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Hydrogeochemical, isotopic, and rare earth element evidence for ntrasting water–rock interactions at two undisturbed Zn–Pb massive sulphide deposits, Bathurst Mining Camp, N.B., Canada

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stract

A detailed hydrochemical study at two undisturbed Ordovician massive sulphide (Zn–Pb) deposits (Restigouche and alfmile Lake deposits, Bathurst Mining Camp, New Brunswick) was initiated to elucidate the processes controlling e oxidation and dissolution of sulphide minerals, the subsequent dispersion of metals in ground and surface waters, d the precipitation of secondary minerals. Groundwater hydrogeochemical signatures are different for the two deposits. lements that form sulphide minerals in the deposits correlate positively in surface waters and increase with proximity to e Restigouche deposit, whereas metal contents for Halfmile Lake surface waters are lower, though still typically higher han background levels. Variations in the composition of ground and surface waters draining the two deposits reflect in part ifferences in the depth and geometry of the massive sulphides and host lithologies. The Halfmile Lake deposit is deeper, nore steeply dipping, and overturned compared to the shallower Restigouche deposit. Groundwaters at the Halfmile Lake leposit up to 760 m below surface are low-TDS (<250 mg l^{-1}), Ca–HCO_3 to Na–HCO_3 waters with oxygen and hydrogen isotopic compositions identical to surface waters. Groundwater REE patterns are flat to LREE-enriched and are similar to host lithologies, unlike the surface waters which are LREE-depleted compared to shale. The Restigouche groundwaters range up to 21,000 mg l^{-1} TDS (Na–Cl waters) and display heavier oxygen and hydrogen isotopic compositions than local surface waters. Variations in groundwater composition require that the two deposits have different hydrologies which influence the natural oxidation of the massive sulphides and thus the environmental hydrochemical signature.

Keywords: hydrochemistry; groundwater; water–rock interaction; stable isotopes; trace elements

1. Introduction

In recent years, increasing attention has been given to the problems of acid-mine drainage (AMD) and to the processes and pathways by which metals are transported away from active and abandoned mine sites (e.g. Curtis and Walker, 1994; Goodyear et al., 1996; Pratt et al., 1996; Thornton, 1996; Wayne et al., 1996). However, there has been less attention paid to the impact of undisturbed massive sulphide deposits on the environment and the potential that they have as natural laboratories to predict

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mining impacts on the environment and establish remediation guidelines. This latter point is critical given the paucity of good analogue sites for active and abandoned mines (Maest, 1996). The Halfmile Lake and Restigouche deposits in the Bathurst Mining Camp of New Brunswick, Canada are well suited for this type of study given that they are the same age, hosted in the same lithologies and exist under the same climatic and physiographic regime as several past and active producing mines in this camp. Both the Halfmile Lake and Restigouche deposits are Zn–Pb volcanogenic massive sulphide deposits with minor Ag and Cu. These two deposits were chosen on a number of criteria, including availability of exploration drill holes likely to be open for sampling of groundwaters, contrasts in deposit geometry, and complementary geological, geophysical, lithogeochemical and Quaternary studies. The main purpose of the present research was to determine the sources and water–rock reactions of groundwaters at the two study sites using geochemical and isotopic data, aqueous geochemical modelling and interpretations of the physical hydrology. The importance of baseline studies for understanding natural and anthropogenic sulphide oxidation and dispersion of metals away from massive sulphide deposits is emphasized by the different geochemical responses of groundwaters at the two deposits studied here. The timeliness of this kind of study in the Bathurst Mining Camp is emphasized by the recent excavation of the Restigouche deposit as an open pit mine and the ongoing assessments of the Halfmile Lake deposit as an underground mine.

2. Study area

The Halfmile Lake and Restigouche massive sulphide deposits are located in the Bathurst Mining Camp (BMC), part of the Miramichi terrane of northern New Brunswick, Canada (Fig. 1). Tetagouche Group rocks host the massive sulphide deposits and are interpreted to have formed within an Ordovician (465–471 Ma) ensialic rift basin (van Staal et al., 1992; van Staal and Sullivan, 1992).

2.1. Halfmile Lake deposit

The stratigraphy at Halfmile Lake consists of felsic quartz–porphyry units (QFP), felsic pyroclastic rocks and minor felsic flows, fine-grained volcaniclastic sediments, stringer zone sulphides, massive sulphides with associated argillite and chert, and overlying mafic to intermediate flows and pyroclastic rocks of the Upper Tetagouche Group. The deposit was overturned by D_1 deformation and dips steeply to the north and northwest (Fig. 2A). The massive sulphides locally crop out, with well developed gossan at the Upper AB zone, although the bulk of the massive sulphides occurs deeper in the stratigraphy (Fig. 2A). The stockwork zone is characterized by pyrrhotite–chalcopyrite–quartz stringers and ranges from 3 to 150 m in thickness (Adair, 1992). Massive sulphides occur as both breccia matrix sulphides dominated by pyrrhotite with lesser chalcopyrite, pyrite, sphalerite, and galena and as laminated massive sulphides composed of pyrite, pyrrhotite, sphalerite and galena (Adair, 1992). Regional metamorphism is lower greenschist facies with pervasive chlorite alteration and increasing sericitic alteration close to the ore deposit (Adair, 1992). Carbonate alteration is best developed in the deeper parts of the deposit within the stratigraphic hanging wall (structural footwall to the deposit) (Adair, 1992). There are no sedimentary carbonate or evaporite units within or near the study area.

Hydrologically, the Halfmile Lake deposit is characterized by steep-sided hills with typical relief of 100–150 m. The area is primarily forested with thin till and soil cover. Groundwater flow is dominantly fracture-controlled, and structures are steeply dipping.

2.2. Restigouche deposit

The Restigouche deposit is hosted by metasedimentary and metavolcanic rocks of the Mount Brittain Formation (McCutcheon, 1997) which is in fault contact to the north with Late Ordovician – Early Silurian mafic volcanic rocks, and to the northwest with Late Silurian to Early Devonian conglomerate, sandstone, and intercalated volcanic units (Fig. 2B, Fig. 3B). The Mount Brittain Formation is conformable with the Patrick Brook Formation and Mi-

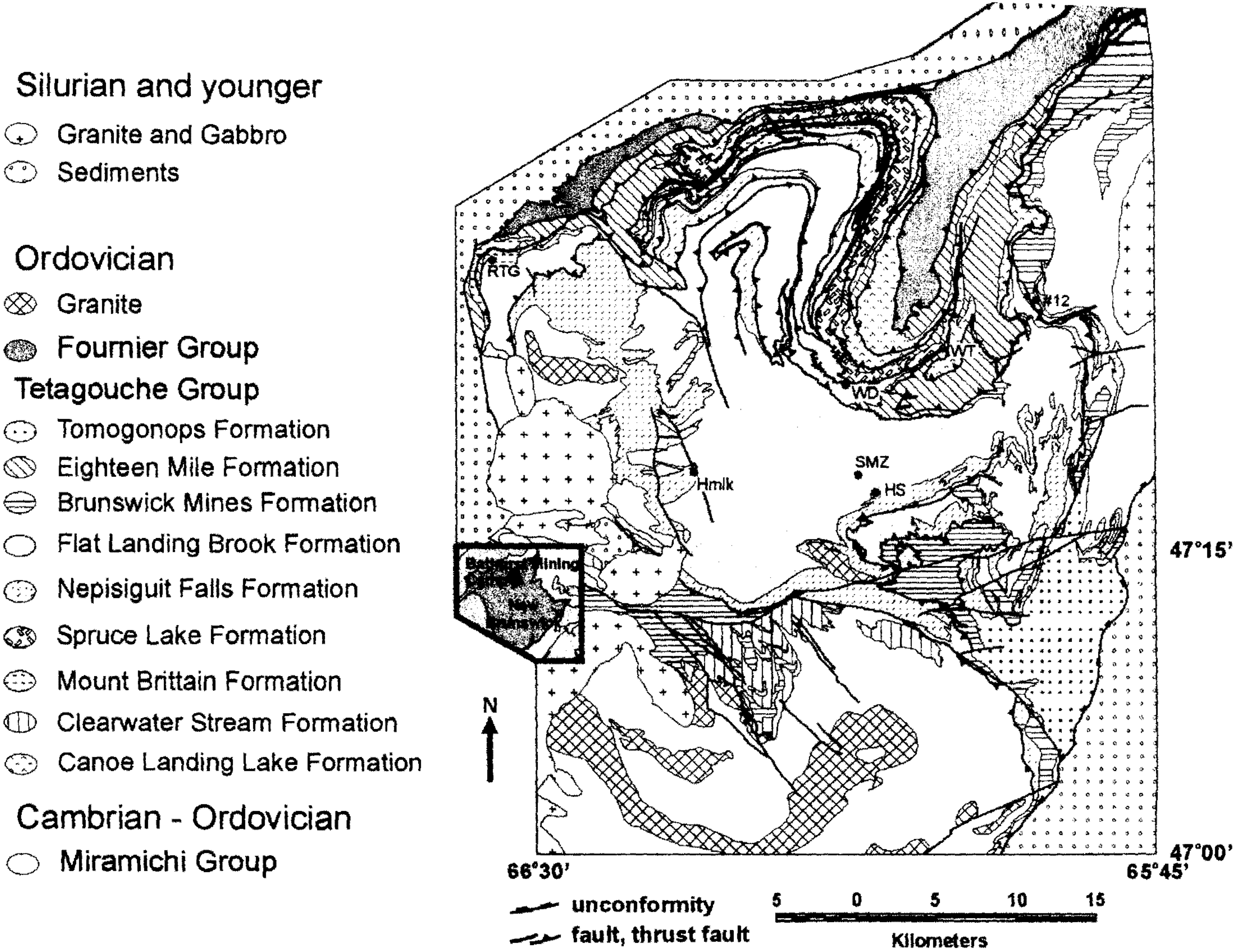
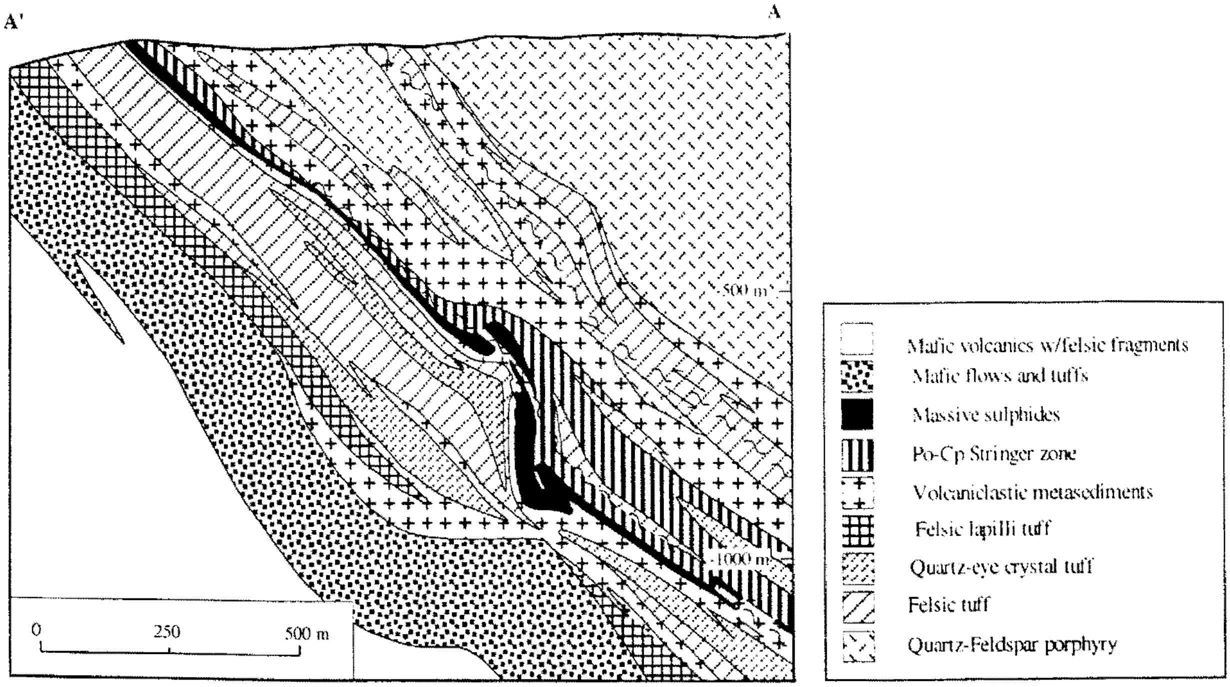


Fig. 1. Simplified geological map of the Bathurst Mining Camp showing the location of the Restigouche (*RTG*) and Halfmile Lake (*Hmlk*) deposits. Other deposits in the [illegible] groundwaters are the Stratmat Main Zone (*SMZ*), Heath Steele (*HS*), Brunswick #12 (*#12*), Wedge (*WD*) and Willett (*WT*) deposits.

