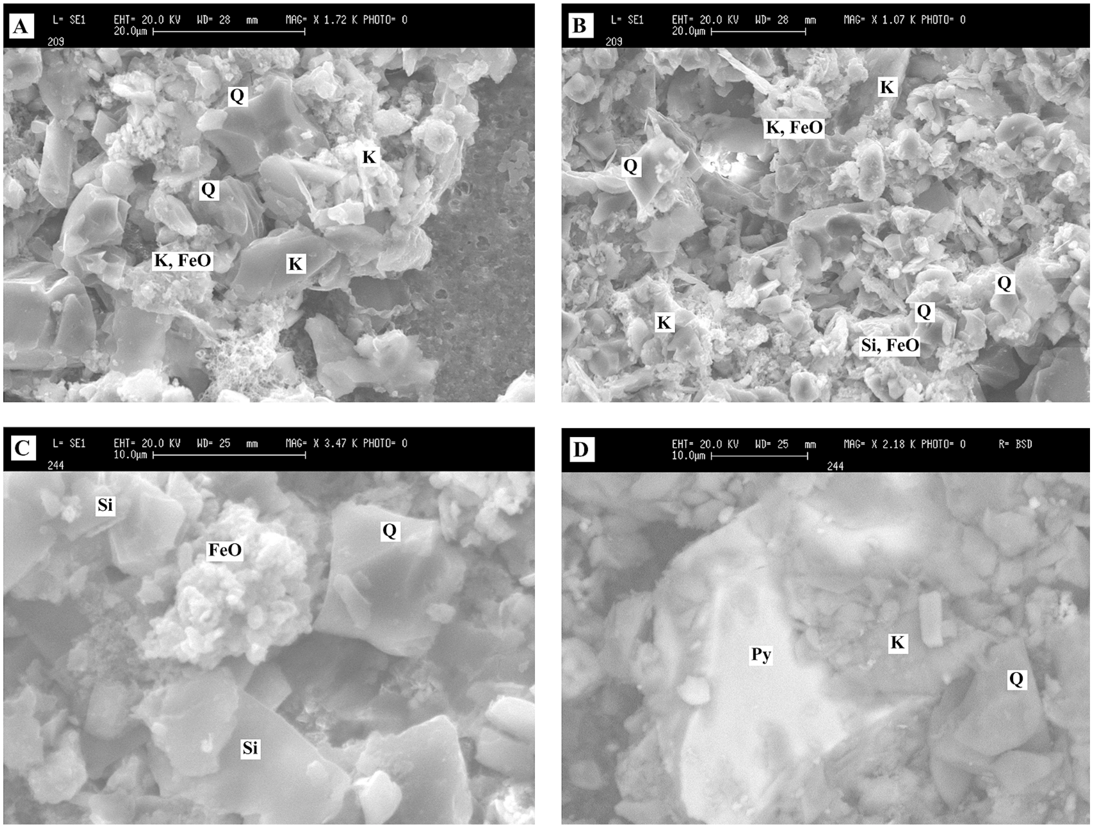

FIG. 3. Secondary SEM images of suspended sediment from groundwater at the Halfmile Lake deposit. Q: quartz, K: K silicates, FeO: Fe oxides, Si: sheet aluminum silicates. A, B) Sample MLF94–209, borehole HN93–50. C, D) Sample MLF94–244, borehole HN94–65.

dominant sulfur-bearing phase in these shallow boreholes. However, the SEM data show strong Fe and Pb peaks, and variable-intensity Zn peaks, coupled with strong S peaks and variable, though generally weaker, O peaks. These data suggest that at least some of the metals are present as sulfates and, perhaps, oxides. For example, XRD analysis of sample MLF95–317 yielded peaks consistent with anglesite ($PbSO_4$). However, speciation and saturation-index calculations on groundwaters from these shallow (60–65 m depth) boreholes indicate that all the waters are below saturation for sulfate minerals [based on thermodynamic data in both the EQ3NR (Wolery 1992) and PHREEQC (Parkhurst 1995) databases], although anglesite comes closest to saturation, with $SI_{anglesite}$ as high as –0.833 (SI: saturation index). The SEM images of these metal–sulfur species reveal a more porous, "semi-amorphous" appearance than is typical of metal sulfides (Figs. 4A, B).

Suspended sediments from a borehole that intersects the massive sulfides at greater depth (65–80 m) are dominated by illite and white mica (Table 1, Fig. 4). However, the composition of these sediments indicates that Al oxide or kaolinite (or both) should be abundant (Al_2O_3 ranges from 21.0 to 31.4 wt.%, see below). The fact that only small peaks of kaolinite were observed in the XRD pattern suggests that amorphous Al oxides are common phases in these sediments. As with the shallow boreholes, suspended sediments have abundant metal–sulfur species (Fe, Zn), which may be present as sulfides, sulfates, or both (Fig. 4).

Suspended sediments from the saline groundwaters (> 20,000 mg/L total dissolved solids, TDS) contain primarily K-bearing silicates and quartz, with minor barite (Fig. 5). These waters have SO_4 contents less than the detection limit (50 μg/L) and have elevated Ba contents (90,000 μg/L) (Leybourne 1998). Halite is another common phase noted in SEM and XRD data on suspended sediments from the saline groundwaters, although the waters are well below halite saturation (SI_{halite} reaches a maximum of $10^{-2.9}$) (Leybourne 1998).

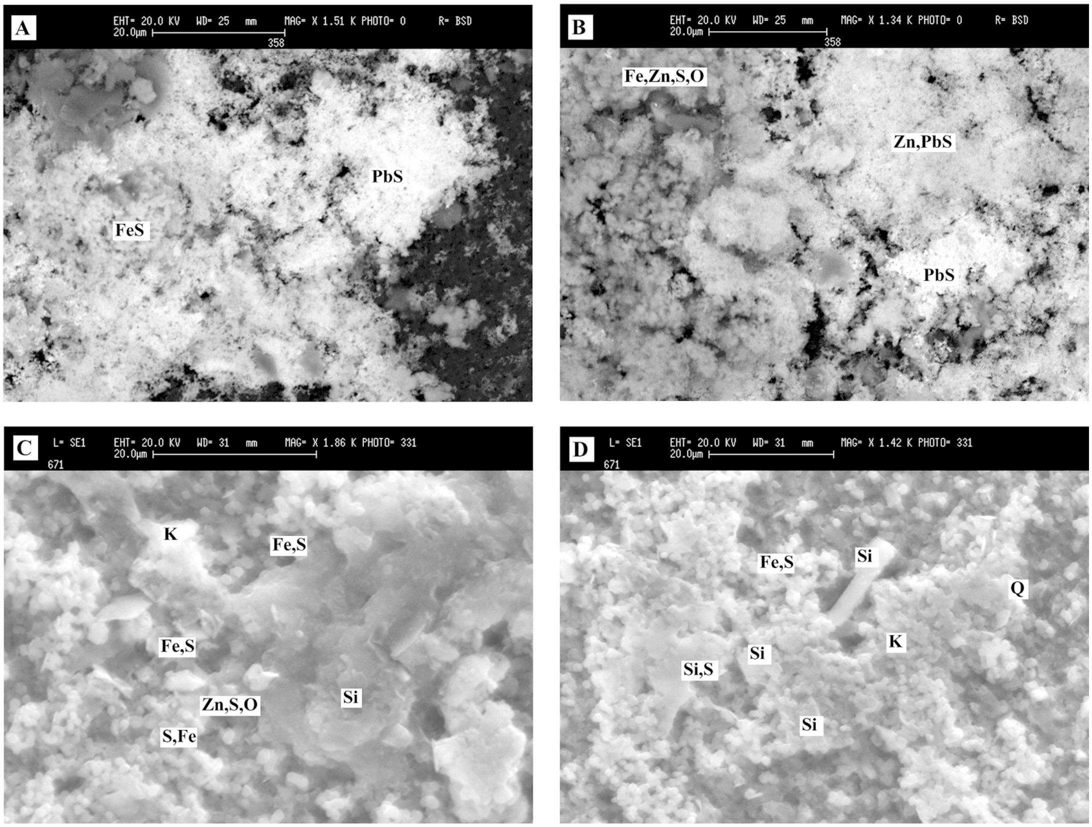

FIG. 4. Secondary SEM images of suspended sediment from groundwater at the Restigouche deposit. Q: quartz, K: K silicates, Si: sheet aluminum silicates. S, Fe, Zn, Pb refer to the dominant peaks of elements on the porous sulfates. A, B) Sample MLF95–358, borehole MM–88–06. C, D) Sample MLF96–671, borehole MM–88–01.

The most likely explanation is that the halite is secondary, due to post-collection evaporation on the surface of the filters.

Silicates dominate the suspended sediments from boreholes distal from the Restigouche deposit (Fig. 2B), which is consistent with low metal and generally low sulfate contents of the groundwaters. Quartz, white mica, chamosite, and kaolinite with accessory albite and K-feldspar are the dominant phases (Fig. 6). One sample also contains accessory *REE* phosphate minerals (Table 1, Fig. 6) and minor NaCl. The latter is most likely due to post-sampling evaporation of this brackish NaCl-type groundwater (salinity up to 2600 mg/L TDS).

