

Mobility and fractionation of rare earth elements during supergene weathering and gossan formation and chemical modification of massive sulfide gossan

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Abstract

Primary massive sulfide gossans (MSG) in the Bathurst Mining Camp (BMC), New Brunswick, Canada, are characterized by relative enrichment of Au, Sb, and As, formation of jarosite group minerals (jarosite, plumbojarosite, and argentojarosite) and little or no fractionation in the rare earth elements (REE), including preservation of large positive Eu anomalies (average $[Eu/Eu^*]_{NASC} = 4.14$ in MSG; 6.61 in massive sulfide mineralization; 0.60 in host rocks). The chemical and mineralogical characteristics of MSG (e.g., Halfmile Lake deposit) imply low pH (<3) and relatively oxidizing conditions during gossan formation; oxidation of a volcanogenic massive sulfide body (comprising pyrite, pyrrhotite, sphalerite, galena, and chalcopyrite) with a falling water table. The lack of light REE or heavy REE fractionation and preservation of positive Eu anomalies characteristic of the original (465 Ma) hydrothermal fluid is consistent with relatively large water–rock ratios during massive sulfide mineralization oxidation, and removal of the REE predominantly as sulfate complexes ($LnSO_4^+$, $Ln(SO_4)_2^-$). Low pH groundwaters recovered from past producing mines in the BMC display REE patterns reflecting those inferred to have occurred during gossan formation. Gossan at the Restigouche deposit, in contrast to the Halfmile Lake deposit, displays mineralogical and chemical evidence for having been chemically reworked since primary gossan formation. Evidence for chemical reworking includes loss of primary massive sulfide mineralization textures, replacement of plumbojarosite with anglesite, almost complete removal of jarosite minerals, loss of Au, Sb, and As and apparent preferential removal of Eu, resulting in loss of positive Eu anomalies for most samples (average $[Eu/Eu^*]_{NASC} = 1.21$ in the gossan, with many displaying strong negative anomalies; 3.65 in massive sulfide mineralization; 0.54 in host rocks). Based on geochemical modeling, conditions inferred for the chemical reworking of the Restigouche deposit include near neutral conditions and either relatively oxidizing conditions with Eu^{2+} hosted in a preferentially weathered mineral host (possibly through substitution for Pb in plumbojarosite and beudantite) or cycling between reduced and oxidized conditions during gossan reworking.

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1. Introduction

The rare earth elements (REE) have been studied extensively in igneous rocks, as aids to understanding

rock petrogenesis because the REE, although they behave similarly across the series, show systematic fractionation as a function of crystal fractionation, degree of partial melting and source characteristics (e.g., Ayres and Harris, 1997; Kepezhinskas et al., 1997; Hansen and Nielsen, 1999; e.g., Klingenberg and Kushiro, 1996; Leybourne et al., 1997; Kerrich et al., 1999). The REE have also been the focus of research in hydrothermal and ore deposit

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systems, to help constrain conditions of ore formation and footwall hydrothermal alteration (e.g., Michard and Albarède, 1986; Klinkhammer et al., 1994; Mills and Elderfield, 1995; Langmuir et al., 1997; Bau and Dulski, 1999; Peter et al., 2003a). The REE are increasingly being studied in low temperature aqueous systems to better understand fractionation of the REE (especially Eu and Ce, which have variable redox states), as proxies for actinide migration and for understanding weathering processes, especially in acidic environments (Walter et al., 1995; Johannesson et al., 1996a,b; Nesbitt and Markovics, 1997; Gimeno Serrano et al., 2000; Leybourne et al., 2000b; Andersson et al., 2001; Aubert et al., 2001; Worrall and Pearson, 2001; Verplanck et al., 2004; Gammons et al., 2005a,b; Leybourne and Cousens, 2005). However, there have been few studies that have investigated the fate and fractionation of the REE during weathering of massive sulfide mineralization to form gossans (Fe-oxide-rich caps). Massive sulfide mineral oxidation and the resulting transport of metals away from primary mineralization is important in base-line environmental studies (i.e., what constitutes a geochemical background; Maest, 1996) and mineral exploration. Sulfide oxidation has been extensively studied in the laboratory with pure mineral phases (e.g., McKibben and Barnes, 1986; Moses and Herman, 1991; Nicholson and Scharer, 1994; Williamson and Rimstidt, 1994) and mine tailings (e.g., Al et al., 1994; Blowes and Ptacek, 1994; Pratt et al., 1996; Nesbitt and Jambor, 1998; Al et al., 2000; Dill et al., 2002; Jamieson et al., 2005). Despite these previous studies of sulfide oxidation and the resultant acidic conditions, there is still a paucity of understanding of REE behavior under these conditions (Gammons et al., 2003, 2005b; Verplanck et al., 2004).