A



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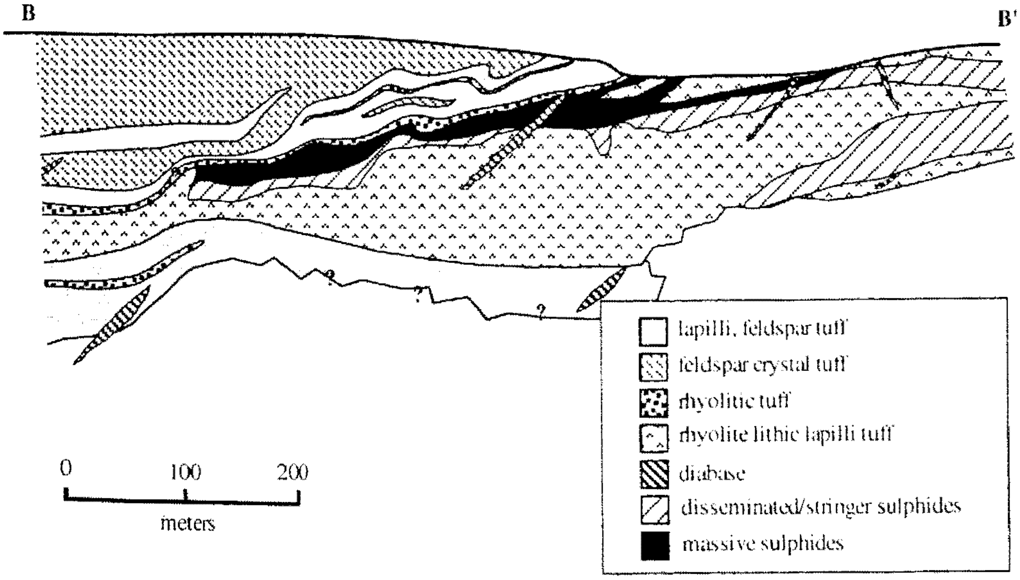
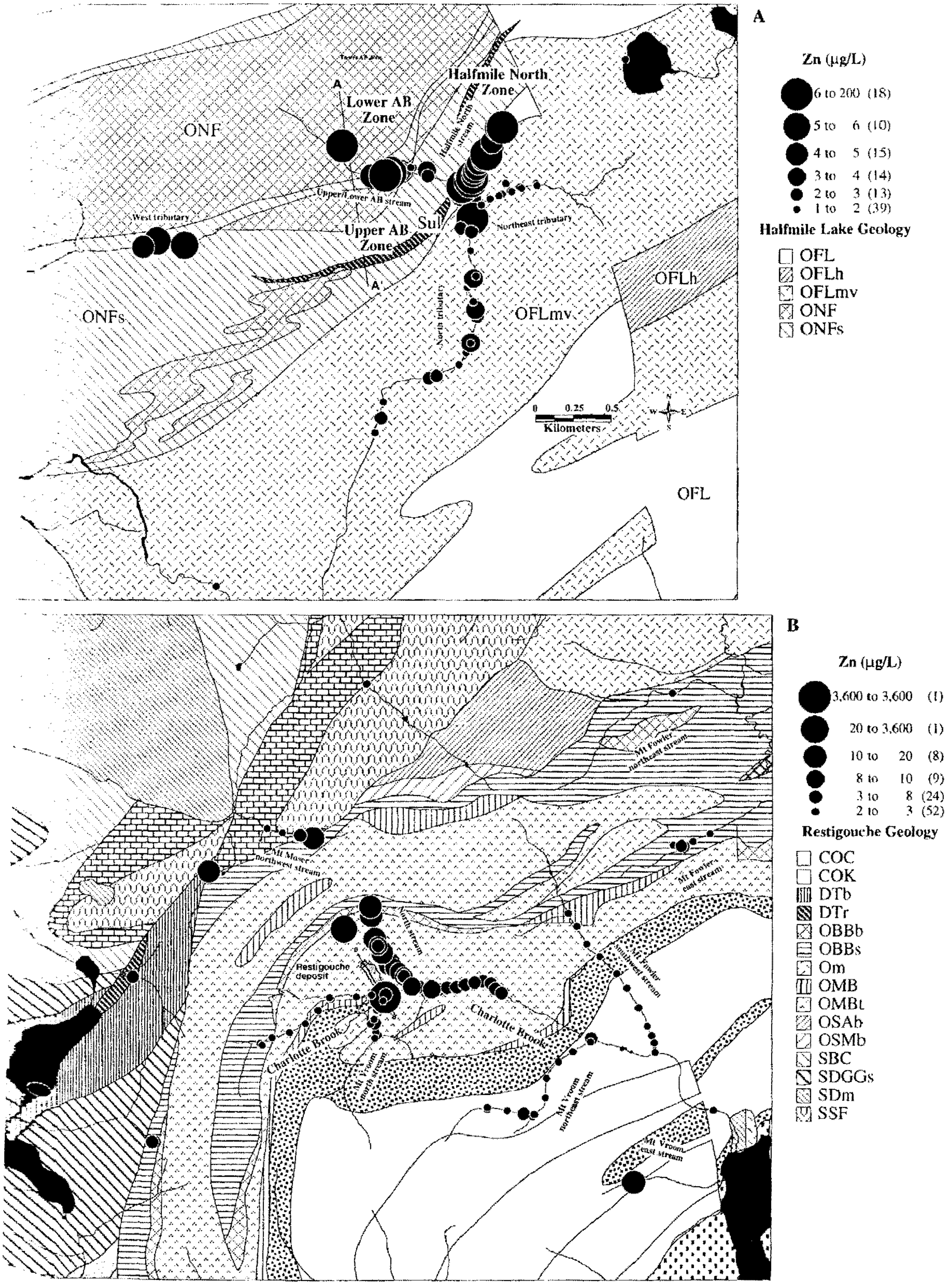


Fig. 2. (A) Cross-section of the Halfmile Lake deposit, after Adair (1992). (B) Cross-section of the Restigouche deposit, modified from Barrie (1982).

Fig. 3. Proportional circle maps showing distribution of Zn in surface waters for the (A) Halfmile Lake deposit, and (B) Restigouche deposit. (A) Geology: *OFL*, Flat Landing Brook rhyolite; *OFlh*, Flat Landing Brook hyaloclastite; *OFLmv*, Flat Landing Brook mafic volcanics; *ONF*, Nepisiguit Falls rhyolite and porphyry; *ONFs*, Nepisiguit Falls sediments. (B) Geology: *COC*, Chain of Rocks Formation sediments; *COK*, Knight's Brook Formation sediments; *DTb* and *DTr*, Tobique Group; *OBBb*, Eighteen Mile Formation basalt; *OBBs*, Eighteen Mile Formation sediments; *Om* and *SDm*, mafic intrusives; *OMB*, Mount Brittain Formation dacite; *OMBt*, Mount Brittain tuff; *OSAb* and *OSMb*, Sormany Formation; *SBC*, Budworm City Formation; *SDGGs*, Greys Gulch Formation; *SSF*, Simpsons Field Formation. The lines *A–A'* and *B–B'* show the positions of the stratigraphic cross-sections in Fig. 2. Geology as in Fig. 2.


A
Halfmile North Zone
Lower AB Zone
ONF
Halfmile North stream
Upper/Lower AB stream
West tributary
Upper AB Zone
Sul
Northeast tributary
A
A'
ONFs
North tributary
OFLmv
OFLh
OFL
0 0.25 0.5
Kilometers
N
W
E
S
Zn (μg/L)
6 to 200 (18)
5 to 6 (10)
4 to 5 (15)
3 to 4 (14)
2 to 3 (13)
1 to 2 (39)
Halfmile Lake Geology
☐ OFL
▨ OFLh
☐ OFLmv
▨ ONF
▨ ONFs
B
Mt Fowler northeast stream
Mt Moser northwest stream
Mt Fowler east stream
North stream
Restigouche deposit
Mt Fowler southwest stream
Charlotte Brook
Charlotte Brook
Mt Vroom north stream
Mt Vroom northeast stream
Mt Vroom east stream
Zn (μg/L)
3,600 to 3,600 (1)
20 to 3,600 (1)
10 to 20 (8)
8 to 10 (9)
3 to 8 (24)
2 to 3 (52)
Restigouche Geology
☐ COC
☐ COK
▥ DTb
▧ DTr
▨ OBBb
▤ OBBs
☐ Om
▥ OMB
☐ OMBt
▨ OSAb
☐ OSMb
▨ SBC
▧ SDGGs
▨ SDm
▨ SSF

ramichi Group metasedimentary rocks to the south. The Restigouche property is dominated by metasedimentary (sandstones, argillites, graphitic and mafic tuff, and ferruginous and graphitic argillites) and felsic metavolcanic units (Barrie, 1982). The general stratigraphy for the Restigouche deposit follows the sequence: banded argillite to siltstone in sharp contact and intercalated with feldspar crystal and lapilli tuff, grading upwards to coarse pyroclastic lithic tuff, lithic lapilli and fragmental units intercalated with massive and disseminated sulphides (Barrie, 1982). The massive pyritic sulphides are in sharp contact with overlying massive rhyolite tuff which grades upwards from lapilli and lithic tuffs to crystal tuff. There is a northeast-trending mafic dyke swarm that cross-cuts the deposit and in places appears to infill fault zones (Barrie, 1982). The diabase is variably altered to carbonate. Quartz and carbonate veins are common in both the footwall and hanging wall units, with local development of feldspar veins. The massive sulphides crop out on the south side of Charlotte Brook as a small gossan. Massive sulphides are dominantly pyrite, marcasite, sphalerite and galena with minor chalcopyrite (Barrie, 1982). Stockwork and vein carbonate is more extensive at the Restigouche deposit than at the Halfmile Lake deposit.

The Restigouche deposit area is topographically similar to the Halfmile Lake deposit, although relief varies from 200 to 400 m. As with the Halfmile Lake area, soils are thinly developed and till cover is thin, commonly less than 1 m in thickness. Groundwater flow is dominantly fracture-controlled. As with the Halfmile Lake deposit, there are no carbonate or evaporite units within the immediate Restigouche deposits stratigraphy (Fig. 2B). However, Silurian carbonate rocks do occur to the northwest of the Restigouche deposit (Fig. 3B).

3. Sampling and analytical methods

Ground and surface waters were collected from the two deposits during the summers of 1994–1996. Groundwaters were sampled from exploration diamond drill holes using both flow-through bailer and straddle-packer systems. The straddle-packers were inflated at the sample depth using N_2 gas. The sample interval is approximately 2 m in length when the packers are fully inflated. Water flowing through the packed-off zone enters the sample head above the top packer through a uni-directional 1-psi cracking valve. The packed zone is purged until the electrical conductivity reaches a steady state. The straddle-packer provides a more accurate representation of down-hole chemical changes than the flow-through bailer because it permits sampling at discrete depth intervals. The bailer method of groundwater sampling is useful in that it is a more rapid technique than the straddle-packer. However, although downhole increases in salinity are evident in bailer samples, the magnitude of the changes are attenuated by diffusion and advection in the borehole. Parameters measured in the field were pH, Eh, conductivity, temperature, and dissolved oxygen (DO). All samples were filtered in situ through 0.45-μm sterile filters and refrigerated and acidified (cations) with ultrapure nitric acid at the base camp. Major cations were analyzed by inductively coupled plasma emission spectrometry (ICP–ES; Si, Ti, Fe, Mg, Ca, Na, K, B), trace elements by ICP–MS (mass spectrometry), anions by ion chromatography, and alkalinity by titration at the Geological Survey of Canada (Table 1). Rare earth elements and selected trace elements were analyzed by ICP–MS following 5× pre-concentration and chelation, using the method of Hall et al. (1995) (Table 1). For the REE, the following isotopes were measured in order to minimize isobaric interferences: ^{139}La, ^{140}Ce, ^{141}Pr, ^{144}Nd, ^{147}Sm, ^{153}Eu, ^{160}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb, and ^{175}Lu. Oxygen and hydrogen isotopes were analyzed at the University of Ottawa. Reproducibility is better than ±0.15‰ for ^{18}O and ±1.5‰ for D. Data are presented in standard δ notation:

$$\delta^{18}\text{O} = 10^3 \times \left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{Sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right)$$

where SMOW is standard mean ocean water (Craig, 1961).