Geochemistry of the Suspended Sediments

Thirty-one samples were analyzed for trace and major elements by ICP–MS and ICP–ES (Table 2). Owing to insufficient material, SiO_2, LOI, P_2O_5, and total S contents were not determined. A potential source of error is the likely formation of salt due to drying, at least for the more saline waters. To evaluate detrital *versus* hydromorphic components, suspended sediments are compared to the least-altered felsic rocks from the Halfmile Lake and Restigouche deposits. Full geochemical data for the host rocks of both deposits are available (Adair 1992, Leybourne 1998). From these, ten samples of felsic volcanic rocks from each deposit were chosen in order to normalize the data on suspended sediments, in order to investigate relative fractionation of elements. The least-altered samples were chosen on the basis of a low value of loss on ignition (LOI), H_2O, CO_2 and S contents.

The Halfmile Lake deposit

Eleven samples of groundwater from three boreholes yielded sufficient suspended sediment for geochemical analysis (Table 2). Two of the boreholes penetrate the massive sulfide zones at depth (around 720 m in bore-

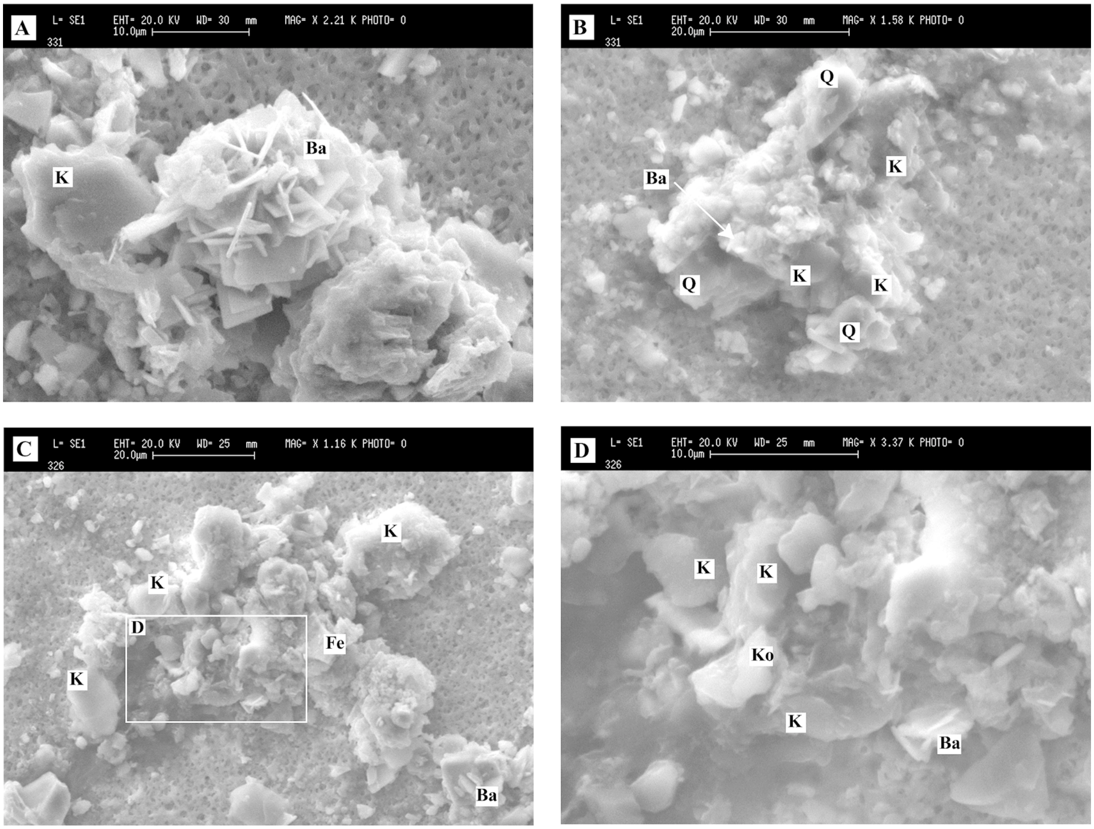

FIG. 5. Secondary SEM images of suspended sediment from groundwater at the Restigouche deposit. Q: quartz, K: K silicates, Ko: kaolinite, Ba: barite. A, B) Sample MLF95–331, borehole MM–88–02. C, D) Sample MLF95–326, borehole MM–88–02.

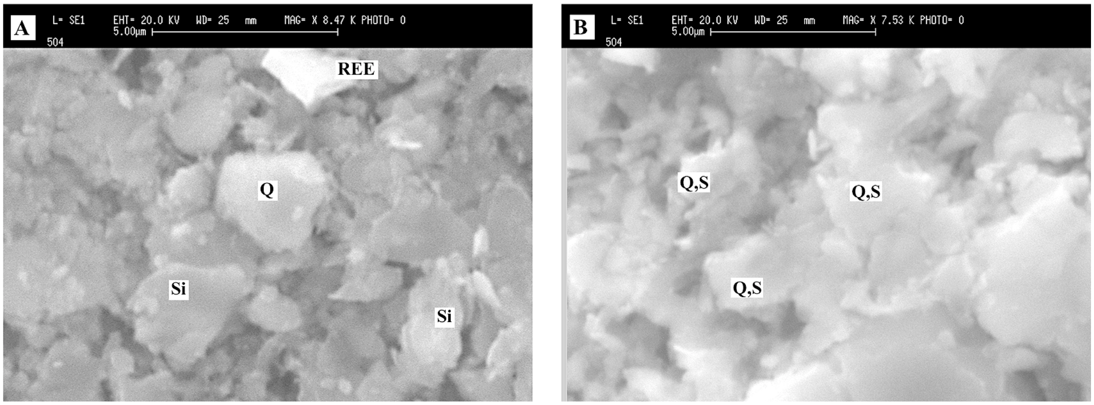

FIG. 6. Secondary SEM images of suspended sediment from groundwater at the Restigouche deposit. Q: quartz, Si: sheet aluminum silicates, S: sulfur peak, *REE*: *REE* phosphate. A, B) Sample MLF95–504, borehole MM–89–106.

hole HN92–40 and 470 and 640 m in borehole HN95–65), and one borehole penetrates the gossan near the surface expression of the deposit (Fig. 2A).

The geochemistry of the suspended sediments from the gossan borehole broadly reflects what is expected from gossan formed by the weathering of massive sulfides in the BMC. Total Fe contents are elevated (39.3 to 64.0 weight %, as Fe_2O_3). Base-metal contents (Zn, Pb, and Cd) are generally low compared to the other suspended sediments at Halfmile Lake, although the gossan sediments have higher Cu contents (690–1400 ppm *versus* a maximum of 490 ppm). The sediments associated with the gossan generally have a higher Mn content than other suspended sediments, suggesting the presence of Mn oxides. Although the XRD data indicate that the main phases in these sediments are quartz and aluminum silicates, Fe (and Mn?) oxides predominate visually. Compared to average unaltered felsic rock-types at Halfmile Lake, these sediments show depletions in levels of large-ion lithophile elements (LILE) such as Cs, Rb, U and in many of the high field-strength elements (HFSE) such as the *LREE* (light *REE*) and, to an even greater extent, Nb, Hf, and Zr (Fig. 7). Conversely, these sediments are highly enriched in Fe, Pb, Co, Zn, Ag, and Eu relative to the host rocks (Fig. 7).

Figure 8 shows the composition of the groundwater normalized to that of the corresponding suspended sediment. Note that the water samples have been multiplied by 1000 (major and trace elements in waters are typically at the ppm and ppb level *versus* weight % and ppm levels for the sediments). Thus, the 1:1 line in Figure 8 actually represents 1:1000. There is a variation of about six orders of magnitude in the differences between suspended sediment and the corresponding water. For the gossan-associated suspended sediments, elements that are relatively fractionated into the solid phase include Al, Fe, Pb, and Cu. Zinc, Mn and K are also fractionated into the solid phase, but less strongly so. Relative to these metals, Mg, Na and, especially, Ca, are fractionated into the groundwater. Cadmium exhibits relatively greater affinity for the aqueous phase than Zn (Fig. 8).

Suspended sediments from the deeper boreholes are characterized by lower Fe contents, and higher Al, K, and Na than those from the gossan (Table 2). The higher alkali metals and Al are consistent with abundant silicate minerals identified by XRD and SEM (Table 1, Fig. 3). Zinc and Pb contents are high in these sediments (1400–4000 ppm Zn, 560–1600 ppm Pb). Indeed, the Zn and Pb contents are considerably higher than in any of the stream sediments from the Halfmile Lake deposit (maximum of 730 and 100 ppm, respectively) (Leybourne 1998), and the Pb contents are similar to Pb contents of stream sediments immediately downstream from the Restigouche deposit. Compared to the host felsic rocks, the suspended sediments from the deeper boreholes have generally flat patterns overall, indicating little elemental fractionation (Fig. 7). However, the suspended sediments are depleted in Cs, Rb, K, and Ba compared to the host rocks (with the exception of the sample from borehole HN92–40, which is relatively enriched in Cs, Rb and the *LREE*), and enriched in Eu, Fe, Pb, Co, Zn, and Ag (Fig. 7). Zinc and Pb contents are up to 100 times the host-rock values. Compared to the coexisting groundwaters, these sediments show similar relationships to the suspended sediments in the case of the borehole in gossan (Fig. 8). However, samples from the deeper boreholes show less relative fractionation between the groundwater and the suspended sediment for Mn, Ca, Na, K, and Ba, but generally greater relative fractionation in Pb and Zn.