The presence of well-formed gossan deposits capping many of the massive sulfide deposits in the Bathurst Mining Camp (BMC) is evidence for natural sulfide oxidation in the past (Late Tertiary; Symons et al., 1996). In this paper, we focus on REE patterns of gossans and coexisting massive sulfides to better understand REE fractionation under the conditions of gossan formation/supergene weathering. Both the Halfmile Lake and Restigouche deposits have well-developed gossans overlying massive sulfide mineralization, however, there is strong evidence that the gossan at the Restigouche deposit has been reworked since its formation in the Late Tertiary (Boyle, 2003). Although the REE generally behave similarly under surface conditions, we show here that this gossan reworking may have profound effects on relative REE mobility, in particular Eu.

2. Geological setting

The Halfmile Lake and Restigouche Zn–Pb massive sulfide deposits are located in the BMC, which comprises part of the Miramichi terrane of northern New Brunswick, Canada. Middle Ordovician (465–471 Ma) Tetagouche Group

and California Lake Group rocks host the massive sulfide deposits, and are interpreted to have formed within an ensialic rift basin (van Staal et al., 2003). Details of the regional geology and mineralization in the BMC are described in Goodfellow et al. (2003) and the detailed geology of the Halfmile Lake and Restigouche deposits has also been described elsewhere (Barrie, 1982; Adair, 1992; Gower, 1996; McCutcheon, 1997).

The Halfmile Lake deposit contains approximately 26 Mt of massive sulfide mineralization, is overturned, and dips steeply to the north and northwest. Massive sulfide mineralization is hosted in felsic quartz–porphyry units, felsic pyroclastic rocks and minor felsic flows, and fine-grained volcanoclastic sedimentary rocks of the Nepisiguit Falls Formation. Massive sulfide mineralization locally crops out with a well-developed gossan at the Upper AB zone (Fig. 1A). The stockwork zone ranges from 3 to 150 m in thickness (Adair, 1992). Mineralization occurs as both breccia matrix sulfides and laminated massive sulfides (Table 1) (Adair, 1992).

The Restigouche deposit is hosted by felsic volcanic and associated sedimentary rocks of the Mount Brittain Formation (McCutcheon, 1997). This formation gradationally overlies clastic rocks of the Patrick Brook Formation and is conformably overlain by mafic volcanic and sedimentary rocks (Boucher Brook Formation) (Fig. 1B). Quartz and carbonate veins are common in both footwall and hanging wall units; feldspar veins are developed locally in the footwall. Massive sulfide mineralization crops out on the south side of Charlotte Brook as a small gossan (Fig. 1B).

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, structures are steeply dipping and groundwater chemistry suggests rapid recharge to depth (Leybourne et al., 1998). The Restigouche deposit area is topographically similar to the Halfmile Lake deposit, although relief varies from 200 to 400 m. Soils are thinly developed and till cover is thin, generally less than one meter in thickness. Although groundwater flow is also fracture-dominated at the Restigouche deposit, shallow dipping structures produce a different groundwater hydrogeochemical regime compared to the Halfmile Lake deposit. The gossan at the Halfmile Lake deposit is on a topographic high, whereas, at the Restigouche deposit, the gossan crops out proximal to Charlotte Brook, a west-to-east flowing stream.