4. Results

4.1. Surface waters

Surface waters at Halfmile Lake are dominantly Ca–HCO_3 waters. Anions in surface waters at

Halfmile Lake are dominated by HCO_3 with a very slight trend to increasing SO_4 for waters closest to the deposit. All Halfmile Lake deposit surface waters typically have very low concentrations of total dissolved solids (TDS). TDS values are all <110 mg l^{-1}, with most samples ranging from 14 to 60 mg l^{-1} (only two sample have >100 mg l^{-1}). The small range in TDS is consistent with the small area and limited range in silicic rock types within the catchment (Leybourne et al., 1995). There is a bimodal distribution to the TDS values with waters from the west half of the study area which drain primarily felsic volcanic and volcaniclastic rocks, having low TDS contents (typically <35 mg l^{-1}) and those on the east half of the study area, which drain more mafic lithologies, having higher TDS contents (typically >35 mg l^{-1}). Stream waters on the east side of the study area typically have higher HCO_3, Ca, Sr, and pH and lower K, Ba, and Rb contents. Trace metals in surface waters at the Halfmile Lake deposit are typically low (only 12 of 144 samples with Pb >0.2 μg l^{-1} and 69 samples with Zn >2 μg l^{-1}). Zinc, Cd and to a lesser extent Pb and Cu contents in surface waters delineate the main orebody despite low metal abundances (Fig. 3A).

Surface waters at the Restigouche deposit are primarily Ca–HCO_3 waters and are broadly similar to Halfmile Lake surface waters in major element composition, although the latter are slightly more Na + K-rich. Exceptions include Ca–Mg–SO_4 waters in streams 4 km to the northeast of the deposit. Streams draining the southeastern part of the study area are characterized by lower TDS and pH than the other streams and drain older metasedimentary units than the other streams which flow over younger metavolcanic and metasedimentary units (Leybourne et al., 1996). Surface waters at the Restigouche deposit range from 9 to 143 mg l^{-1} TDS ($\bar{x} = 45$ mg l^{-1}). The main stream in the study area, Charlotte Brook, crosses the deposit close to where it comes to surface (Fig. 3B). TDS values are highest in Charlotte Brook, especially upstream from the deposit. Downstream from the deposit, TDS values in Charlotte Brook are lower due to dilution from several tributaries. Zinc contents are commonly below detection (<2 μg l^{-1}), but are clearly elevated in the immediate vicinity of the deposit and in Charlotte Brook downstream from the deposit (Fig. 3B). Chloride concentrations are somewhat elevated in the streams closest to, and downstream from, the ore body, suggesting that there may be some degree of mixing between deeper saline groundwaters (see Section 4.3 below) and the low-TDS meteoric waters which feed the stream system, or shallow groundwater leaching of Cl-bearing hydrothermal alteration minerals associated with the deposit.

Surface waters from both deposits have similar δD and $\delta^{18}O$ stable isotopic compositions, with average values of −89.2‰ and −13.3‰ for the Halfmile Lake deposit and −93.0‰ and −13.4‰ for the Restigouche deposit. Excess deuterium values are similar for both deposits, although the Halfmile Lake deposit has slightly higher average excess deuterium (14.3 vs 17.5). Rare earth element patterns are also similar for surface waters from both deposits with LREE depleted profiles and large negative Ce anomalies, although surface waters at the Restigouche deposit commonly have lower average total REE contents and larger negative Ce anomalies (Leybourne, 1998).

4.2. *Groundwaters at the Halfmile Lake deposit*

Halfmile Lake deposit groundwaters are dominantly low-TDS Ca–HCO_3 waters (Fig. 4a, Fig. 5) and are more Na- and K-rich compared to local surface waters, but show little distinction in terms of the major anions. There is a weak evolutionary trend with depth in groundwater composition towards higher Na and K and lower Ca contents and a weaker trend towards increasing Cl contents (Fig. 6). Groundwaters from borehole HT55-43 which penetrates gossanized sulphides where the deposit crops out are an exception, being Mg–SO_4 in composition. The highest-TDS groundwaters recovered from the Halfmile Lake deposit area are from borehole HN94-63 (TDS = 226 mg l^{-1}). These waters are Na–HCO_3 waters with low Ca and Cl contents (Fig. 4a). The lowest-TDS groundwaters are from boreholes located at the top of the Upper AB and Lower AB zones (boreholes HT55-43 and HN87-8). These waters also have the highest DO contents suggesting that these are zones of recharge. Dissolved oxygen decreases with decreasing elevation of drill hole collar.

There are chemical differences in waters in different boreholes, in both absolute contents and in

Table 1
Water chemistry data for selected Halfmile Lake and Restigouche deposit groundwaters

Sample #: Hole #:	MLW94-156 HN87-08	MLW94-171 HN87-08	MLW94-209 HN93-50	MLW94-256 HT55-43	MLW95-608 HN94-65	MLW95-613 HN94-51	MLW96-708 HN94-63	MLW95-315 MM-88-07	MLW95-358 MM-88-06	MLW95-364 MM-88-06	MLW95-503 MM-89-106
Depth (m)	110	760	375	50	223	117	450	20	15	65	243
Deposit	Halfmile Lake	Halfmile Lake	Halfmile Lake	Halfmile Lake	Halfmile Lake	Halfmile Lake	Halfmile Lake	Restigouche	Restigouche	Restigouche	Restigouche
Method	Bailer	Bailer	Bailer	Bailer	Packer	Packer	Packer[a]	Bailer	Bailer	Bailer	Packer
Water type	$CaNaHCO_3$	$NaHCO_3$	$CaNaHCO_3SO_4$	$MgCaSO_4$	$CaNaHCO_3$	$CaHCO_3$	$NaHCO_3$	$CaNaClSO_4$	$CaSO_4$	$CaNaSO_4HCO_3$	NaCl
DO (mg/l)	9.0	7.5	4.6	9.7	nd	nd	2.4	3.3	2.3	2.0	0.0
pH	6.26	6.48	6.39	5.43	7.94	7.26	9.86	5.72	6.84	7.06	9.33
Eh (mV)	277	68	169	348	64	220	−236	nd	169	42	197
EC (μS/cm)	28	85	56	15		58	277	235	165	309	4870
TDS (mg/l)	20.6	47.9	37.5	8.1	95.2	45.0	226.1	127.8	93.2	201.7	2657.1
Ion chromatography (mg/l)											
HCO_3	9.61	25.02	17.20	2.49	50.87	25.07	139.97	15.53	22.11	66.34	211.77
SO_4	1.99	1.91	6.70	3.20	5.67	3.97	7.13	36.50	40.00	51.20	0.21
Cl	0.96	5.14	0.84	0.42	9.24	1.15	6.83	31.80	2.86	22.90	1485.00
ICP–ES and MS (μg/l)											
Si	3600	3300	3400	1100	4100	4600	6818	3000	3200	3400	2200
Al	6.5	43	26	29	58	12	281	3.6	6.1	2	110
Fe	6	430	170	130	230	6	151	2300	4600	3200	3
Mn	11	26	72	25	440	49	24	270	240	260	280
Mg	390	320	940	430	1400	670	121	6200	6200	10000	5000
Ca	1900	1500	3700	360	10000	6600	1825	16000	15000	21000	11000
Na	1600	10000	3500	50	13000	2500	62681	18000	3300	26000	940000
K	530	670	1200	73	900	430	740	760	500	820	1900
As								49	76	110	13
Ba	12	18	59	33	250	270	11	48	32	98	550
Cd								6.1	0.9	0.5	0.5
Co	0.2	0.2	0.88	2.7	1.7	1.9	0	1.9	0.8	0.6	0.8
Cr	0.2	0.2	0.2	0.2	0.8	0.2	0.2	0.2	0.2	0.2	2.7
Cu	1.5	1	2.1	7.8	0.7	0.8	0.5	1.7	0.5	0.5	2
Li					2	5		2		4	1800
Mo	0.5	8.6	3.1	0.5	5.6	1.9	47	0.5	0.5	1.7	19
Ni	1	1.5	2.3	2.5	2	3		5	2	1	6
Pb	1.2	0.46	0.65	0.62	0.6	0.2	0.4	410	530	22	1.3
Rb	0.68	1.1	1.4	0.34	1.5	0.4	1.6	0.9	0.6	1.1	3.7
Sr	8.8	12	29	2.1	160	37	19	70	38	120	610
Zn	29	10	69	61	220	470	2	2300	1300	1000	14
Chelation ICP–MS (μg/l)											
Ti	0.05	0.51	0.31	0.07	0.45	0.06	1.52	0.05	0.05	0.05	0.12
V	0.02	0.09	0.02	0.01	0.04	0.02	0.18	0.01	0.01	0.01	0.16
Co	0.123	0.144	0.814	2.578	1.66	1.938	0.21	1.378	0.585	0.465	0.82
Ni	0.3	1.5	2.2	2.6	1.9	2.8	0.1	4.3	1.3	1.3	6.1
Cu	1.37	0.82	2.47	8.02	0.73	1.06	0.19	1.25	0.57	0.32	2.1
Zn	22.7	9.3	48.9	61	171	358.2	2.1	1702.8	963.6	750	16.5
Y	0.028	0.105	0.111	0.119	0.194	0.014	0.159	0.143	0.064	0.048	0.039
Cd	0.165	0.034	0.142	1.528	0.16	0.105	0.005	5.487	0.848	0.075	0.384
Pb	0.971	0.435	0.62	0.607	0.554	0.241	1.072	323.044	376.956	20.112	1.113
U	0.02	0.028	0.109	0.006	0.238	0.06	0.049	0.01	0.021	0.296	0.915
$\delta^{18}O_{SMOW}$	13.42	13.43		13.70	−13.15	−13.35	13.38			11.58	12.42
δD_{SMOW}	88.8	90.9		97.1	−89.1	91.5	81.5			93.4	85.4

Table 1 (continued)