For suspended sediments at the Halfmile Lake deposit, there is a relationship between Zn/Pb and proximity to massive sulfides. Although base-metal contents

TABLE 2. GEOCHEMICAL DATA ON SUSPENDED SEDIMENT, IN GROUNDWATER ASSOCIATED WITH UNDISTURBED Zn–Pb MASSIVE SULFIDE DEPOSITS, BATHURST MINING CAMP, NEW BRUNSWICK

Sample #	94-236	94-237	94-238	94-242	94-248	94-249	94-255	94-257	94-258	94-259	96-696	95-307	95-309	95-312	95-313	95-606
Borehole	HN94-65	HN94-65	HN94-65	HN94-65	HN94-65	HN94-65	HT55-43	HT55-43	HT55-43	HT55-43	HN92-40	MM-88-01	MM-88-01	MM-88-01	MM-88-01	MM-88-02
Deposit	H	H	H	H	H	H	H	H	H	H	H	R	R	R	R	R
Type	bailer	bailer	bailer	bailer	bailer	bailer	bailer	bailer	bailer	bailer	packer	bailer	bailer	bailer	bailer	packer
Depth (m)	50	100	150	250	500	550	40	60	70	80	214	50	80	125	140	511
TiO_2 wt.%	0.39	0.39	0.43	0.44	0.40	0.44	0.12	0.19	0.30	0.25	0.58	0.05	0.08	0.12	0.12	0.21
Al_2O_3	9.19	9.50	9.41	9.70	8.64	8.85	2.66	3.77	9.50	6.27	14.00	31.40	26.90	21.00	21.90	11.60
Fe_2O_3t	12.50	12.70	12.80	12.50	12.90	14.10	64.00	53.80	39.30	43.80	17.50	7.01	9.60	13.40	13.00	6.45
MnO	0.06	0.06	0.06	0.06	0.05	0.05	0.30	0.23	0.16	0.19	0.52	0.02	0.03	0.05	0.05	0.03
MgO	1.88	2.01	1.99	2.09	1.93	1.91	0.66	0.89	1.25	1.12	2.06	0.40	0.65	1.13	1.07	1.38
CaO	0.27	0.28	0.29	0.30	0.31	0.45	0.05	0.06	0.73	0.05	0.63	0.19	0.22	0.29	0.24	1.27
Na_2O	1.11	1.14	1.15	1.12	1.07	1.38	0.14	0.20	0.31	0.50	1.02	0.52	0.50	0.53	0.53	6.18
K_2O	1.95	2.01	2.01	2.00	1.80	1.87	0.32	0.46	1.62	1.08	3.17	0.38	0.59	0.94	0.89	4.04
Ag ppm	15	15	17	13	14	29	4.6	8.0	4.3	6.8	11	9.1	12	9.4	45	22
Ba	490	510	510	510	470	500	2400	2500	1100	70	560	110	140	240	190	3300
Be	1.6	1.6	1.6	1.7	2.7	6.3	0.5	0.5	1.1	0.6	11	7.6	7.2	6.2	6.4	8
Bi	3.6	3.5	3.8	3.5	4.2	5.1	8.7	11	7.3	46	6.1	3.2	4.2	5.8	5.2	2
Cd	6.4	6.9	6.7	7.1	5.6	6.6	1.1	0.9	0.6	0.8	7.1	4.6	6.5	10	17	1.9
Co	30	29	29	37	70	180	60	47	26	57	180	110	100	51	80	15
Cr	83	89	95	100	110	190	61	64	70	52	250	91	88	140	110	120
Cs	1.5	1.6	1.6	1.6	1.4	1.3	0.36	0.57	1.3	1.1	42	0.8	1.2	2.3	2.2	14
Cu	380	390	390	400	410	490	1400	1400	690	1800	240	360	480	600	590	110
Ga	14	13	12	13	17	31	5.4	5.7	12	9.2	20	6.1	7.9	10	10	19
Hf	5.4	4.8	6.2	5.8	5.2	6.8	1.1	1.7	2.7	2.9	5.7	2.3	2.3	3.3	3	5.4
In	1.4	1.4	1.4	1.5	1.7	1.7	0.61	0.9	0.45	2	1.9	1	0.94	1.3	1.3	0.71
Mo	24	23	23	21	21	22	20	15	10	11	50	6.1	6.2	46	16	5.9
Nb	11	11	11	12	11	12	3	4.4	6.8	5.6	14	1.8	2.6	7.2	4.3	10
Ni	39	40	42	44	58	110	130	98	65	69	79	55	55	170	80	30
Pb	1400	1500	1500	1500	1600	1500	190	230	120	270	560	3500	4800	6700	6500	230
Rb	80	82	80	88	81	81	16	22	74	53	150	19	29	54	45	160
Sc	7.4	7.7	7.7	7.9	7.4	8	3.6	4.5	9.4	6.8	17	6.6	7.2	8.1	8.1	9.5
Sn	18	16	29	29	16	350	13	44	12	29	54	29	77	16	74	130
Sr	26	24	25	25	24	28	24	22	26	20	47	11	15	25	21	530
Ta	0.9	0.8	0.5	0.9	0.5	1.2	0.4	0.8	0.6	0.4	1.5	1.0	0.5	3.3	2.8	1.1
Th	9.5	9.9	9.9	10	9.9	9.7	2.6	3.7	7.7	5.6	13	3.7	5.4	9.1	8.9	21
Tl	0.79	0.79	0.79	0.77	0.76	0.85	0.11	0.13	0.46	0.42	1.1	0.83	1.6	2.9	2.7	0.98
U	4.7	4.4	4.5	4.4	4.3	4.7	0.86	1.1	2.2	1.8	6.1	65	58	49	50	4.6
V	47	48	48	49	46	47	22	26	58	41	96			13	5	12
Y	27	27	34	35	28	36	7.9	10	19	14	34					48
Zn	3800	4000	3900	4000	2800	2700	420	400	340	230	1400	2100	2800	3400	3100	3900
Zr	200	180	230	220	190	250	46	64	89	92	200	69	81	110	95	210
U/Mo	0.20	0.19	0.20	0.21	0.20	0.21	0.04	0.07	0.22	0.16	0.12	10.66	9.35	1.07	3.13	0.78
Zn/Pb	2.71	2.67	2.60	2.67	1.75	1.80	2.21	1.74	2.83	0.85	2.50	0.60	0.58	0.51	0.48	16.96

are variable with depth (Table 2), the Zn/Pb value decreases toward the depth at which massive sulfides occur. The lowermost samples from the boreholes have Zn/Pb less than 1. Similar relationships exist for proximity to the Restigouche deposit (see below).

The Restigouche deposit

Twenty samples of suspended sediment from six boreholes at the Restigouche deposit were sufficiently large for geochemical analyses. Four of the boreholes intersect massive sulfide. Boreholes MM–88–06 and MM–88–07 are shallow (65 and 60 m depth, respectively) and intersect sulfides close to the surface (7–55

TABLE 2 (continued). GEOCHEMICAL DATA ON SUSPENDED SEDIMENT, IN GROUNDWATER ASSOCIATED WITH UNDISTURBED Zn–Pb MASSIVE SULFIDE DEPOSITS, BATHURST MINING CAMP, NEW BRUNSWICK