3. Methods

Typically, large samples (1–1.5 kg) of gossan were collected owing to the mineralogical and chemical heterogeneity observed. Samples were coarse ground and ball milled for geochemical analysis. In addition, several groundwater samples were collected from two active mines (Heath Steele

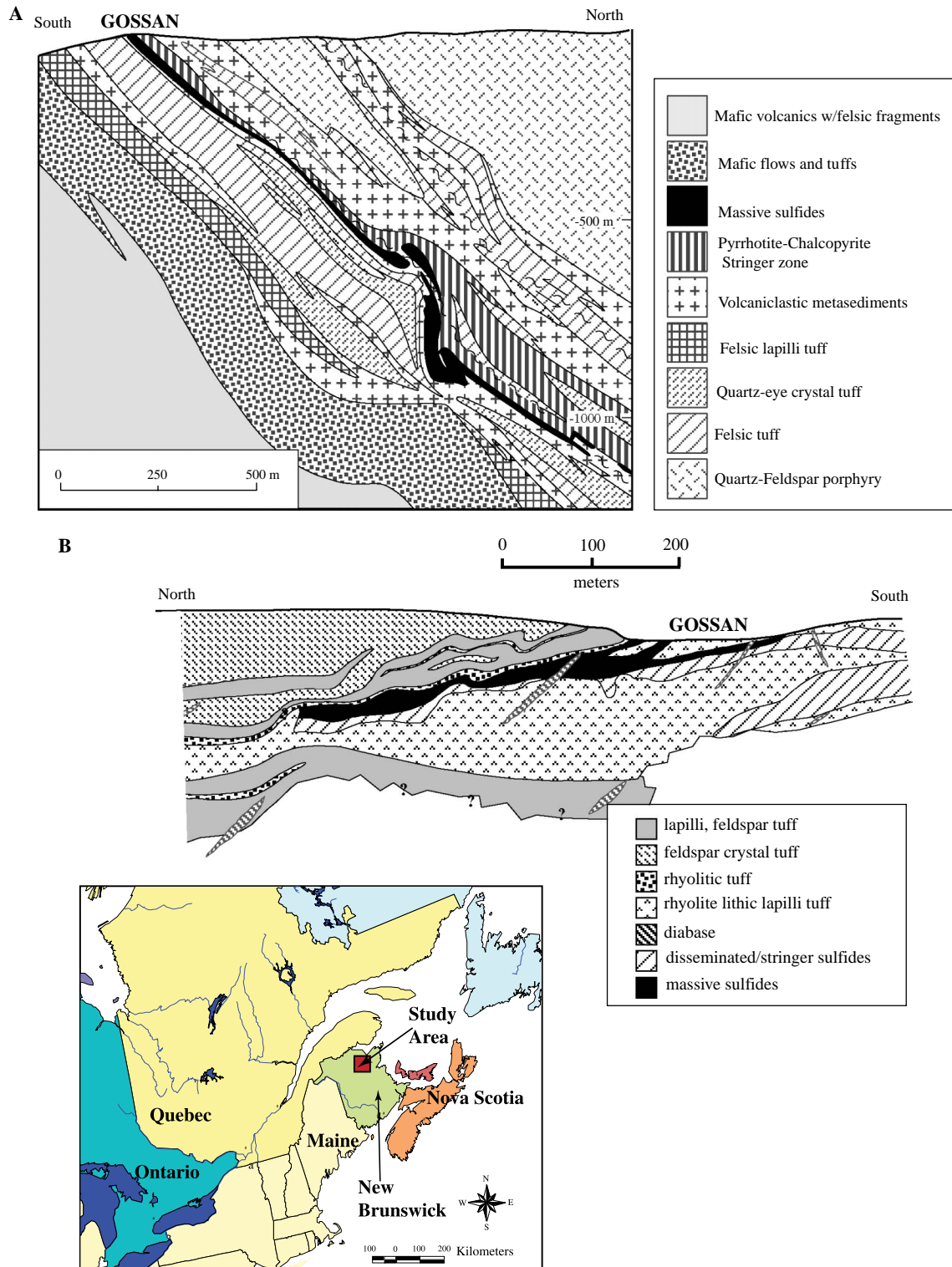


Fig. 1. (A) N-S geological cross-section of the Halfmile Lake deposit, after (Adair, 1992). (B) NW-SE geological cross-section of the Restigouche deposit, after (Barrie, 1982). Note that the Halfmile Lake deposit is overturned, so that the stringer sulfide zone overlies the massive sulfide. Inset shows the location of the study area in northern New Brunswick.