Sample #:	MLW95-528	MLW95-546	MLW95-547	MLW95-563	MLW95-570	MLW95-586	MLW95-590	MLW95-593	MLW95-597	MLW95-600
Hole #:	MM-89-106	MM-89-104	MM-89-109	B-80-15	MM-89-102	B-80-7	B-80-7	MM-89-107	MM-88-02	MM-88-02
Depth (m)	53	210	Surface	100	350	223	116	169	251	511
Deposit	Restigouche	Restigouche	Restigouche	Restigouche	Restigouche	Restigouche	Restigouche	Restigouche	Restigouche	Restigouche
Method	Packer	Bailer	Artesian	Bailer	Bailer	Packer	Packer	Packer	Packer	Packer
Water type	$CaHCO_3$	$CaHCO_3$	$CaHCO_3$	$CaHCO_3$	$NaClHCO_3$	$NaHCO_3Cl$	$CaNaHCO_3$	$CaHCO_3$	NaCl	NaCl
DO (mg/l)	nd	5.4	nd	4.5	3.2	nd	nd	nd	nd	nd
pH	7.18	7.31	8.11	7.84	8.67	8.23	8.67	7.98	7.94	7.83
Eh (mV)	165	−13	−70	193	97	−60	95	161	−150	−113
EC (μS/cm)	66	272	373	262	1520	702	305	144	41600	40800
TDS (mg/l)	55.9	215.5	314.6	230.3	989.3	508.6	255.6	122.5	20792.3	20714.1
Ion chromatography (mg/l)										
HCO_3	33.99	141.89	207.79	144.42	316.65	227.70	152.21	78.29	130.10	136.91
SO_4	3.97	16.30	22.10	25.10	3.07	10.30	19.40	11.40	0.05	0.05
Cl	1.35	3.76	4.64	1.983	51.00	118.00	14.90	0.82	13440.00	13255.00
ICP–ES and MS (μg/l)										
Si	3500	2900	4300	4500	3100	2500	3000	2700	3100	3100
Al	4.3	1.3	3.4	1.5	12	11	4.1	10	200	14
Fe	5	1600	500	93	3	38	3	3	950	1300
Mn	5.1	580	86	200	17	45	32	14	140	81
Mg	2600	12000	15000	14000	4500	3300	7600	5900	320000	320000
Ca	8100	27000	40000	34000	10000	6000	22000	20000	790000	780000
Na	2000	11000	20000	5900	300000	140000	36000	2900	6090000	6200000
K	390	680	730	430	960	770	510	480	19000	19000
As	1	6	11	8	7	2	8	2	1	7
Ba	19	280	79	48	220	59	75	69	91000	93000
Cd	1.1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Co	0.2	1	0.2	0.2	0.2	0.2	0.2	0.2	2.5	2.1
Cr	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	3.3	1.6
Cu	0.5	0.8	0.5	0.5	0.5	0.5	0.5	0.5	11	12
Li	1	3	13	3	910	950	6	1	1900	2600
Mo	0.5	1.6	1.5	1.1	1.6	0.8	0.7	1.3	0.7	0.5
Ni	1	9	1	1	2	1	1	2	26	21
Pb	0.2	0.6	0.2	0.2	0.2	0.2	0.2	0.3	0.8	0.8
Rb	0.5	1	0.7	0.6	1.5	1.2	0.6	0.7	29	25
Sr	20	100	250	180	290	180	200	95	88000	89000
Zn	58	21	2	12	2	11	2	22	370	1700
Chelation ICP–MS (μg/l)										
Ti	0.05	0.05		0.05	0.06		0.05	0.06		
V	0.02	0.01		0.03	0.29		0.01	0.02		
Co	0.137	0.96		0.129	0.161		0.035	0.141		
Ni	0.2	8.6		0.2	1.9		0.2	1.1		
Cu	0.37	0.58		0.12	0.31		0.44	0.3		
Zn	53.4	20.8		12.3	0.9		3.1	20		
Y	0.007	0.014		0.035	0.121		0.014	0.006		
Cd	0.986	0.021		0.005	0.072		0.005	0.012		
Pb	0.207	1.735		0.524	0.059		0.082	0.248		
U	0.028	0.981		0.368	0.525		0.476	0.271		

element ratios. This is consistent with fracture-dominated flow and with the steep structures in the deposit. There are no consistent trends with depth between boreholes, although there is a tendency for TDS, Cl, Na, K, Al and Mo contents to increase with depth, and Ca, Eh and DO contents to decrease with depth. Because most of the samples collected from the Halfmile Lake deposit were sampled using the flow-through bailer, the relationship between groundwater composition and proximity to the ore zones is difficult to quantify. However, typically the base metal (Zn, Pb, Cu and Co) and SO_4 contents tend to be somewhat elevated near massive sulphide mineralization (e.g., Zn; Fig. 7A). In boreholes

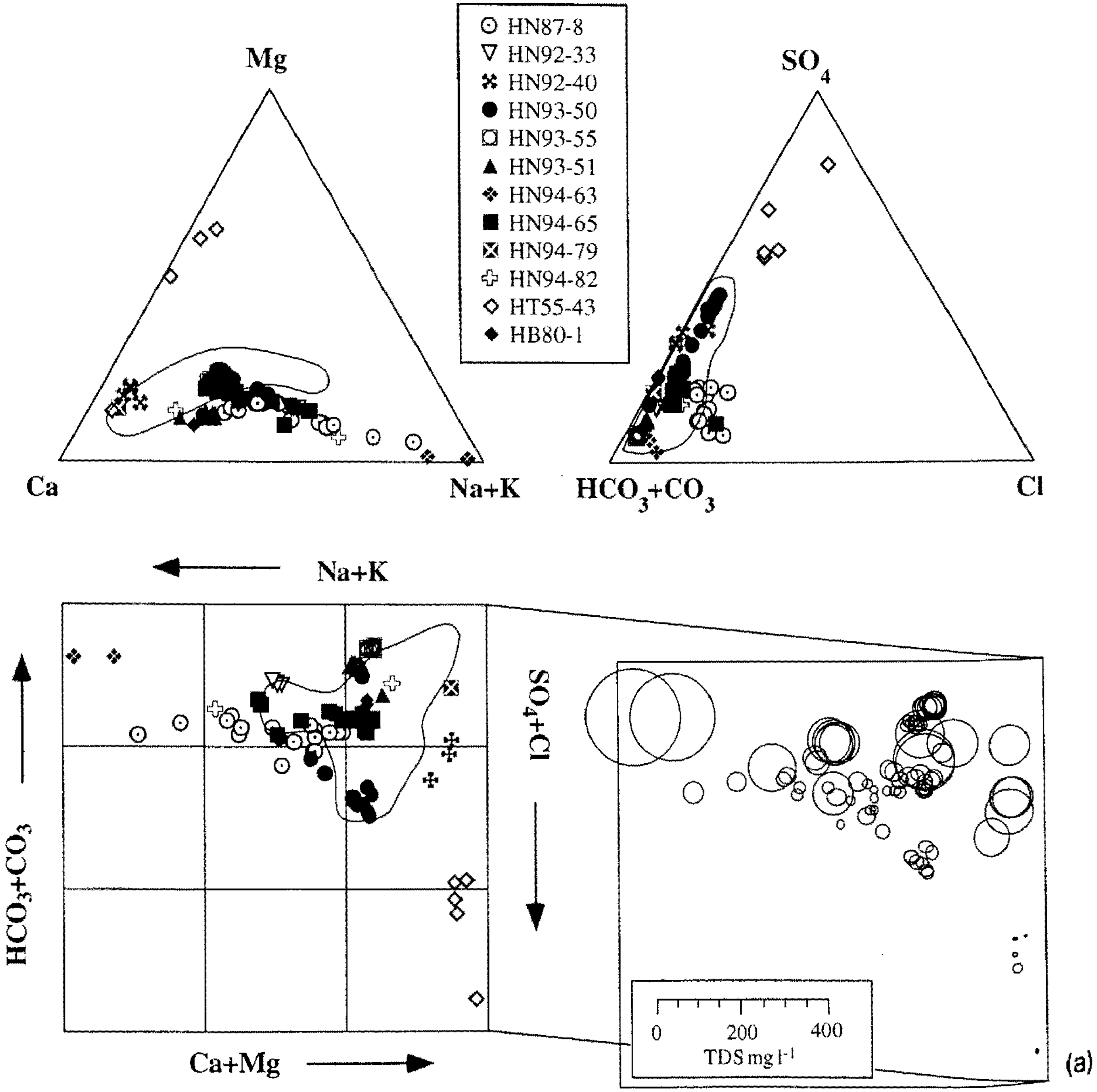


Fig. 4. Modified piper diagram for groundwaters associated with the (A) Halfmile Lake deposit, and (B) Restigouche deposit. Shown on both figures are the fields for surface waters from each deposit.

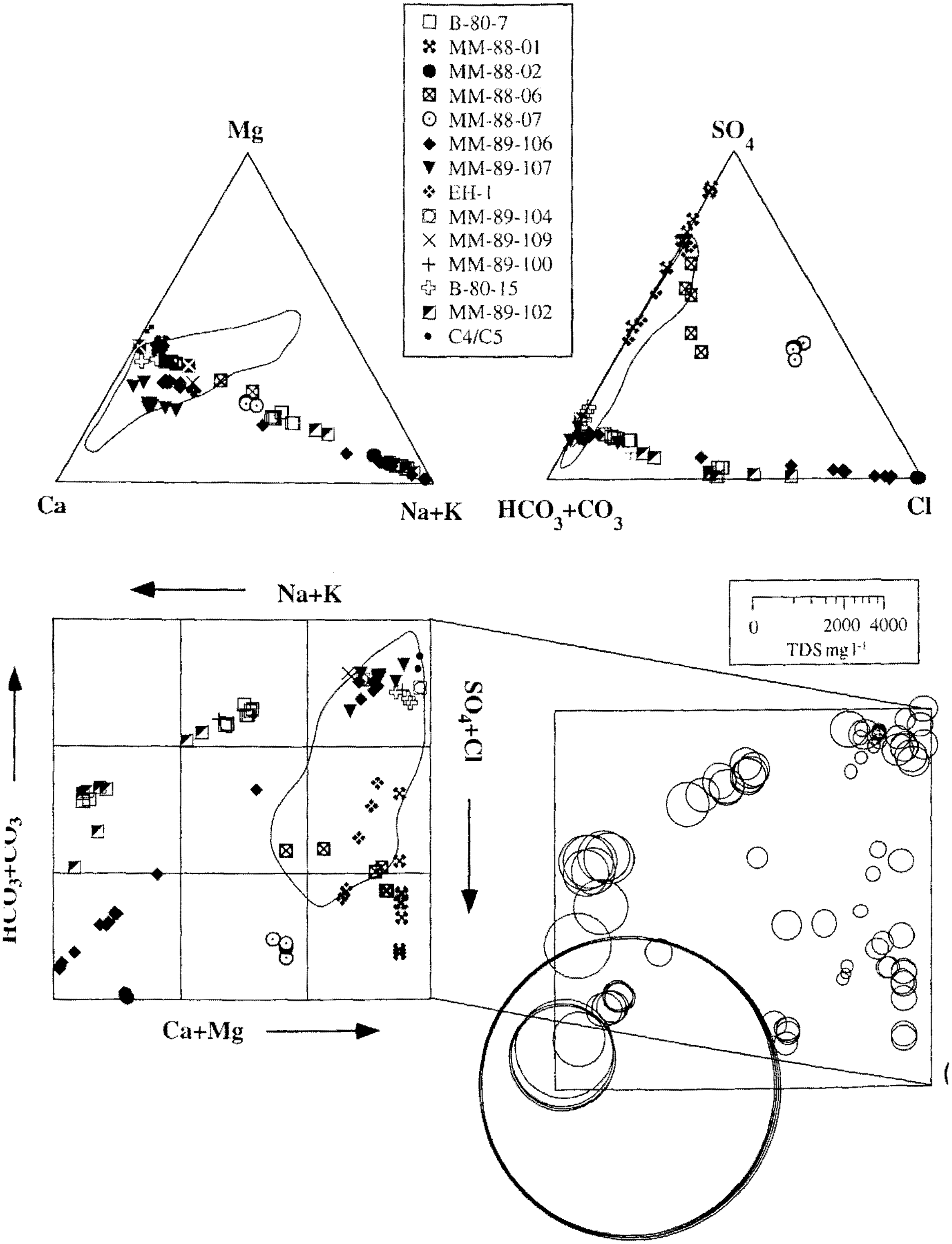


Fig. 4 (continued).