Sample #	95-361	95-362	95-364	95-315	95-317	95-318	95-332	95-335	95-336	95-341	95-343	95-508	95-354	95-355	95-592
Borehole	MM-88-06	MM-88-06	MM-88-06	MM-88-07	MM-88-07	MM-88-07	MM-89-106	MM-89-106	MM-89-106	MM-89-106	MM-89-106	MM-89-106	MM-89-107	MM-89-107	MM-89-107
	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
	bailer	bailer	bailer	bailer	bailer	bailer	bailer	bailer	bailer	bailer	bailer	packer	bailer	bailer	packer
	25	35	65	20	40	55	25	100	125	200	250	195	160	180	169
TiO_2 wt.%	0.14	0.25	0.21	0.05	0.07	0.08	0.40	0.42	0.42	0.39	0.40	0.36	0.37	0.17	0.33
Al_2O_3	5.08	7.45	8.14	3.97	3.46	3.63	13.90	14.10	14.00	12.70	13.50	14.50	11.90	6.00	15.40
Fe_2O_3t	16.80	20.50	22.10	35.60	38.20	37.10	10.30	9.90	10.70	10.00	9.11	6.71	8.12	3.65	4.88
MnO	0.05	0.08	0.09	0.01	0.02	0.02	0.69	0.61	0.64	0.56	0.57	0.10	1.17	0.52	0.06
MgO	0.76	1.05	1.16	0.35	0.42	0.51	1.29	1.32	1.32	1.25	1.29	1.46	1.05	0.51	1.49
CaO	0.21	0.28	0.39	0.12	0.14	0.15	0.40	0.41	0.42	0.41	0.44	0.57	0.53	0.22	0.41
Na_2O	0.26	0.28	0.29	0.08	0.08	0.10	1.51	1.56	1.54	1.33	1.51	1.83	1.64	0.93	2.58
K_2O	1.17	1.44	1.54	0.26	0.30	0.40	2.64	2.68	2.64	2.52	2.63	2.99	1.86	0.97	2.88
Ag ppm	27	39	40	99	110	140	2.2	2.0	2.0	13	15	4.7	7.0	7.5	6.9
Ba	2700	220	1400	150	250	310	1100	1100	1100	1100	1200	1300	1300	600	1100
Be	2.6	1	1.3	2.1	1.2	1	2.8	2.9	2.9	3.5	3.6	5.3	6.6	5.9	3.9
Bi	6.1	7.4	8.4	4.6	5.7	6.1	0.8	0.6	1.1	0.9	1.2	1.8	2.7	1.7	2.1
Cd	320	280	230	40	47	52	2.9	2.6	2.9	2.7	2.5	9.3	4.6	2	4.8
Co	94	39	48	13	15	13	50	46	57	64	41	120	170	180	91
Cr	63	39	48	36	29	30	64	69	73	78	92	180	160	120	23
Cs	2.2	2.5	2.7	0.46	0.48	0.76	8.2	8.5	8.8	8.7	9.6	16	9.4	4.5	15
Cu	2200	3100	3000	2000	2500	2600	150	150	160	170	150	180	130	59	55
Ga	14	16	17	7.8	7.4	8.3	18	20	20	21	22	23	23	13	21
Hf	3.1	4.7	3.9	1.4	1.8	2.2	6.6	7	7	6.3	6.8	6	7.9	4	8
In	1.6	1.4	1.5	0.9	0.71	0.76	0.16	0.08	0.22	0.14	0.21	0.4	1.1	0.56	0.16
Mo	32	26	23	32	25	23	6.2	6.2	7.7	10	8.8	7.4	20	12	0.7
Nb	5.3	8.1	6.6	3.5	2.2	2.6	13	14	13	14	13	12	15	7.7	15
Ni	65	37	42	20	16	12	41	44	51	54	47	120	120	95	210
Pb	153000	129000	109000	112000	119000	111000	120	110	110	120	120	430	300	96	110
Rb	62	71	74	13	14	18	110	110	120	120	120	150	110	57	150
Sc	5.4	7.2	7.6	7.8	8.8	9	14	14	14	13	14	16	20	9.4	13
Sn	39	85	59	62	70	120	7.4	10	8.2	16	12	16	27	30	76
Sr	71	95	96	10	14	16	80	95	100	93	120	140	110	52	71
Ta	0.6	0.7	0.6	0.7	0.5	0.4	0.9	1.0	1.1	0.9	0.8	0.9	1.2	0.9	0.9
Th	10	12	13	5.5	6.6	6.9	18	19	19	20	21	21	21	9.4	21
Tl	46	38	32	5.5	5.9	6.7	1.1	1	0.92	1	1	1.1	1.3	0.73	1
U	6.5	7.6	8.9	37	35	29	9.2	9.7	9.4	9.3	9.4	7.3	12	3.3	7.4
V	18	26	27	17	16	17	45	46	45	43	44	57	37	14	27
Y	16	26	20	24	20	19	59	62	60	59	60	48	68	24	41
Zn	77000	72000	64000	8900	11000	12000	280	270	290	290	300	1600	370	200	800
Zr	110	190	150	59	74	82	260	260	260	220	240	200	290	160	320
U/Mo	0.20	0.29	0.39	1.16	1.40	1.26	1.48	1.56	1.22	0.93	1.07	0.99	0.60	0.28	10.57
Zn/Pb	0.50	0.56	0.59	0.08	0.09	0.11	2.33	2.45	2.64	2.42	2.50	3.72	1.23	2.08	7.27

Deposit: H: Halfmile, R: Restigouche. Concentration of major elements expressed as oxides, in weight %; that of trace elements, in ppm. The sample numbers all have the prefix MLF.

m and 2–51 m, respectively). Groundwaters from those holes have high metal contents (Zn up to 2300 μg/L, Pb up to 1400 μg/L) (Leybourne & Goodfellow 2001). Boreholes MM–88–01 and MM–88–02 are deeper (170 and 600 m, respectively) and intersect the sulfides at greater depth (65–80 m). Groundwaters in the latter hole are saline (> 20,000 mg/L TDS) Na–Ca–Cl fluids. Boreholes MM–89–106 (250 m depth) and MM–89–107 (235 m depth) were drilled to the east of the deposit (Fig. 2B) and do not intersect the massive sulfides.

Suspended sediments from the shallow boreholes are characterized by high Fe contents and elevated base-

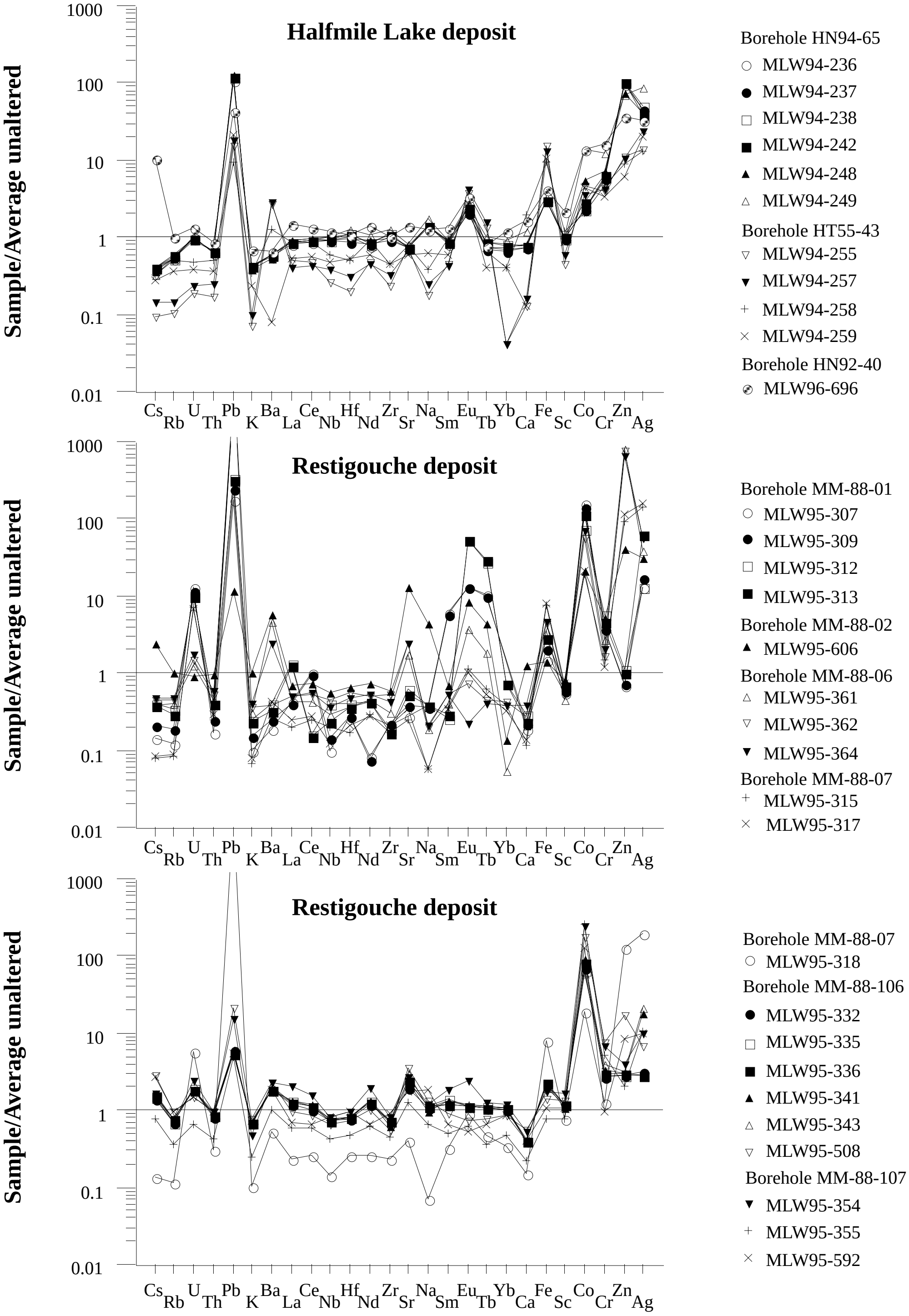

FIG. 7. Trace- and major-element contents of suspended sediments along boreholes at Halfmile Lake and Restigouche deposits, normalized to average unaltered felsic rock-types from each deposit. The normalizing values and *REE* values are given in Leybourne (1998).