and Brunswick No. 12 deposits), a past producer (Wedge deposit) and two other relatively undisturbed deposits (Willett and Stratmat Main Zone deposits) to compare current aqueous-sulfide interaction with inferred gossan-

forming solutions. Details of groundwater sampling and chemistry (including the REE) have been presented elsewhere (Leybourne et al., 2000b, 2002; Leybourne and Goodfellow, 2003).

Table 1
Summary of gossan and massive sulfide mineralogy for the Halfmile Lake and Restigouche deposits

Rock type	Major minerals	Minor minerals
Halfmile Lake deposit		
Massive sulfides	Breccia = pyrrhotite > chalcopyrite, pyrite, sphalerite, and galena Laminated = pyrite, pyrrhotite, sphalerite, and galena	
Stockwork sulfides	Pyrrhotite, chalcopyrite, and quartz	
Primary massive sulfide gossan	Goethite, silica, jarosite group minerals, and beudantite	Scorodite, barite, bindheimite, cinnabar, native metals (Au, Ag, and Bi), cassiterite, and clay minerals
Gangue	Chlorite, quartz, and carbonate	
Restigouche deposit		
Massive sulfides	Pyrite, sphalerite, and galena	Chalcopyrite, arsenopyrite, and tetrahedrite
Secondary massive sulfide gossan	Anglesite, hematite	Scorodite, barite, bindheimite, cinnabar, native metals (Au, Ag, and Bi), and cassiterite
Gangue	Chlorite, quartz, carbonate, and sericite	

Gossan samples were analyzed for the major oxides by X-ray fluorescence (XRF) on pressed-powder pellets and inductively coupled plasma optical emission spectrometry (ICP-OES). Trace elements and the REE were determined by ICP-mass spectrometry. For ICP-OES and ICP-MS analyses, rocks were taken into solution by multi-acid digestion (HCl–HF–HNO₃–HClO₄), with any residue undergoing lithium metaborate fusion and further acid dissolution. Au was determined by neutron activation (for detailed description of gossan analytical methods, see Boyle, 2003). Representative analyses for the base metals, sulfur, and the REE are presented in electronic annex EA-1 for massive sulfides, gossans and host lithologies. Groundwaters were analyzed by a combination of ICP-OES, ICP-MS with the REE determined by ICP-MS following pre-concentration using the method of Hall et al. (1995). REE data for groundwaters at the Halfmile Lake and Restigouche deposit are given in Leybourne et al. (2000b).

4. Results

4.1. Mineralogy and composition of BMC gossan

BMC Fe-oxide rocks have been classified by Boyle (2003) and include, (1) massive sulfide gossans (MSG), formed in situ by weathering of massive sulfide mineralization, (2) mineralized wall-rock gossans, proximal to MSG, (3) ferricrete, or transported gossan, including glacial and stream sediment cemented by Fe-oxides, and (4) ironstones, or weathered and oxidized Fe-rich rocks, such as mafic volcanic rocks and pyritic shales. Massive sulfide gossans in the BMC generally overlie supergene sulfide zones, which overlie primary massive sulfide mineralization. BMC supergene sulfide zones are composed of pyrite–quartz sand layers overlying supergene-enriched copper zones, which have gradational contacts with unweathered massive sulfide mineralization (Boyle, 2003). The pyrite–quartz lenses are interpreted to have formed by post-glacial oxidation of the altered massive sulfide zone; present-day water tables coin-

cide with these lenses (Boyle, 2003). Secondary or reworked gossans are present at the Restigouche and Brunswick #6 deposits and are interpreted to represent in situ primary massive sulfide gossan that have been reworked by later groundwaters (Boyle, 2003).