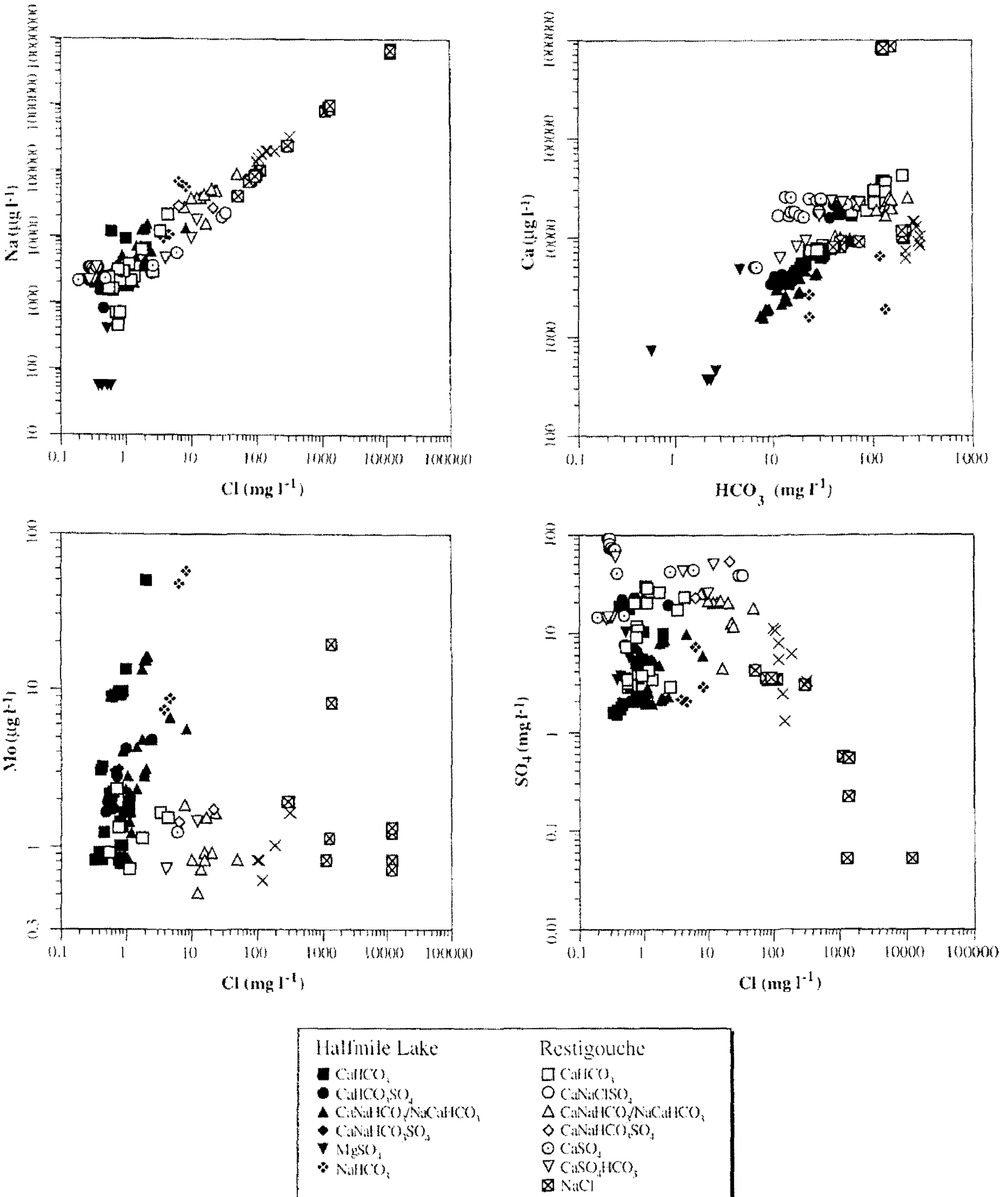
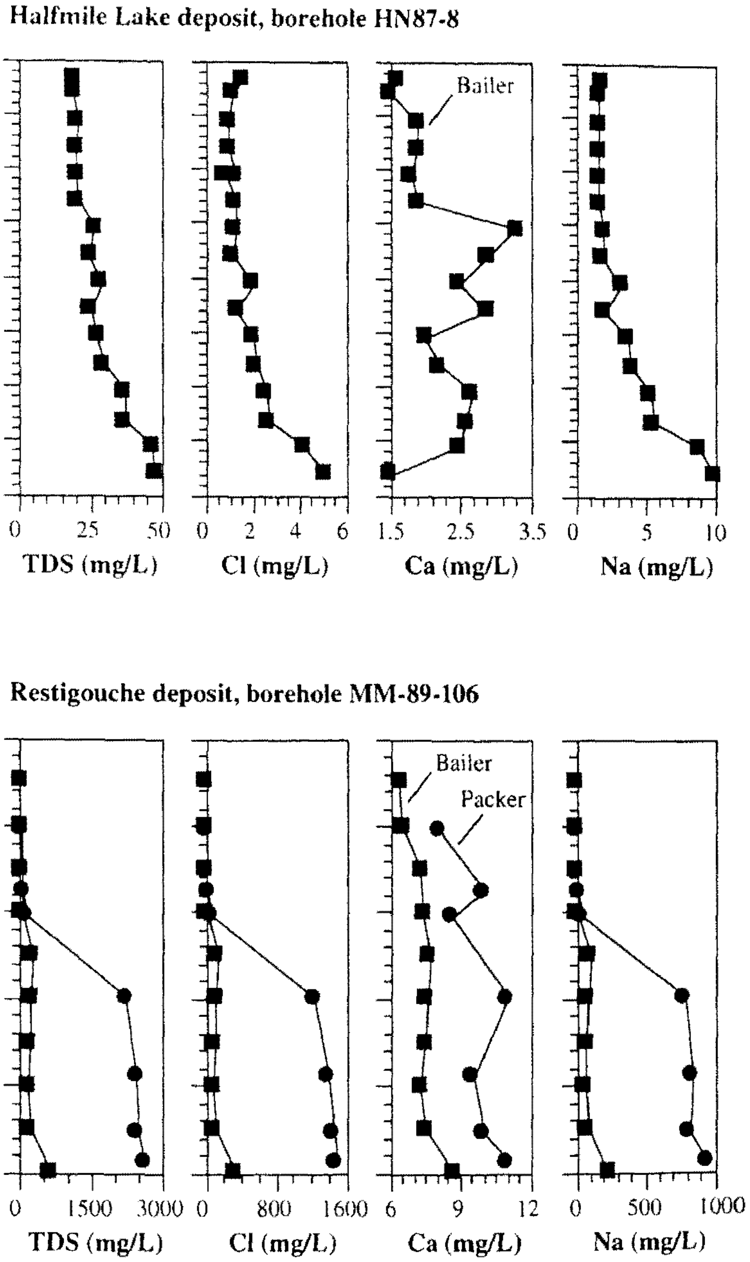


Fig. 5. Element–element plots showing the differences in groundwater geochemistry between the two deposits. The waters have been classified according to water-type. (a) Na vs Cl, (b) Ca vs HCO_3, (c) Mo vs Cl, and (d) SO_4 vs Cl.



g. 6. Downhole variation for selected geochemical parameters for borehole HN87-8 from the Halfmile Lake deposit (bailer oundwaters) and borehole MM-89-106 from the Restigouche deposit (bailer and straddle-packer groundwaters).

N87-8, HN93-50 and HN93-55, Fe concentrations crease with decreasing Eh, whereas in borehole N94-55 both Eh and Fe decrease in the vicinity f the massive sulphide zones. Many groundwaters the Halfmile Lake deposit have elevated Al and Mo contents (Fig. 5c) but lower base metals and SO_4 contents compared to the Restigouche deposit (Fig. 5d).

The stable isotopic compositions of borehole waters are remarkably uniform and essentially identi-

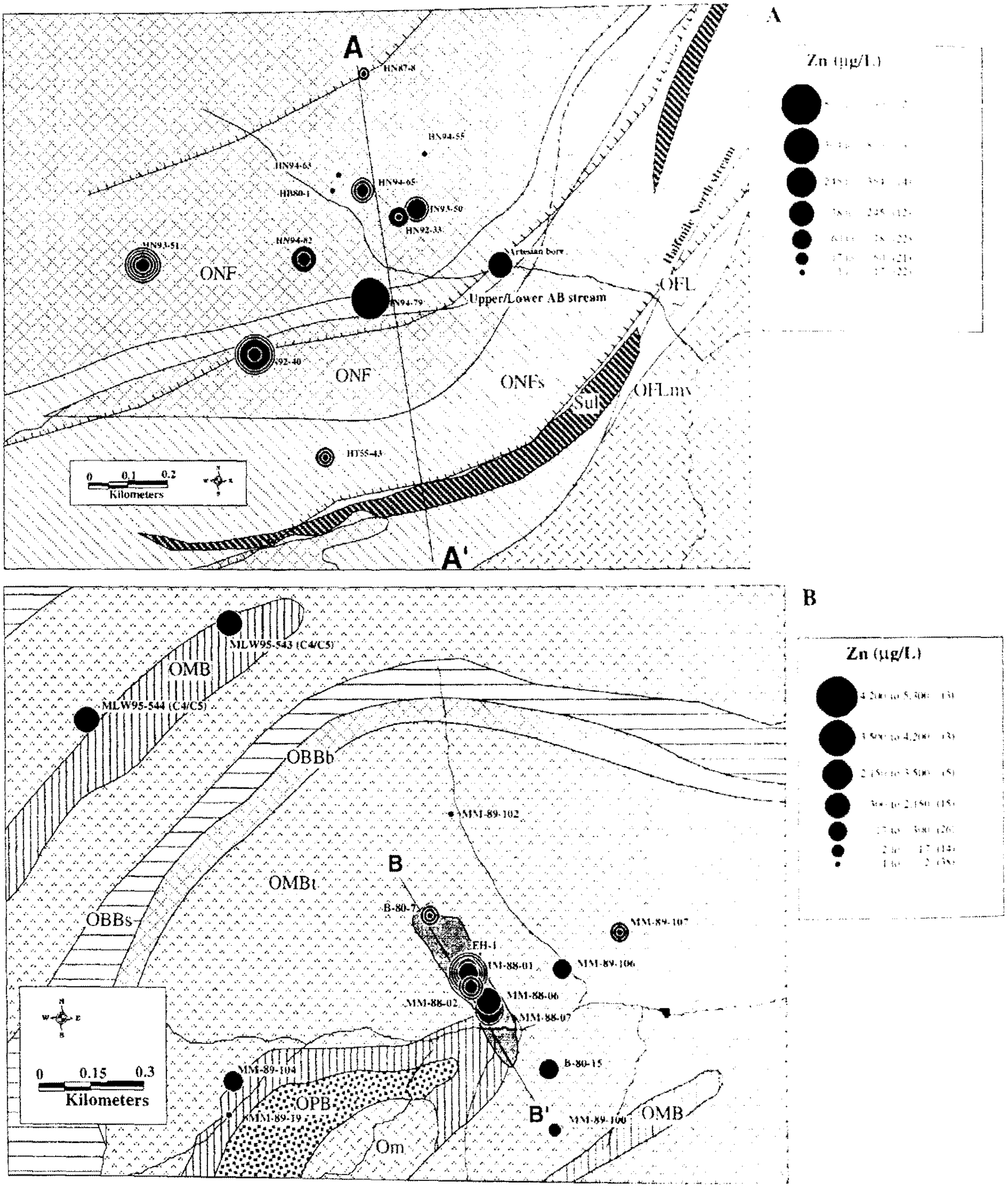
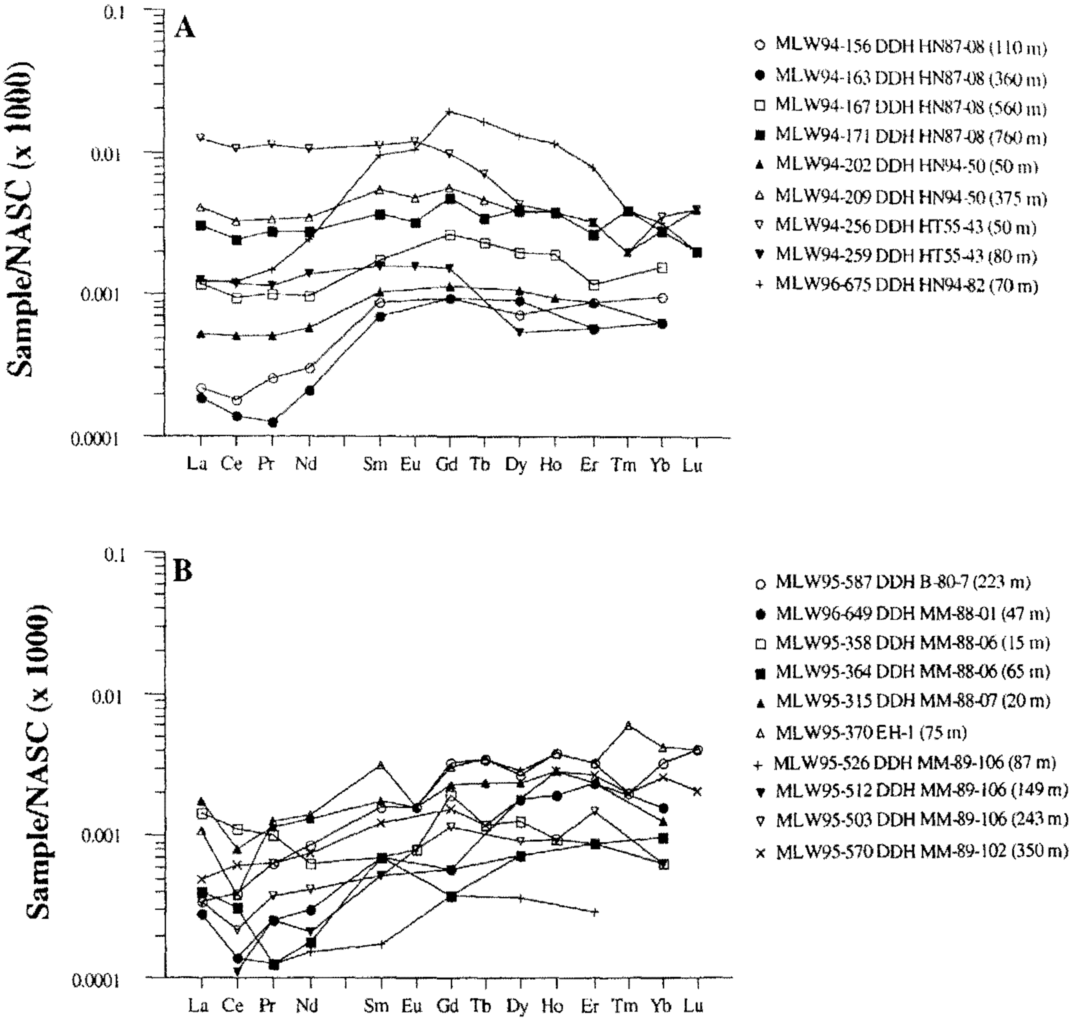


Fig. 7. Proportional circle maps of Zn contents of groundwaters from the (A) Halfmile Lake deposit, and (B) Restigouche deposit. The lines *A–A′* and *B–B′* show the positions of the stratigraphic cross-sections in Fig. 2. Geology as in Fig. 2.