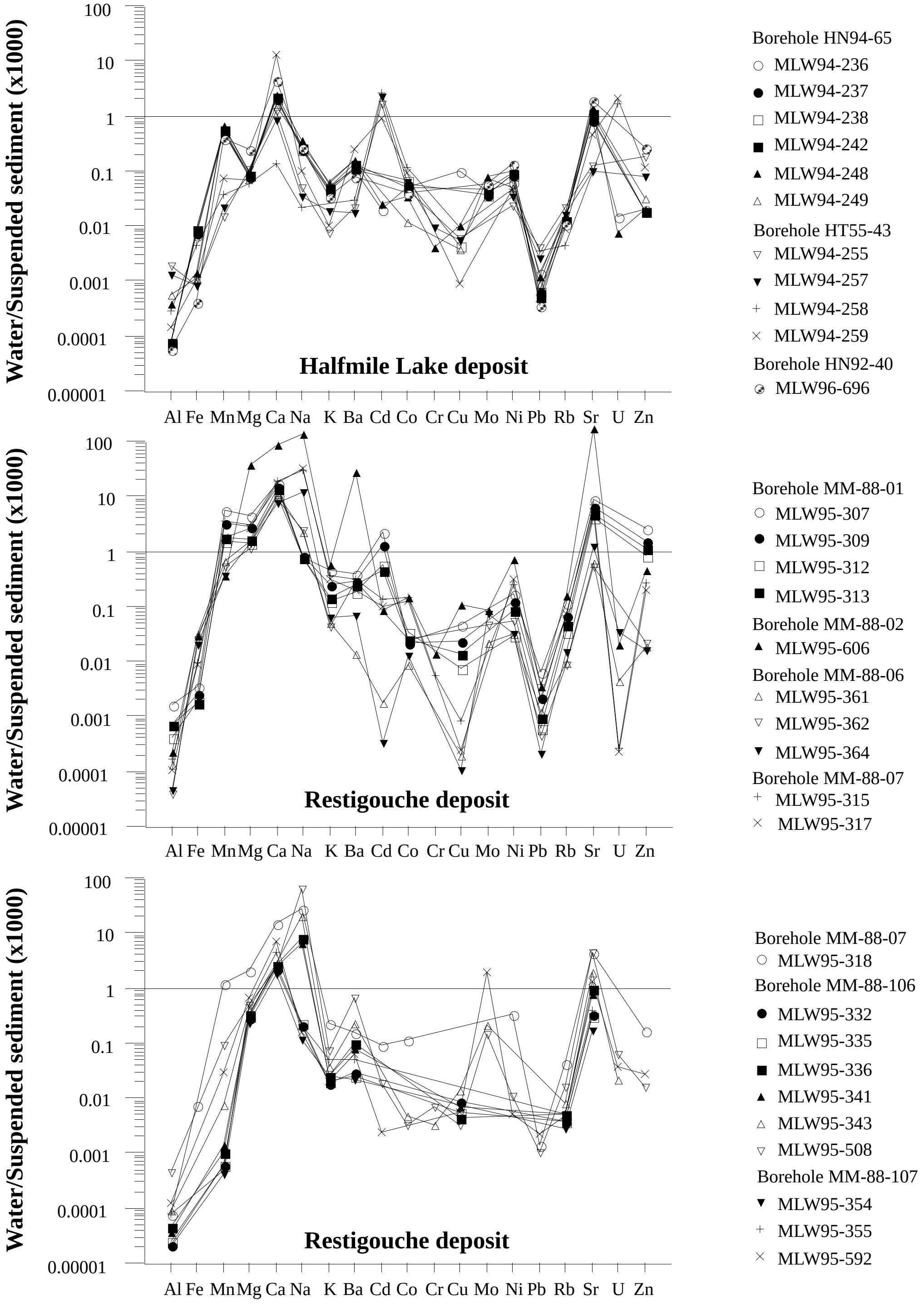

FIG. 8. Trace- and major-element contents of borehole waters at Halfmile Lake and Restigouche deposits, normalized to the corresponding suspended sediment. Groundwater geochemistry given in Leybourne & Goodfellow (2001), Leybourne *et al.* 1998).

metal contents. In this latter respect, they are quite different from the high-Fe sediments from the gossan borehole at the Halfmile Lake deposit. For example, Pb contents range from 11.1 to 15.3 wt.% (Table 2). Zinc contents are also high, ranging from 0.89 to 7.7 wt.%, but are lower than Pb. Other sulfide-associated elements are similarly enriched, including Cd, Tl, and Bi. These sediments also have high Ag contents, up to 140 ppm. Compared to average unaltered host-rocks, suspended sediments from these boreholes are depleted in most elements associated with terrigenous and clastic rocks (*i.e.*, *LILE*, *HFSE*, and the *REE*) and enriched in Pb, Co, Ag, Fe, and Zn (Fig. 7). Compared to the corresponding groundwaters, these sediments are relatively enriched particularly in Cu, Pb, Zn, and Al (Fig. 8).

Suspended sediments from deeper holes within the sulfides differ from those from the more shallow boreholes. These deeper sediments have lower base-metal contents, although elevated compared to sediments distal from the deposit. Zinc and Pb contents range from 2100 to 3400 ppm and from 3500 to 6700 ppm, respectively. These deeper sediments also have unusually high Al contents, ranging from 21.0 to 31.4 wt.% Al_2O_3 (Table 2). All the other suspended sediments analyzed in this study have <15 wt.% Al_2O_3, and most are <10 wt.%. However, despite the high Al contents, Na, K, Mg, and Ca contents are generally low, suggesting that the Al occurs primarily as kaolinite or Al oxide phases (the SEM and XRD data are most consistent with the latter). Compared to the host rocks, these deeper sediments have low concentrations of most elements, with the exception of elevated U, Pb, Nb, Fe, Co, and Ag. In addition, these sediments are *LREE*-depleted and have large positive Eu anomalies relative to the host rocks (Fig. 7). In contrast, the sediment from the deep saline borehole is characterized by elevated Ba (3300 ppm) and Sr (530 ppm) compared to the other sediments. The groundwaters from this borehole also have very high Ba and Sr, on the order of 90,000 μg/L (in contrast, all other groundwaters at the Restigouche deposit have Ba and Sr contents less than 1000 μg/L) (Leybourne 1998).

Suspended sediments from the boreholes distal from the Restigouche deposit have compositions that closely approximate the host rocks (Fig. 7). These sediments have generally low base-metal contents and moderately low Fe contents compared to the sediments proximal to the deposit. As discussed in the methods section, the straddle-packer was designed to permit discrete-depth sampling of groundwater. Generally, the bailer system of sampling indicates geochemical changes with depth, but not always the full magnitude of the changes. For example, groundwater from one of the distal holes from the Restigouche deposit has salinities up to 660 mg/L TDS for bailer samples, but up to 2600 mg/L TDS for straddle-packer samples. Similarly, although data on major and some trace elements in suspended sediments collected by both methods are broadly similar for this hole, there are differences in, for example, the base-metal contents, with somewhat higher Zn values in the straddle-packer sediments (Zn around 300 ppm at 200 m depth for the bailer sample, 1600 ppm for the straddle-packer sample at the same depth). Compared to the host rocks, suspended sediments from both boreholes have generally flat patterns with slight enrichments in the *LREE*, Cs, U, and Sr, and strong enrichment in Pb and Co. The only element showing consistent depletion is Ca, probably related to dissolution of carbonate (Fig. 7). Compared to the corresponding groundwaters, these sediments show similar relationships to the other suspended sediments. Differences include a stronger partitioning of Mn into the suspended sediment phase and greater partitioning of Na into the aqueous phase (Fig. 8).

DISCUSSION

Mineralogy

The mineralogy of the suspended sediments is generally consistent with the make-up of the rocks crossed by fracture zones (Leybourne 1998). Close to the ore deposits, hydrothermal alteration at the time of ore formation produced an assemblage of silicate alteration minerals dominated by quartz, white mica, and chlorite. More distal from the deposits, felsic metavolcanic and metasedimentary host-rocks are dominated by quartz, feldspar (albite and K-feldspar), white mica, and chlorite (Lentz & Goodfellow 1993, 1996). This raises the question as to whether the suspended sediments represent only disaggregated fracture-zone material, or are they controlled in part by the composition of the present groundwaters? Degueldre *et al.* (1996a) suggested that there are three main sources of colloids and suspended sediments in groundwater systems: 1) alteration of host-rock minerals by groundwaters, with subsequent suspension, 2) mechanical abrasion or disaggregation of non-cemented particles of aquifer material, and 3) precipitation of minerals directly from the groundwater. The Pb contents of the suspended sediments from the shallow boreholes at the Restigouche deposit are interesting in this respect. The Pb contents are much higher than assay samples collected during mineral exploration (Westoll 1990) and are higher than most samples of massive sulfide analyzed in this study (from 2.8 to 16.6 wt.% Pb) (Leybourne 1998), suggesting that Pb is released from the host rocks as a product of oxidation of the massive sulfides, and then concentrated in suspension both as Pb sulfates and adsorbed onto Fe oxyhydroxides. In contrast, although Zn abundances are elevated in suspended sediments from boreholes that intersect shallow zones of massive sulfides, Zn contents are lower than Pb (*i.e.,* low Zn/Pb values, Table 2), which indicates that Zn is preferentially partitioned into the aqueous phase relative to Pb (Fig. 8). Zn/Pb values in groundwater are all much greater than 1, which is consistent with this interpretation.

Fractionation among rocks, waters, and suspended sediments

No attempt was made to quantify the amount of suspended sediment present. The sampling methodology (especially with respect to the flow-through bailer) can dislodge material from borehole walls during raising and lowering of the sampling apparatus, thus potentially biasing the sample. However, I do not believe that this factor affects the results presented here for several reasons. Firstly, it is unlikely that normalizing elemental abundances in suspended sediment to the amount of suspended sediment accurately indicates relative fractionation. Miekeley *et al.* (1992) used such normalizing techniques to show that U is present predominantly in the dissolved phase, despite high U contents in the suspended sediment, owing to the low abundances of suspended sediment in the groundwater. However, the abundance of suspended sediment does not represent the only source and sink of elements in a groundwater system; fracture walls consist of minerals and oxide coatings that are typically similar mineralogically to the suspended sediment load. For example, the mineralogy of suspended sediment in groundwaters of the Halfmile Lake and Restigouche deposits are mineralogically very similar to the fracture-zone minerals. Additional sources of elements and sites for adsorption and coprecipitation reactions thus are present that are not "recorded" by a groundwater sample. Secondly, much of the discussion presented below is based on normalization of the composition of waters and sediments to that of the host rocks and the sediments to the waters from which the sediments were collected. The conclusions regarding element partitioning can thus be achieved in a relative sense.