Detailed descriptions of the mineralogical and bulk geochemical compositions of gossans and primary massive sulfide samples have been presented elsewhere (Boyle, 1994, 1995, 2003; de Roo and van Staal, 2003; Goodfellow and McCutcheon, 2003) and are summarized in Table 1.

Boyle (2003) concluded, based on textural analysis and the strain equation of Brimhall and Dietrich (1987), that BMC gossans are essentially undeformed and are isovolumetric with precursor massive sulfide mineralization. Boyle (1995) showed that for the Murray Brook massive sulfide gossan, there was no difference in mass-balance calculations of element loss or gain based on detailed porosity and density determinations compared to those based on Sn as the most conservative element during gossanization. Sn is primarily present in massive sulfide mineralization and gossans as cassiterite, and as such is very stable even during the conditions of gossan formation. Thus, Boyle (2003) calculated percent mass loss/gain factors for all the gossan deposits in the BMC using conservative Sn, using the following equation:

$$\% \text{gain/loss} = \frac{\left[\left(C_{\text{Em G}} \times \frac{C_{\text{Snm MS}}}{C_{\text{Snm G}}} \right) - C_{\text{Em MS}} \right]}{C_{\text{Em MS}}} \times 100,$$

where, S_{nm} and E_m are the mean concentrations in gossan (G) and massive sulfide (MS) of Sn and the element (E) of interest. Mass-balance adjustment factors range from 0.18 to 0.57 for all the gossans in the BMC, with the Halfmile Lake deposit gossan at 0.36 and the Restigouche deposit gossan at 0.18 (Boyle, 2003).

Compared to massive sulfide mineralization from the same deposit, Halfmile Lake deposit gossans have similar Pb and Cu contents, but significantly lower Zn contents