8. Representative REE patterns normalized to North America Shale Composite (*NASC*) for (A) Halfmile Lake groundwaters, and Restigouche groundwaters. Data from (Leybourne, 1998). Sample depths are given in metres below ground surface.

l to the surface waters with an average $\delta^{18}O$ of 13.4‰ and δD of −90.2‰, and an average excess uterium value of 17.2.

Shale-normalized (North America Shale Com- site; NASC) REE patterns for Halfmile Lake undwaters vary from slightly LREE-enriched highly LREE-depleted with dish-shaped con- ve-up profiles between the LREE and the MREE ig. 6). Many samples show a slight upward con- xity about the MREE with $[La/Sm]_{NASC} < 1$ and d/Yb$]_{NASC} > 1$ (Fig. 8). Several samples from reholes HN94-65 and HT55-43 have relatively flat tterns from La to Eu, with progressive depletion from Gd to Yb. Despite the overall relative chemical uniformity of Halfmile Lake groundwaters there are significant variations in the REE with depth. For example, in borehole HN87-8, $[La/Sm]_{NASC}$ and $[La/Yb]_{NASC}$ increase systematically with depth (Fig. 8). The REE patterns of the deeper samples in this borehole are distinct from the shallower samples in that the latter are depleted in the LREE with pronounced dish-shaped concave-up profiles in the LREE. The deeper samples show a flatter pattern overall (Fig. 8; compare the profiles for samples MLW94-156 and 163 with those of samples MLW94-167 and 171). Leybourne (1998) has shown that the REE patterns of the deeper waters are very similar to REE patterns for the host lithologies.

4.3. Groundwaters at the Restigouche deposit

Groundwaters at the Restigouche deposit display a wide variation in composition (Fig. 4b, Fig. 5). Shallow oxidizing groundwaters in contact with the massive sulphides are dominantly Ca–(Na)–SO_4 waters. Some of these waters have highly elevated metal contents (Zn up to 5300 µg l^{-1}, Pb up to 1400 µg l^{-1}). Shallow groundwaters from boreholes away from the main ore zone are dominantly Ca–HCO_3^- to Ca–Mg–HCO_3^- waters (Fig. 4b) with generally low base metal loads. With increasing depth, groundwaters increase in total dissolved solids (up to 3000 mg l^{-1}) and trend towards Na–HCO_3–Cl and ultimately to Na–Cl waters (e.g., borehole MM-89-106; Fig. 6). In the deepest borehole (600 m depth), Na–Cl waters were recovered with up to 21,000 mg/l TDS. The highest salinity waters from MM-88-02 have lower Na/Ca than the brackish waters from borehole MM-89-106 (Fig. 4b). Groundwaters also show a strong trend with increasing TDS and Cl concentration away from Ca–Mg-dominated compositions to Na-dominated compositions (Fig. 4b). This relationship is evident from the strong correlation between Na and Cl concentrations (Fig. 5a). Both Ca and Mg correlate positively with Cl, but groundwaters with Cl concentrations >10 mg l^{-1} decrease somewhat in Ca and Mg with further increases in Cl. This may indicate saturation of these waters with respect to carbonate minerals, consistent with hydrogeochemical modelling (see Section 5).

Trace elements show similar patterns as the major cations. In general, the trace metals increase with increasing chloride content (e.g. Sr, Ba, Li). Potassium and Rb contents are higher in the lowest salinity groundwaters from boreholes penetrating hanging wall and footwall alteration zones, than in more saline waters, and probably originate from sericitic clays in the fractures by cation exchange and silicate hydrolysis reactions. Potassium and Rb contents are lowest for groundwaters with Cl concentrations from 0.7 to 20 mg l^{-1} above which concentrations of both elements increase. Solubility modelling is consistent with K and Rb contents being controlled by saturation with respect to sericite and illite.

The SO_4 concentrations are generally highest in the vicinity of the sulphides. Boreholes MM-88-06 and MM-88-07 are close to the surface outcrop of the deposit (Fig. 2B) and have elevated sulphate (Fig. 4b). Borehole MM-88-01 is further removed from the outcrop, but still intersects the main zone of mineralization and has the highest SO_4 values (38–87 mg l^{-1}). The waters in this borehole are more O_2-rich than those from 88-06 or 88-07 (DO = 4–5 mg l^{-1} vs <3 mg l^{-1}). Iron contents are generally low, probably reflecting the precipitation of Fe-oxyhydroxides. The most elevated Fe contents are in groundwaters from boreholes MM-88-06 and MM-88-07. Groundwaters from borehole MM-88-01 have relatively low Fe compared to MM-88-06 and MM-88-07. Boreholes away from the deposit are low in all the base metals and SO_4. Groundwater base metal contents (Zn, Pb, Cu, Sb, Cd) are highest closest to the Restigouche deposit (e.g., Zn; Fig. 7B).

Groundwaters at the Restigouche deposit show greater variation in stable isotopic compositions compared to groundwaters from the Halfmile Lake deposit. Surface waters and low TDS shallow groundwaters are isotopically similar to those from the Halfmile Lake deposit, ranging from between −13.4 and −13.8‰ for $\delta^{18}O$ and −90 and −98‰ for δD. Brackish groundwaters from the lower portions of MM-89-102 and MM-89-106 (990–2660 mg l^{-1} TDS) are isotopically heavier, whereas the saline waters from borehole MM-88-02 are the most isotopically enriched with $\delta^{18}O$ values of around −11‰ and δD values of −67 to −72‰.

The range in REE is restricted, varying from 5.4 ng l^{-1} to 240 ng l^{-1} with an average of 65.9 ng l^{-1}. These values are much lower than for the Halfmile Lake groundwaters despite higher TDS in Restigouche deposit groundwaters (REE could not be accurately determined in MM-88-02 waters). Compared to NASC, most Restigouche deposit groundwaters display REE patterns with positive slopes from the LREE to the MREE with $[La/Sm]_{NASC} < 1$. Slopes from the MREE to the HREE are variable but generally flat. Exceptions to the LREE-depleted nature of the groundwaters are waters from borehole MM-88-06 which show a concave-up pattern from La to Gd. As with the Halfmile Lake groundwaters, Ce anomalies are poorly developed compared to the local surface waters, although w groundwaters have well developed negative nalies (Fig. 8). Unlike the deeper Halfmile Lake ndwaters, groundwaters from the Restigouche sit have REE patterns that are different to the lithologies.

iscussion

Surface water geochemical response of the fmile Lake and Restigouche orebodies

The geochemistry of the surface waters at both osits is largely controlled by the composition echarge waters, water–rock reactions, length of way from recharge to discharge site and the ologies through which they flow. In addition. e metal contents at both deposits are controlled solubility factors and proximity and depth to the bodies.

At both deposits the major cations and HCO_3 are ngly correlated with each other and vary between ams. Given that the different streams, in a broad se, flow over different lithologies (Fig. 3), this gests that lithology is a major control on dis- ved load. For example, TDS shows a bimodal tribution at the Halfmile Lake deposit. Streams on east half of the study area have generally higher S and Ca, consistent with more easily weathered fic to intermediate lithologies compared to the sic lithologies on the west half of the study area ybourne et al., 1995). Although there is good dence at the Restigouche deposit for hydrologi- connection between the high salinity MM-88-02 ters and boreholes MM-88-07 and MM-88-06 (as denced by elevated Cl and Na compared to other llow groundwaters interacting with the deposit), low SO_4 contents of Charlotte Brook waters acent to the deposit suggest that there is no ob- us connection between the high-sulphate shallow undwaters and the surface waters in Charlotte ook which flow over the deposit. Although metal ntents in Charlotte Brook downstream from the body are anomalous (e.g. Zn, Fig. 3B), sulphate ntents are not. Chloride contents are slightly ele- ted but this may also be due to interaction with Cl- h alteration minerals in the alteration halo about deposit.

Further oxidation of sulphides is evident in streams on the east and west boundaries of the Restigouche deposit study areas. Streams in these locations have thick accumulations of Fe-oxyhydroxides in the stream sediments, although metal contents in the waters are not as high as in Charlotte Brook downstream from the Restigouche deposit (e.g. Fig. 3B). Either Fe-sulphide minerals are being oxidized in the subsurface rather than Zn–Pb massive sulphides as found in the Restigouche deposit, or Zn and Pb have been scavenged by adsorption onto Fe-oxyhydroxides. Two very Fe-rich stream sediment samples from the Mt Fowler east stream have similar Zn contents as the sediments downstream from the Restigouche deposit, but much lower Pb contents (Leybourne, 1998). These data suggest that if there is Zn–Pb massive sulphide mineralization in the subsurface, it must be at greater depth than the main Restigouche deposit; the low Pb levels in the Mt Fowler east stream sediments would therefore be due to low Pb solubility in natural waters compared to Zn.

At both deposits, natural oxidation and dispersion of massive sulphides is apparent (Fig. 3). At the Halfmile Lake deposit, base metal anomalies in waters are relatively subdued due to the physical hydrology and the depth of the orebody. Downstream, even the signature of relatively mobile Zn decreases to background values ($<2\ \mu g\ l^{-1}$; Fig. 3A). At the Restigouche deposit elevated Zn and Pb contents are associated with the main orebody and Fe-oxyhydroxide-rich stream sediments west and east of the deposit indicate other sites of natural oxidation of Fe-sulphides in the area.

5.2. Groundwater chemical differences between the Halfmile Lake and Restigouche deposits

Groundwater compositions between the two deposits are distinctly different. Whereas the Halfmile Lake deposit groundwaters are Ca–HCO_3 to Na–HCO_3 in composition, groundwaters at the Restigouche deposit trend away from such compositions to high salinity Na–Cl waters (Figs. 4 and 5a). Even where groundwaters have a similar classification (Fig. 4), Restigouche groundwaters tend to be higher in TDS, Ca, Na, Cl, HCO_3, SO_4 (Fig. 5). Halfmile Lake groundwaters have higher DO, Al, and Mo and lower pH and base metal compositions than those associated with the Restigouche deposit (e.g. Fig. 5c). For the Restigouche groundwaters, those shallow groundwaters distal to the deposit are chemically most similar to the groundwaters recovered from the Halfmile Lake deposit (Fig. 4). Shallow groundwaters from both deposits have similar stable isotope compositions that overlap with local surface water isotopic compositions indicating modern recharge.