In many respects, the suspended sediments are compositionally similar to the host lithologies. For example, normalized to average unaltered felsic host-rocks, many of the samples of suspended sediment display flat patterns, especially for the "detrital" elements identified previously. The suspended sediments that most closely approximate unaltered host-rocks are those distal from massive sulfides at the Restigouche deposit and from the deeper boreholes at the Halfmile Lake deposit (Fig. 7). Suspended sediment from groundwaters proximal to massive sulfides and gossan show relative depletions in mobile elements (K, Na, Ca, Rb, Cs) and strong to very strong enrichments in relatively immobile hydromorphic elements, such as Fe^{3+} and Pb.

Thus, for some of the suspended sediments, there is an apparent fractionation of some elements compared to the host rocks. However, much of this fractionation disappears or is reduced in magnitude if these sediments are normalized to rocks with which they are more spatially related. The low trace-element contents and generally lower base-metal contents of suspended sediments from the gossan (Halfmile Lake deposit) most likely reflect mechanical erosion and transport of gossan and ferruginous material rather than fractionation of elements during weathering of primary felsic volcanic rocks. The suspended sediments from the gossan borehole show patterns normalized with respect to felsic host-rock that are similar to some gossan samples from the Halfmile Lake deposit (Fig. 9). Although the suspended sediments from the gossan borehole are fractionated compared to the host felsic rocks, they are less fractionated than the gossans themselves. Many of the gossan samples show a more fractionated pattern than the suspended sediments (Fig. 9A).

Suspended sediments from the shallow boreholes at the Restigouche deposit were sampled from within the massive sulfides. Again, compared to the host rock-types (Fig. 7), these sediments show very fractionated patterns. However, compared to the massive sulfides, there are some similarities (*cf.* Figs. 7, 9B). The suspended sediments and massive sulfides show strong depletions in detrital elements and very strong enrichments in hydromorphic elements (see below). Interestingly, both show less depletion or enrichment in Sr, U, and Eu compared to the host rocks. The enrichment in Eu in the suspended sediment relative to host rocks is greater than for the massive sulfides. Europium thus is preferentially being mobilized during rock and sulfide weathering, but is strongly adsorbed to the suspended phases. Similarly, U shows relatively little depletion in the massive sulfides compared to the host rocks, whereas the suspended sediment is enriched in U for these boreholes. Compared to the corresponding groundwater, U is apparently strongly partitioned into the suspended sediment phase. Speciation modeling of these groundwaters indicates that between 70 and 85% of the U in the waters is present as U^{6+}. Uranium is highly soluble in the 6^+ state, but is insoluble in the 4^+ state. Previous work has shown that U^{6+} has a strong affinity for adsorption to Fe oxyhydroxides. Waite *et al.* (1994) showed that U^{6+} adsorption onto ferrihydrite approaches 90–100% in the pH range 5–8 for a variety of experimental conditions with variable ionic strength, and activities of U and Fe. Unlike U, Sr shows a relatively strong partitioning into the aqueous phase (Fig. 10). However, strontium also behaves in a similar way to U in that the massive sulfides show little fractionation compared to the host rocks (Fig. 11B), but suspended sediments can show significant enrichment (Fig. 9).

Suspended sediments from borehole MM–88–01 cannot easily be related to any of the host rocks or massive sulfides. These sediments show strong fractionation in many elements compared to the host rocks (Fig. 9) and are strongly enriched in Al relative to all the host rocks and other suspended sediments (Table 2). These sediments show the strong influence of the aqueous phase compared to that of the host rocks. This contrast is emphasized by the rare-earth-element systematics of these sediments. They display a strong *LREE* depletion compared to NASC (North America Shale Composite;

not shown) and the host rocks have a strong negative Ce anomaly unlike any of the other suspended sediments, and are similar only to local surface-waters (Leybourne *et al.* 2000).

Size distribution of suspended sediments

There is a functional difference between colloidal material and suspended particles. Degueldre *et al.* (1996b) referred to particles less than 1000 nm across as colloidal, and particles greater than 1000 nm as suspended matter. In this study, only material >450 nm was analyzed owing to the filter size chosen. However, based on previous studies (*e.g.,* Degueldre *et al.* 1996b), the finer-grained material observed by SEM is probably a good approximation of the colloids less than 450 nm in size that may have passed through the filter and thus influenced the "dissolved" load of the waters. In this study, no quantitative analyses of the size distribution of the suspended sediments was attempted. However, it is obvious from the SEM data (Figs. 3–6) that the majority of the suspended sediment in Halfmile Lake and Restigouche deposit groundwaters is between <1 and 10 μm in size. This size distribution is consistent with previous studies of the >0.45 μm fraction of groundwaters. For example, Gómez *et al.* (1992) showed that suspended sediments from groundwaters associated with granites in Spain have maxima in grain diameters of 1 and 10 μm. The truly colloidal fraction of these Spanish groundwaters (<0.45 μm) shows maxima at 50–100 nm and 350 nm, and the mineralogy of the suspended sediments is similar to those of BMC groundwaters, *i.e.,* silica, K-feldspar, clay minerals and Al-oxyhydroxides (Gómez *et al.* 1992).

Hydromorphic and detrital components

Previous work (Peter & Goodfellow 1993, 1996) has shown that sediments proximal and distal to massive sulfide deposits and modern sea-floor hydrothermal vent

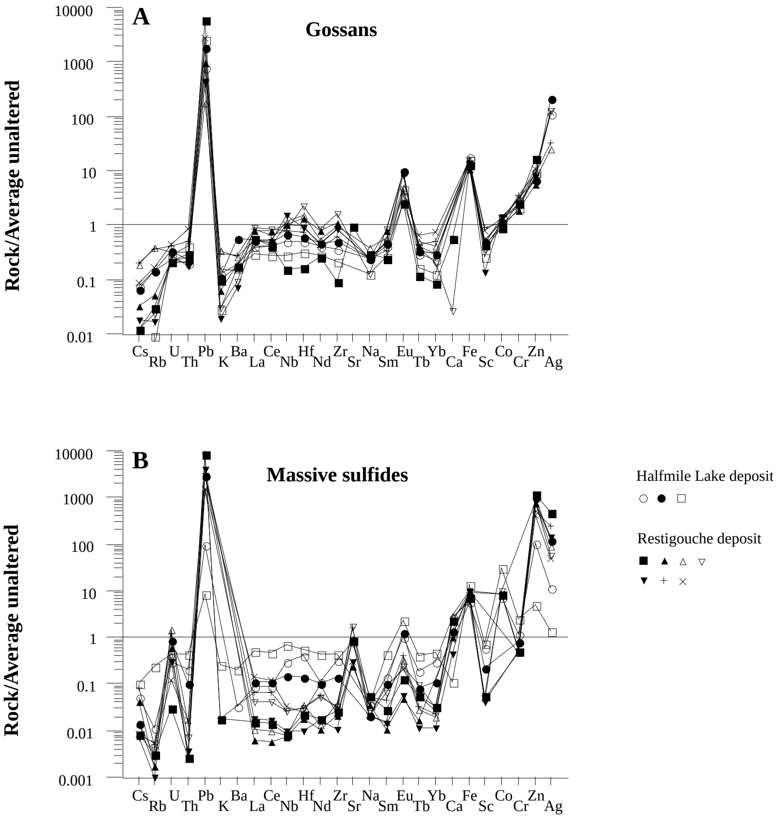

FIG. 9. A) Gossan (weathered massive sulfide) from the Halfmile Lake (Boyle 2001) normalized to average unaltered felsic rocks from the Halfmile Lake deposit (Leybourne 1998). B) Massive sulfides of the Halfmile Lake and Restigouche deposits normalized to average unaltered felsic volcanic rocks of the Restigouche deposit (Leybourne 1998).

sites exhibit mixing trends between elements associated with hydrothermal fluids and those associated with clastic sediments. These elements have been subdivided into hydrothermal, hydrogenous, and detrital components. Peter & Goodfellow (1993) demonstrated that iron formation along the Brunswick Belt showed mixing relationships with respect to Fe/Ti and Al/(Al + Fe + Mn). The Fe/Ti ratio increases with increasing hydrothermal input to the iron formations (Fe/Ti ∝ hydrothermal/detrital), whereas the ratio Al/(Al + Fe + Mn) increases with increasing detrital input {Al/(Al + Fe + Mn) ∝ detrital/(detrital + hydrothermal + hydrogenous)}. The suspended sediments from the Halfmile Lake and Restigouche deposits have been plotted on a similar diagram (Fig. 10). It is very interesting that the BMC suspended sediments fall on a mixing line very similar to that between hydrothermal and detrital components defined for the Brunswick Belt iron formations. The suspended sediment data can best be fit with a power-law function:

$$Fe / Ti = 9.864 \bullet [Al / (Al + Fe + Mn)]^{-1.0585}$$
$$(r^2 = 0.80)$$

The suspended sediments with high base-metal contents attributed to proximity to the massive sulfides, and high Fe due to proximity to gossan, plot closest to the massive sulfide end-member. Samples more distal from the Restigouche deposit plot close to the least-altered felsic host-rocks from both the Halfmile Lake and Restigouche deposits, indicating a high detrital component. The exceptions are the suspended sediment from borehole MM–88–01. These sediments have relatively high metal contents (Table 2), but have anomalously high Al contents owing to formation of Al oxides ± kaolinite.

The fact that suspended sediments show Fe/Ti *versus* Al/(Al + Fe + Mn) values similar to those of hydrothermal sediments suggests that weathering and dissolution of massive sulfides by meteoric groundwaters impart a similar composition between end-members as that in ancient products of hydrothermal fluids. Instead of mixing between hydrothermal and detrital components, the relationship for suspended sediments in groundwater can be thought of as representing mixing between detrital (host-rock-derived) and hydromorphic (sulfide-derived) components. Thus, as massive sulfides are oxidized, Fe and base metals are released to the aqueous phase. If the pH and Eh conditions are

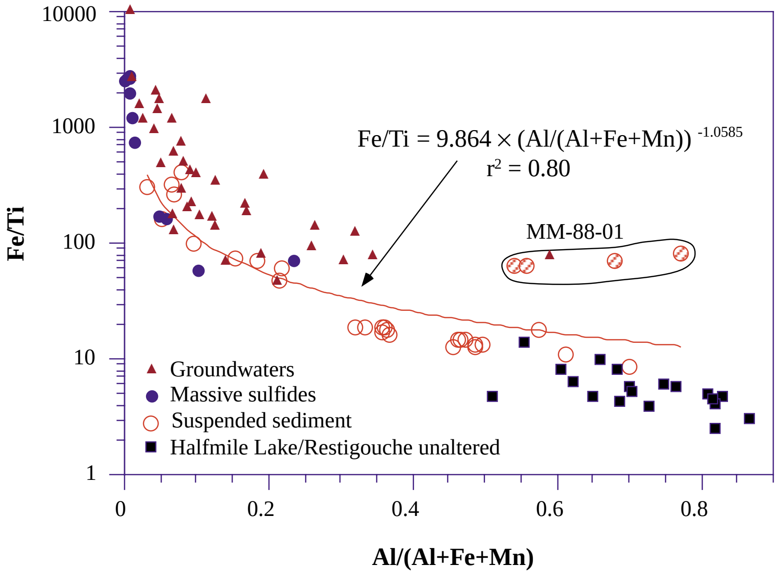

FIG. 10. Plot of Fe/Ti *versus* Al/(Al + Fe + Mn) for suspended sediments in groundwaters at the Halfmile Lake and Restigouche deposits. Also shown are values for unaltered felsic volcanic host- rocks and massive sulfides from the Halfmile Lake and Restigouche deposits. The suspended sediment data fit a power law curve. This curve is very similar to a best-fit curve through samples of iron formation from the Brunswick Belt massive sulfide deposits (Peter & Goodfellow 1996). Host rock, massive sulfide, and groundwater data from Leybourne (1998). The suspended sediments from borehole MM–88–01 have high base-metal contents (high Fe, Zn), but also have anomalously high Al owing to formation of Al oxides. Thus, these sediments do not fit the curve well.

favorable, as they will be in most natural groundwaters, Fe and metals will strongly, though variably, partition into the suspended sediment phase relative to the aqueous phase.

This subdivision of elements in suspended sediments into hydromorphic and detrital components is also indicated by inter-element correlation and factor analysis. Elements typical of the detrital component (*e.g.,* Ti, K, Al, Ca, Mg, Na, Ga, Nb, Hf, Sc, Rb, Th, and Zr) show strong positive inter-element correlations, whereas these elements are typically negatively correlated with Fe and base metals. Similarly, hydromorphic elements released by dissolution of massive sulfide and gossan show strong correlations (*e.g.,* $r^2 = 0.805$ for Zn–Pb, $r^2 = 0.726$ for Ag–Pb, and $r^2 = 0.821$ for Cd–Pb). The strength of the inter-element correlations among the hydromorphic elements very much depends on their relative mobility, which is controlled by the pH and Eh conditions, which in turn reflect the affinity for the aqueous phase.

Of particular interest are the Zn/Pb values. Whereas Zn/Pb invariably exceeds 1 in the groundwaters at the Restigouche deposit, suspended sediments from boreholes close to the Restigouche orebody have values less than 1. Similarly, suspended sediments in boreholes HN94–65 and HT55–43 show decreasing Zn/Pb downhole toward the massive sulfides. This relationship between Zn and Pb is consistent with the greater solubility of Zn compared to Pb; Pb is more readily adsorbed (or coprecipitated) with the suspended sediment than Zn. With increasing distance from the deposit, Zn/Pb is greater than 1 as Pb is not readily hydromorphically transported away from the immediate area of the deposit.

The Zn/Pb values in the suspended sediments closest to the orebody at Restigouche are extremely low. Note that the values in boreholes that intersect shallow massive sulfides are all less than 1. In contrast, in suspended sediments from boreholes distal from mineralization and from the Halfmile Lake deposit, the values all exceed 1. The very low values found in boreholes intersecting the most shallow massive sulfide indicate that the suspended sediments are not merely material scraped from the orebody as the bailer was lowered into the borehole. Assay Zn/Pb values given in Westoll (1990) are greater than 1 except in borehole MM–88–06, where leached limonitic gossans were recovered from 8.43 to 13 m below surface and where the Zn/Pb values for two assays are much less than 1. Either the suspended sediments represent gossan material, or there is preferential loss of Pb from the water owing to adsorption or formation of secondary minerals such as anglesite.

Environmental implications

Clearly, metals are associated, to a variable degree, with particulate matter in BMC groundwaters. These suspended sediments can be considered "stable" at the pH, Eh and geochemical conditions under which they were sampled. Under the present conditions, many metals show a strong preference for the suspended phase and are strongly adsorbed. However, perturbations to the present conditions could result in enhanced uptake of metal or, more likely, enhanced desorption of metal and release to the dissolved phase and potentially to the surface environment. For example, at the time of sampling, the Restigouche deposit was relatively undisturbed (with the exception of exploration drilling). Previous work has shown that, on the basis of stable isotope data, the surface waters at the Halfmile Lake and Restigouche deposits represent base-flow from shallow groundwater discharge. Despite high metal contents in groundwaters from the shallow boreholes adjacent to Charlotte Brook (*e.g.,* Zn up to 2300 μg/L, Pb to 1400 μg/L, As to 120 μg/L) (Leybourne 1998), metal contents of Charlotte Brook waters are not as high as would be expected if this stream was being fed by base-flow in the vicinity of the deposit (*e.g.,* Zn reaches a maximum of 9 μg/L, Pb to 2.5 μg/L, As to 3 μg/L in Charlotte Brook) (Leybourne *et al.* 2001). Groundwater flow under "natural" conditions, therefore, was presumably away from Charlotte Brook where the stream crosses the deposit. The Restigouche deposit has since gone into production as an open-pit operation (and, subsequently, ceased operation). Mining and excavation will perturb groundwater flow, increase the exposure of sulfide minerals to atmospheric oxygen, and may result in increased acidity of groundwater and surface water. If this happens, there is the potential for significant release of adsorbed metals (especially Pb) from suspended sediments. Swartz *et al.* (1997) noted that the mobilization and transport of colloids are strongly affected by perturbations in the pH, Eh, ionic strength, and chemical composition of groundwaters and pore fluids.

SUMMARY

Suspended sediments recovered from groundwaters at the Halfmile Lake deposit are dominantly quartz and aluminum silicate minerals. Fe oxyhydroxides are probably present as surface coatings and amorphous Fe-bearing phases. Suspended sediments in groundwaters remote from the main Restigouche orebody are mineralogically similar. However, suspended sediments from boreholes that intersect the Restigouche orebody consist primarily of Fe sulfides and Pb and Zn sulfate minerals. The mineralogical variation in the suspended sediment is reflected in the chemical composition.

The suspended sediments at Halfmile Lake are depleted in the mobile elements Cs, Rb, and K compared to host rocks. These suspended sediments show generally flat patterns normalized to the host rocks for most other elements, but strong enrichments in the hydrothermal suite of elements Pb, Fe, Co, Zn, Ag, and Eu. Iron-oxide-rich suspended sediments from borehole HT55–43, which penetrates the gossan, are more depleted in most elements than the other sediments. The geochemistry of the suspended sediments from the Restigouche deposit shows similar relationships, although the degree of enrichment in metals associated with massive sulfide mineralization is greater.

Compared to coexisting groundwaters, the suspended sediments are relatively enriched in Al, Fe, Pb, and relatively depleted in Ca, Sr, and Mg. Potassium and Rb are generally more strongly fractionated into the suspended sediment phase than other mobile elements, indicating that their abundance in the groundwaters is controlled by secondary phases.

Suspended sediments proximal to massive sulfide mineralization have elevated Fe/Ti and base-metal contents, *i.e.*, elements that can be considered hydromorphic. In contrast, with increasing distance away from mineralization, "detrital" elements are more significant, with decreasing Fe/Ti values and base-metal contents and increasing Zn/Pb and Al/(Al + Fe + Mn) ratios. The elevated base-metal contents of suspended sediments associated with massive sulfides is important, as mining activities in the BMC can result in changes in groundwater Eh–pH conditions, potentially resulting in greater dispersion of the metals that are presently strongly sorbed onto sediments.

ACKNOWLEDGEMENTS

The field work was funded by the Geological Survey of Canada as part of the EXTECH–II program. Peter Bélanger is thanked for overseeing the geochemical analyses, and Judy Vaive, for the chelation ICP–MS analyses. Technicians R. Forconi and K. Lalonde of the GSC Instrument Development Section are thanked for their efforts in constructing the straddle-packer system. Excellent reviews by Tom Al and an anonymous reviewer helped improve the manuscript. Associate Editor Dan Kontak and Robert F. Martin are also thanked for constructive comments on the manuscript. This is UTD Geosciences contribution number 960.