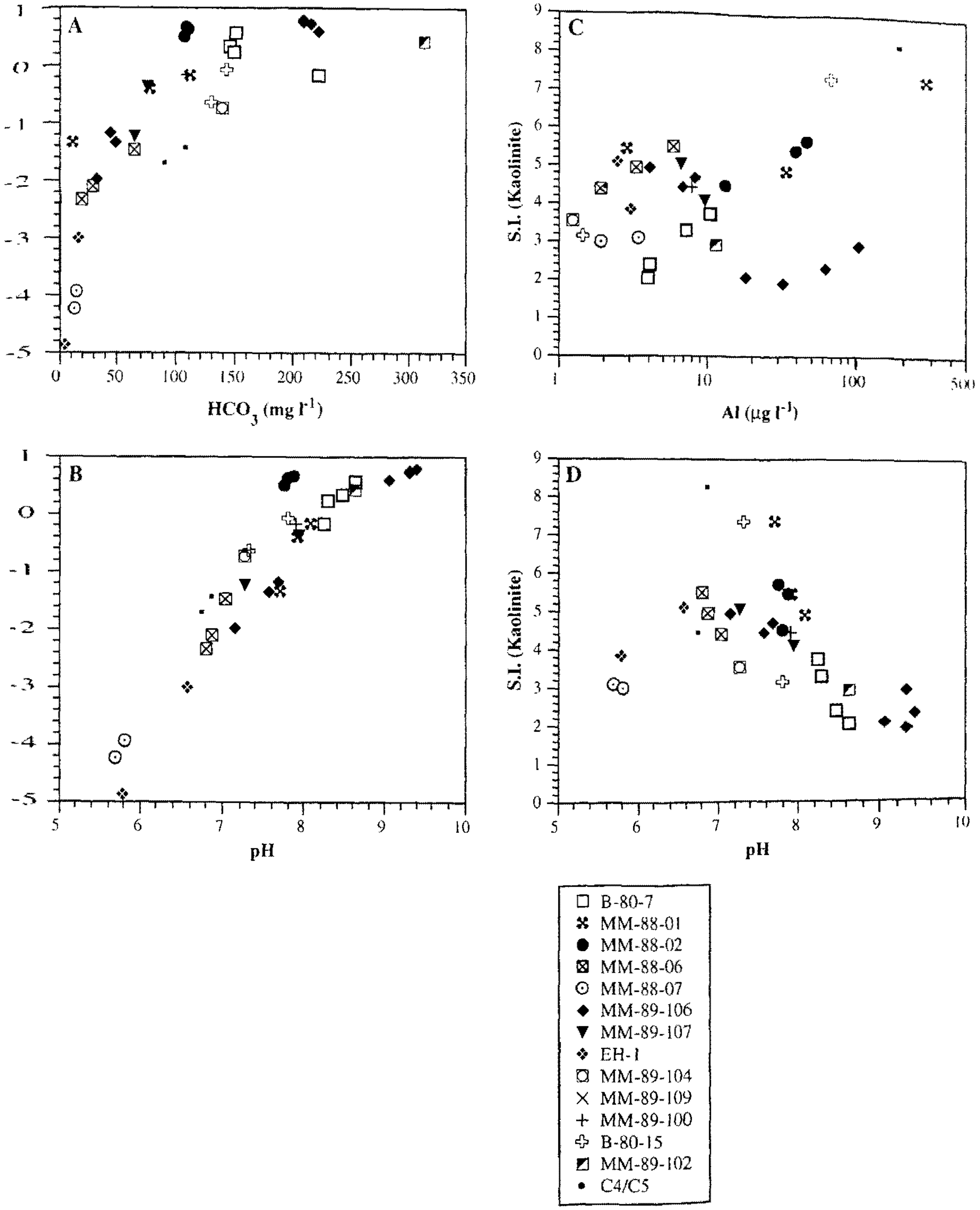
There are a number of possible explanations for the absence of saline waters at the Halfmile Lake deposit. More than 100 exploration holes have been drilled at the Halfmile Lake deposit since 1987, and many of the holes are >1000 m in length. If saline waters existed in the subsurface at Halfmile Lake, it seems likely that they would have been intersected by drilling. In order to fully address this question, it is important to establish how representative the different groundwater sampling techniques used in this study are of the true groundwater compositions. The success of the flow-through bailer in fracture-flow-dominated systems is highly dependent on the variations in hydraulic gradients and hydraulic conductivities with depth. For example, bailer samples from borehole MM-89-106 showed an increase in salinity with depth with waters less than 125 m depth having low TDS contents and groundwaters below this depth showing increasing Na and Cl contents. However, although the bailer samples indicated progressive change with depth, the magnitude of the change was suppressed due to mixing within the open borehole. Straddle-packer samples from this hole indicate that waters flowing near the bottom of the hole have salinities in excess of 2500 mg l^{-1}, compared to 660 mg l^{-1} as indicated by the deepest bailer sample. Although the straddle-packer system worked well at the Restigouche deposit, results from the Halfmile Lake deposit were less successful (Leybourne, 1998). Therefore, most of the groundwater samples considered in this study were collected using the flow-through bailer. Packer samples from Halfmile Lake deposit are all low-TDS waters (Table 1). Thus, although the bailer samples are unlikely to be fully representative of the salinities in existence at the Halfmile Lake deposit, saline waters would likely have been found if they existed. In addition, saline waters are commonly overpressured/artesian (e.g. Restigouche deposit), suggesting that even the bailer sampling method should indicate the presence of saline groundwaters.

Brackish to saline waters also occur at the Heath Steele and Brunswick #12 deposits indicating that saline waters are not unique to the Restigouche deposit (Leybourne et al., 1997; Leybourne, 1998). The saline waters at the Restigouche deposit could be allochthonous, possibly from younger sedimentary units (e.g., Silurian-age rocks to the northwest of the study area; Figs. 1 and 3b). The Silurian rocks consist of siltstones, sandstones and limestones (McCutcheon, 1997), whereas, there are no equivalent units proximal to the Halfmile Lake deposit. However, the saline waters at the Restigouche deposit are chemically and isotopically closer in affinity to shield-type brines than they are to brines found in sedimentary basins. In addition the Br/Cl ratios are too low to support derivation from a seawater source (Leybourne, 1998).

Dilution of deeper groundwaters by drilling fluid (surface waters) at the Halfmile Lake is inconsistent with the fact that the packer samples are not significantly elevated in TDS compared to bailer samples, the composition of groundwaters from newer holes are similar to those from holes drilled before 1990, and the variation in REE downhole indicates different groundwaters with depth.

The preferred interpretation is that saline waters at the Halfmile Lake deposit have largely been flushed due to rapid recharge to depth of meteoric waters. This is consistent with the low TDS and lower pH of the Halfmile Lake groundwaters compared to those at the Restigouche deposit, with similar stable isotopic compositions in ground and surface waters at the Halfmile Lake deposit and with the variation in REE profiles (Fig. 9). Deeper groundwaters at the Halfmile Lake deposit have REE profiles similar to the host rocks, unlike the shallow groundwaters (Leybourne, 1998).

Therefore, the gross differences in groundwater composition between the two deposits is due to differences in the physical hydrology and the nature of active groundwater circulation. Steep structures at the Halfmile Lake deposit have allowed recharge waters to penetrate deeper, displacing any saline waters that may have existed. In contrast, the shallow and deep groundwater systems are more isolated



g. 9. Saturation index plots for Restigouche deposit groundwaters. SI calculated using the EQ3NR code of Wolery (1992). (A) S.I.$_{\text{calcite}}$ HCO$_3$. (B) S.I.$_{\text{calcite}}$ vs pH. (C) S.I.$_{\text{kaolinite}}$ vs Al. (D) S.I.$_{\text{kaolinite}}$ vs pH.

at the Restigouche deposit due to more shallow structures. A similar situation to the Restigouche deposit was observed at the Oak Ridge Reservation, Tennessee, where brines were found to occur as shallow as 30 m, although tritium and carbon isotope evidence indicates that the brines are influenced by meteoric waters (Nativ, 1996). At the Restigouche deposit, the lack of sulphate and the carbon isotopic composition (Leybourne, unpublished data) of the saline waters indicates that there has been little, if any, mixing with the shallow groundwaters.

5.3. Water–rock reactions and controls on Restigouche deposit groundwater chemistry

Having established that fundamental controls over the gross differences in the groundwater compositions between the two deposits are the hydrology, structure and proximity of massive sulphides to surface, it is possible to also place some constraints on controls over the solute contents of different groundwaters. Likely causes of variable groundwater composition include (1) mixing between different groundwaters (e.g. recharge waters, saline fluids), (2) cation and anion exchange reactions, and (3) water–rock interaction including mineral dissolution and formation of new mineral phases.

Principal component analysis (PCA) of the Restigouche groundwaters suggests that any mixing relationships cannot be explained by simple two-component mixing between shallow recharge waters and deeper saline waters. Several possible end-member groundwater compositions can be identified using PCA. One end-member is represented by shallow, low-TDS Ca–HCO_3 waters distal from the Restigouche ore body (e.g. MM-89-106 and MM-89-107). The second end-member is represented by shallow high-SO_4 groundwaters from borehole MM-88-01. The elevated sulphate in these and other Ca–SO_4 waters (boreholes MM-88-06, MM-88-07 and EH-1) is due to oxidation of massive sulphides. The majority of shallow groundwaters can be accounted for by two-component mixing if the first two factors in the PCA are considered, accounting for 78% of the variance in the data. Consideration of the third factor (17% of the variance) suggests a third shallow groundwater end-member represented by waters in boreholes B-80-15 and MM-89-109, both distal from the main deposit. These waters are also Ca–HCO_3 waters but have higher TDS (>200 mg l^{-1} vs ≤ 100 mg l^{-1}) and higher Mg/Ca and Na/K than other shallow Ca–HCO_3 groundwaters. Considering all three PCA factors, most of the shallow groundwaters could represent three-component mixing. However, the situation is clearly more complicated. A fourth component is indicated by the brackish waters recovered in borehole MM-88-102 and the deeper parts of B-80-7. The highly saline waters in borehole MM-88-02 are distinctly different from any of the above end-members. Finally the deep waters from borehole MM-89-106 may represent mixing between the MM-89-102 end-member and another end-member represented by a mixture between the MM-88-02 waters and the shallow groundwaters. Calcium and Mg contents for the MM-88-02 waters are too high for the MM-89-106 saline waters to be produced by recent mixing between the saline waters and shallow groundwaters. Alternatively, if these waters are mixtures, the mixing is not a recent phenomenon, allowing time for modification of the Mg and Ca values through water–rock and cation exchange reactions. Thus, although the Cl and stable isotopic data suggest that the MM-89-106 saline waters are mixtures between saline (as represented by waters from MM-88-02) and meteoric end-members, if mixing has occurred, it is not a recent, drilling-induced mixing given the differences in the major element compositions.

There is also good evidence for modern (drilling-induced) mixing between the high-salinity waters in MM-88-02 and shallow groundwaters in MM-88-06 and 07. The Cl contents are consistent with some cross-flow between these boreholes, as they are down-gradient from MM-88-02.

Modelling of groundwater chemical speciation and saturation was carried out using the EQ3/6 code (Wolery, 1992). High-sulphate shallow groundwaters at the Restigouche deposit are typically the most undersaturated with respect to carbonate species, consistent with the observation that carbonate minerals have been dissolved from the host rock in the upper parts of the section. With increasing depth, the high-sulphate waters are less undersaturated with respect to carbonate species (e.g. MM-88-01 waters). Shallow groundwaters away from the deposit (boreholes MM-89-100, MM-89-104, B-80-15, MM-

-107, and shallow waters from MM-89-106) are undersaturated or close to saturation but typi- lly have higher HCO_3 contents and higher $S.I._{calcite}$ d $S.I._{dolomite}$ than the high-sulphate groundwaters ig. 9). The deeper, more saline groundwaters from reholes MM-89-102, MM-89-106 and MM-88-02 ; all supersaturated with respect to carbonate min- als (Fig. 9). The lower HCO_3 contents in the deep M-89-106 and MM-88-02 waters compared to M-89-102 waters may indicate loss of HCO_3 due carbonate precipitation, consistent with the obser- tion of carbonate in vugs and along some fracture rfaces in the deeper portions of the section (Ley- urne, 1998). Groundwaters are supersaturated with spect to Fe and Al oxides (e.g. goethite, hematite, bbsite) and aluminosilicates (e.g. kaolinite, illite, uscovite/sericite). There is a strong likelihood that uch or all of this supersaturation is an artifact of lloids that are <0.45 μm in size and pass through e filter paper during sample collection. SEM re- lts of suspended and colloidal material trapped on e filter papers (Leybourne, 1998) suggests that any aterial that may have passed the filters would be minated by quartz and aluminosilicates (clays). his result is consistent with studies of colloids in e 20–1000 nm size range from granitic terrains Degueldre et al., 1996). However, at least some the groundwaters, especially at the Restigouche eposit may be saturated with respect to clay miner- s; kaolinite and K-silicates are common in fracture nes and Al oxides have also been observed (Ley- ourne, 1998). The hydrothermal alteration mineral ssemblage of the host rocks at the time of ore for- ation is dominated by chlorite and sericite so that is not clear as to the timing of silicate formation long fractures. The shape of the kaolinite solubility urve with respect to pH (Fig. 9D) is consistent with eoretical Al speciation and Al-mineral solubilities.