REFERENCES

ADAIR, R.N. (1992): Stratigraphy, structure, and geochemistry of the Halfmile Lake massive-sulfide deposit, New Brunswick. *Explor. Mining Geol.* **1**, 151-166.

ANDERSON, P.R. & CHRISTENSEN, T.H. (1988): Distribution coefficients of Cd, Co, Ni, and Zn in soils. *J. Soil Sci.* **39**, 15-22.

BARRIE, C.Q. (1982): Summary Report, Restigouche Property N.T.S. 21O/7E and 10E. Billiton Canada Limited.

BOYLE, D.R. (2001): Pre-glacial weathering of massive sulfide deposits in the Bathurst Mining Camp: economic geology, geochemistry, and exploration applications. *In* Massive Sulphide Deposits of the Bathurst Mining Camp, New Brunswick and Northern Maine (W.D. Goodfellow, S.R. McCutcheon & J.M. Peter, eds.). *Econ. Geol., Monogr.* **11** (in press).

COSTON, J.A., FULLER, C.C. & DAVIS, J.A. (1995): Pb^{2+} and Zn^{2+} adsorption by a natural aluminum- and iron-bearing surface coating on an aquifer sand. *Geochim. Cosmochim. Acta* **59**, 3535-3547.

DEGUELDRE, C., GRAUER, R., LAUBE, A., OESS, A. & SILBY, H. (1996a): Colloid properties in granitic groundwater systems. II. Stability and transport study. *Appl. Geochem.* **11**, 697-710.

________, PFEIFFER, H.-R., ALEXANDER, W., WERNLI, B. & BRUETSCH, R. (1996b): Colloid properties in granitic groundwater systems. I. Sampling and characterization. *Appl. Geochem.* **11**, 677-695.

EGGLESTON, C.M. & STUMM, W. (1993): Scanning tunneling microscopy of Cr(III) chemisorbed on α-Fe_2O_3 (001) surfaces from aqueous solution: direct observation of surface mobility and clustering. *Geochim. Cosmochim. Acta* **57**, 4843-4850.

GÓMEZ, P., TURRERO, M.J., MOULIN, V. & MAGONTHIER, M.C. (1992): Characterization of natural colloids in groundwaters of El Berrocal, Spain. *In* Proc. 7th Int. Symp. on Water–Rock Interaction. 1. Low Temperature Environments (Y.K. Kharaka & A.S. Maest, eds.). Int. Assoc. Geochemistry and Cosmochemistry and Alberta Research Council, Sub-Group on Water–Rock Interaction **7**, 797-800.

GOWER, S.J. (1996): Geology, lithogeochemistry and mineral occurrences in the Portage Brook area, northwestern Bathurst Mining Camp, New Brunswick (NTS 21 O/7h, part of 21 O/10a). *In* Current Research 1995 (B.M.W. Carroll, ed.). *New Brunswick Department of Natural Resources and Energy, Minerals and Energy Division, Mineral Resources Rep.* **96-1**, 13-43.

LASAGA, A.C. (1990): Atomic treatment of mineral–water surface reactions. *In* Mineral–Water Interface Geochemistry (M.F.J. Hochella & A.F. White, eds.). *Rev. Mineral.* **23**, 17-85.

LENTZ, D.R. & GOODFELLOW, W.D. (1993): Petrology and mass-balance constraints on the origin of quartz-augen schist associated with the Brunswick massive sulfide deposits, Bathurst, New Brunswick. *Can. Mineral.* **31**, 877-903.

________ & ________ (1996): Intense silicification of footwall sedimentary rocks in the stockwork alteration zone beneath the Brunswick no. 12 massive sulphide deposit, Bathurst, New Brunswick. *Can. J. Earth Sci.* **33**, 284-302.

LEYBOURNE, M.I. (1998): *Hydrochemistry of Ground and Surface Waters Associated with Massive Sulphide Deposits, Bathurst Mining Camp, New Brunswick: Halfmile Lake and Restigouche Deposits*. Ph.D. thesis, University of Ottawa, Ottawa, Ontario.

________, BOYLE, D.R. & GOODFELLOW, W.D. (2001): Interpretation of stream water and sediment geochemistry in the Bathurst Mining Camp, New Brunswick: applications to mineral exploration. *In* Massive Sulphide Deposits of the Bathurst Mining Camp, New Brunswick and Northern Maine (W.D. Goodfellow, S.R. McCutcheon & J.M. Peter, eds.). *Econ. Geol., Monogr.* **11** (in press).

________ & GOODFELLOW, W.D. (2001): Processes of metal solution and transport in ground and surface waters draining massive sulfide deposits, Bathurst Mining Camp, New Brunswick. *In* Massive Sulphide Deposits of the Bathurst Mining Camp, New Brunswick and Northern Maine (W.D. Goodfellow, S.R. McCutcheon & J.M. Peter, eds.). *Econ. Geol., Monogr.* **11** (in press).

________, ________ & BOYLE, D.R. (1998): Hydrogeochemical, isotopic, and rare earth element evidence for contrasting water–rock interactions at two undisturbed Zn–Pb massive sulphide deposits, Bathurst Mining Camp, N.B., Canada. *J. Geochem. Explor.* **64**, 237-261.

________, ________, ________ & HALL, G.M. (2000): Rapid development of negative Ce anomalies in surface waters and contrasting REE patterns in groundwaters associated with Zn–Pb massive sulphide deposits. *Appl. Geochem.* **15**, 695-723.

MCCUTCHEON, S.R.C. (1997): Geology and massive sulphides of the Bathurst Camp, New Brunswick. *Geol. Assoc. Can. – Mineral. Assoc. Can., Guidebook, Field Trip* **B7**.

MIEKELEY, N., COUTIHO DE JESUS, H., PORTO DA SILVEIRA, C.L. & DEGUELDRE, C. (1992): Chemical and physical characterization of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *J. Geochem. Explor.* **45**, 409-437.

MÜLLER, B. & SIGG, L. (1992): Adsorption of lead (II) on the goethite surface: voltammetric evaluation of surface complexation parameters. *J. Coll. Interface Sci.* **148**, 517-532.

PARKHURST, D.L. (1995): *User's Guide to PHREEQC – a Computer Program for Speciation, Reaction-path, Advective-transport, and Inverse Geochemical Calculations.* U.S. Geological Survey, Lakewood, Colorado.

PETER, J.M. & GOODFELLOW, W.D. (1993): Bulk and stable sulphur and carbon isotope geochemistry of hydrothermal sediments associated with the Brunswick No. 12 deposit, northern New Brunswick. *In* Current Research (S.A. Abbott, ed.). *New Brunswick Department of Natural Resources and Energy, Mineral Resources, Inf. Circ.* **93-1**, 154-169.

________ & ________ (1996): Mineralogy, bulk and rare earth element geochemistry of massive sulphide-associated hydrothermal sediments of the Brunswick Horizon, Bathurst Mining Camp, New Brunswick. *Can. J. Earth Sci.* **33**, 252-283.

SWARTZ, C.H., ULERY, A.L. & GSCHWEND, P.M. (1997): An AEM–TEM study of nanometer-scale mineral associations in an aquifer sand: implications for colloid mobilization. *Geochim. Cosmochim. Acta* **61**, 707-718.

SYMONS, D.T.A., LEWCHUK, M.T. & BOYLE, D.R. (1996): Pliocene–Pleistocene genesis for the Murray Brook and Heath Steele Au–Ag gossan ore deposits, New Brunswick, from paleomagnetism. *Can. J. Earth Sci.* **33**, 1-11.

VAN STAAL, C.R., WILSON, R.A., FYFFE, L.R., LANGTON, J.P., MCCUTCHEON, S.R., ROGERS, N., MCNICOLL, V. & RAVENHURST, C.E. (2001): Geology and tectonic history of the Bathurst Mining Camp and its relationship to coeval rocks in southwestern New Brunswick and adjacent Maine – a synthesis. *In* Massive Sulphide Deposits of the Bathurst Mining Camp, New Brunswick and Northern Maine (W.D. Goodfellow, S.R. McCutcheon & J.M. Peter, eds.). *Econ. Geol., Monogr.* **11** (in press).

WAITE, T.D., DAVIS, J.A., PAYNE, T.E., WAYCHUNAS, G.A. & XU, N. (1994): Uranium(VI) adsorption to ferrihydrite: application of a surface complexation model. *Geochim. Cosmochim. Acta* **58**, 5465-5478.

WEN, L.-S., SANTSCHI, P.H. & TANG, D. (1997): Interactions between radioactively labeled colloids and natural particles: evidence for colloidal pumping. *Geochim. Cosmochim. Acta* **61**, 2867-2878.

WESTOLL, N.D.S. (1990): Report on exploration diamond drilling, Restigouche Property, Restigouche County, New Brunswick. *Marshall Minerals Corp., New Brunswick Department of Natural Resources and Energy, Mineral and Energy Division, Assessment File* **473864**.

WOLERY, T.J. (1992): EQ3NR, a computer program for geochemical aqueous speciation–solubility calculations: package overview and installation guide (*version 7.0*). *Lawrence Livermore National Laboratory, Livermore, California* **UCRL MA–110662–PT–I**.

Received May 2, 2000, revised manuscript accepted November 3, 2001.