At the Restigouche deposit there is a general crease in Na and Cl with depth, reflecting both creased water–rock reactions, cation exchange re- ctions, and mixing with deeper, older saline ground- aters. The general increase in Na and Na/Ca ith depth can in part be explained by reactions f groundwaters with albitic plagioclase feldspars. lagioclase feldspar observed in the BMC is uni- ormly albite in composition (Lentz and Goodfellow, 993). Elevated Na/Ca in the more saline waters may also be related to precipitation of Ca(+ Mg) carbonate, as suggested by the solubility calculations (Fig. 9). There is also elevated K in the high-sulphate waters associated with the main ore zone. It is likely that these waters are influenced by K-rich silicates associated with hydrothermal alteration at the time of ore formation (Lentz and Goodfellow, 1994, 1996). Some of the increase in Na and decrease in Ca with depth is likely due to cation exchange reactions. In addition, the very high sulphate contents of shallow groundwaters interacting with the massive sulphides indicate that they are actively undergoing oxidation. Although base metal contents are high (Table 1) the $\Sigma(Fe + Mn + Zn + Pb + Cu + Co + Cd)$ does not balance the total sulphate contents of these waters. Given that these waters are O_2-rich and oxidizing (Table 1), it is likely that much of the Fe produced by sulphide oxidation is rapidly reprecipitated as Fe-oxides and Fe-oxyhydroxides. The metals Zn, Pb, and Mn have a strong affinity for adsorption onto Fe-oxyhydroxide surfaces (e.g., Coston et al., 1995). These waters are all strongly supersaturated with respect to Fe-oxyhydroxide minerals (e.g. hematite and goethite), consistent with this interpretation.

5.4. Water–rock reactions and controls on Halfmile Lake deposit groundwater chemistry

Principle component analysis of the Halfmile Lake groundwaters shows no clear relationships between different groundwaters recovered from different boreholes due to variable mixing with surface waters, rapid downward penetration of shallow recharge waters along fractures, possible upward gradients in the lower parts of at least some of the boreholes, and perhaps to the greater reliance on bailer samples which reflect mixing within the borehole water column. At the Halfmile Lake deposit, steep structures result in more variable groundwater chemistry between boreholes, whereas at the Restigouche deposit, the structures are more shallow and more conducive to mixing relationships between groundwater flow systems. There are general downhole trends in some cases, reflecting both in-hole mixing due to upward and downward gradients at the bottom and top of these holes, respectively, and due to cation exchange and water–rock reactions with depth (Figs. 6 and 8).

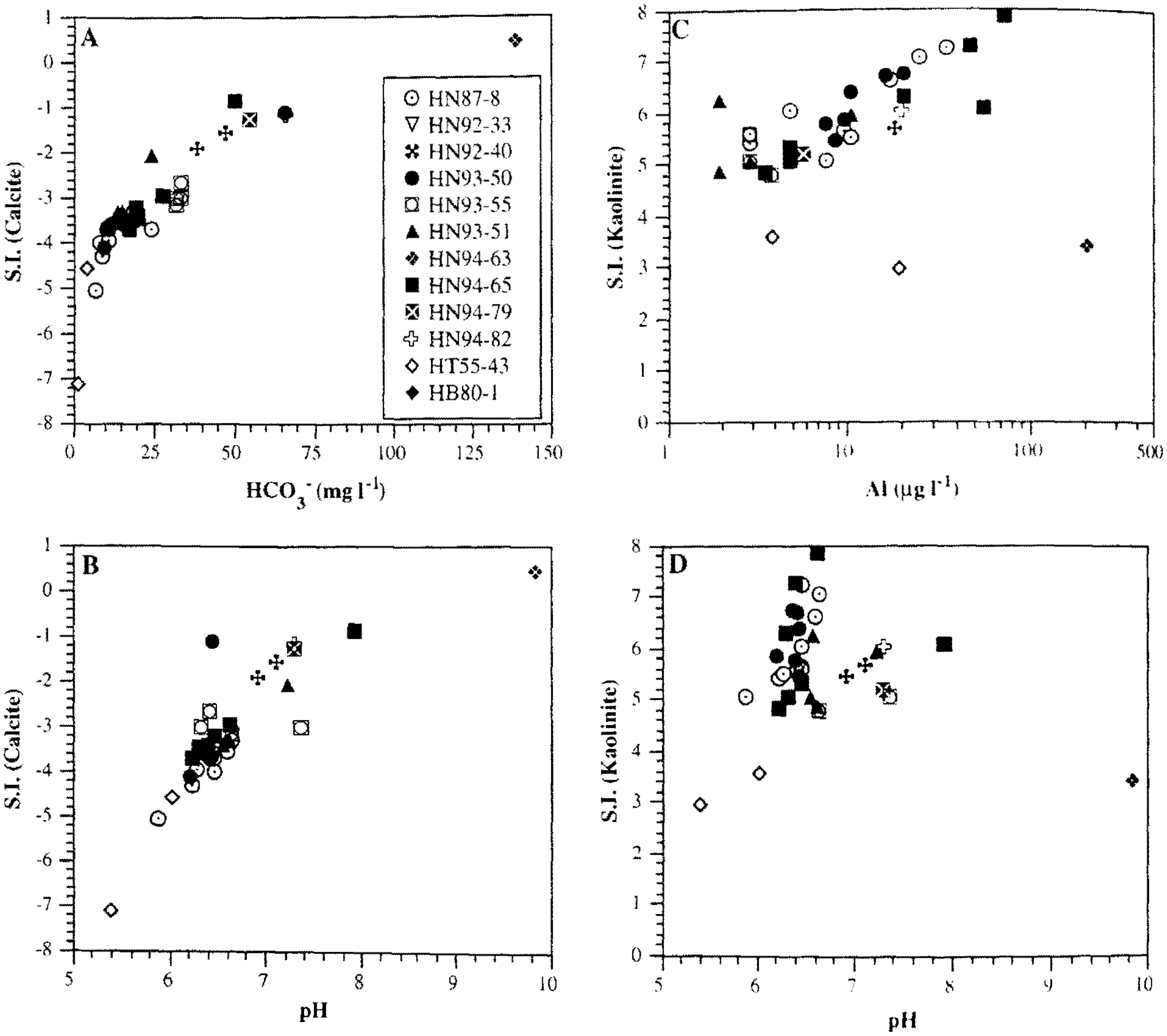


Fig. 10. Saturation index plots for Halfmile Lake deposit groundwaters. SI calculated using the EQ3NR code of Wolery (1992). (A) S.I.$_{\text{calcite}}$ vs HCO$_3$. (B) S.I.$_{\text{calcite}}$ vs pH. (C) S.I.$_{\text{kaolinite}}$ vs Al. (D) S.I.$_{\text{kaolinite}}$ vs pH.

Geochemical modelling of groundwaters from the Halfmile Lake deposit indicates that they are all undersaturated with respect to carbonate minerals with the exception of the groundwaters from borehole HN94-63, which are slightly saturated with respect to both calcite and dolomite (Fig. 10). The general lack of carbonate saturation compared to groundwaters at the Restigouche deposit is a function of both the very low TDS of Halfmile Lake groundwaters and is also probably indicative of the lower carbonate content of the host rock compared to the Restigouche deposit and different hydrology resulting in more rapid and deeper recharge. Groundwaters are typically supersaturated with respect to Fe and Al (hydr)oxides (e.g. goethite, hematite, gibbsite) and aluminosilicates (e.g. kaolinite, illite, muscovite/sericite). As with the Restigouche deposit groundwaters there is a possibility that some or much of this supersaturation is an artifact of colloids that are <0.45 µm in size and pass through the filter paper during sample collection. However, as with the Restigouche groundwaters, the kaolinite saturation and pH relationship is consistent with Al solubility.

Implications for baseline studies

The different groundwater compositions at the lfmile Lake and Restigouche deposits have import implications for baseline studies in the Bathurst ning Camp. For example, groundwaters from llow boreholes intersecting the Restigouche desit have elevated metal contents (up to 1400 μg Pb and 5300 μg l^{-1} Zn), in excess of Canan drinking water standards of 10 and 5000 μg respectively. However, surface waters close to Restigouche deposit have metal contents bev drinking water guidelines (e.g., Fig. 3B). All the und and surface water samples reported here were llected during 1995 and 1996 prior to initiation of en-pit mining at the Restigouche deposit. There therefore, considerable potential for enhanced undwater contribution of metals to the surface vironment due to the disruption in the hydroly caused by mining activities. In addition, upon mpletion of mining operations, the baseline data llected during this study will allow more realistic idelines for reclamation given that metal contents shallow groundwaters proximal to the deposit are turally elevated. At the Halfmile Lake deposit, ound and surface water metal contents are lower an at the Restigouche deposit, as discussed previsly. However, the catchment basin for the Halfmile ke deposit drains directly into the northwest Mimichi River, one of the major salmon rivers in stern Canada. The generally low base metal connts of waters associated with this deposit suggests at disturbance due to mining could more readily rturb the natural metal loads than is the case for e Restigouche deposit. The results of this study ggest that application of a single set of guidenes for the initiation, operation and remediation of ining operations is inappropriate.

Conclusions

The groundwaters at the two studied deposits re very different. Groundwaters at the Halfmile ake deposit are characterized by low-TDS, Ca–CO_3 compositions, and stable isotopic composions which are similar to surface waters. REE in alfmile Lake groundwaters are variable and change with depth suggesting upward gradients in the bottom parts of some boreholes. In contrast, groundwaters at the Restigouche range from shallow Ca–HCO_3 waters to shallow Ca–SO_4 waters and to high-TDS Na–Cl waters with increasing depth. The Restigouche deposit groundwaters show more variable stable isotopic composition with the more saline groundwaters having heavier stable isotopic compositions suggesting that they are much older and were recharged under a different climatic regime. The Halfmile Lake deposit groundwaters are most likely modern meteoric waters rapidly transmitted to depth along steep structures. Any saline groundwaters that may have existed at the Halfmile Lake deposit have been 'flushed' from the system.

The interpretation of the groundwater data at the Restigouche deposit is as follows.

(1) A shallow local recharge system that is dominated by Ca and HCO_3 due to dissolution of carbonate and silicate minerals in the shallow soil and upper parts of the weathered bedrock. There are possibly two end-members here that may reflect different dominant lithologies and different temporal characteristics.

(2) Another shallow groundwater system characterized by oxygenated waters flowing through or along the ore horizon. This water mass is actively oxidizing the ore deposit resulting in elevated SO_4 and base metal contents.

(3) A deeper groundwater flow system characterized by elevated Na and Cl concentrations due to greater water–rock reaction times and elevated HCO_3 due to dissolution of carbonate in the footwall alteration zone to the ore deposit (as in boreholes MM-89-102 and the deeper parts of B-80-7). Finally deeper saline groundwaters occur with no obvious relationships to the shallow groundwater system.

The elevated sulphate and base metal contents of shallow groundwaters recovered from boreholes intersecting the Restigouche deposit indicate that the massive sulphides are undergoing significant oxidation and hydromorphic transport. However, although base metals are elevated in streams flowing across and adjacent to the deposit, there is little evidence for significant contribution of the high-sulphate groundwaters to the surface environment. The lower base metal and sulphate contents of Halfmile Lake groundwaters close to the ore zone is a function of the different hydrology of this deposit and greater depth to the ore body compared to the Restigouche deposit and this is also indicated by more subdued metal anomalies in stream waters at the Halfmile Lake deposit. These results have important implications for baseline studies prior to exploitation of ore deposits in the Bathurst Mining Camp and elsewhere, and to setting water quality limits for the remediation of AMD sites.

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