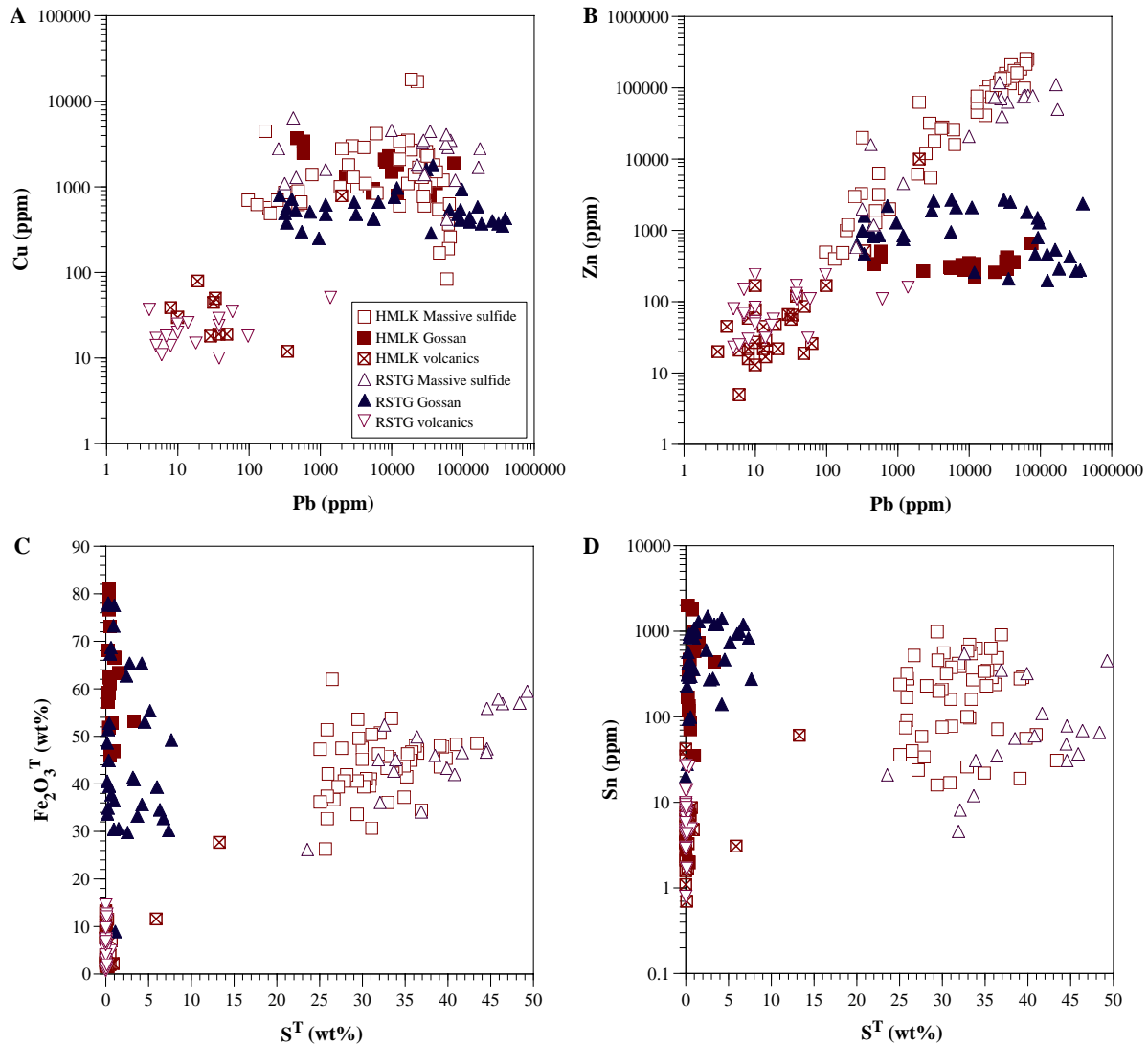


Fig. 2. Plots of (A) Cu versus Pb, (B) Zn versus Pb, (C) $\text{Fe}_2\text{O}_3^{\text{T}}$ versus total S, and (D) Sn versus total S, for Halfmile Lake (HMLK) and Restigouche (RSTG) deposit massive sulfides, gossans, and host lithologies. Note that gossan values have not been adjusted for loss/gain.

(not adjusted for loss/gain; Fig. 2). Sulfur is almost entirely removed from the system during gossan formation, other than S resident in jarosite minerals (Halfmile Lake deposit), anglesite (Restigouche deposit) and trace cinnabar, whereas Fe contents remain high with respect to primary massive sulfide samples (Fig. 2). The Restigouche deposit differs from the Halfmile Lake deposit in that Cu is generally lower in the former relative to the coexisting sulfides (Fig. 2).

4.2. REE in massive sulfides

Massive sulfide mineralization at the Halfmile Lake deposit has generally flat North American Shale Composite (NASC)-normalized REE patterns, with all REE less than NASC values (Fig. 3). Cerium anomalies are lacking ($[\text{Ce}/\text{Ce}^*]_{\text{NASC}} = 0.80$ to 1.04, average = 0.92), although most massive sulfide samples in this study possess large po-

sitive Eu anomalies ($[\text{Eu}/\text{Eu}^*]_{\text{NASC}} = 0.93$ to 27.6, average = 6.61, $n = 50$) (Figs. 3 and 4).

Massive sulfide mineralization at the Restigouche deposit shows broadly similar REE patterns, although REE contents are generally lower than at the Halfmile Lake deposit (Figs. 3–5). Most massive sulfide analyses possess positive Eu anomalies; $[\text{Eu}/\text{Eu}^*]_{\text{NASC}}$ ranges from 0.53 to 11.34, average = 3.65, $n = 16$ (Fig. 6). Massive sulfide mineralization at the Restigouche deposit has slightly more negative Ce anomalies than the Halfmile Lake deposit with $[\text{Ce}/\text{Ce}^*]_{\text{NASC}}$ ranging from 0.73 to 0.97, average = 0.89 (Figs. 4 and 5).

4.3. REE in primary gossan at the Halfmile Lake deposit

Gossan samples at the Halfmile Lake deposit generally have flat NASC-normalized REE patterns with positive Eu anomalies, and are remarkably similar to

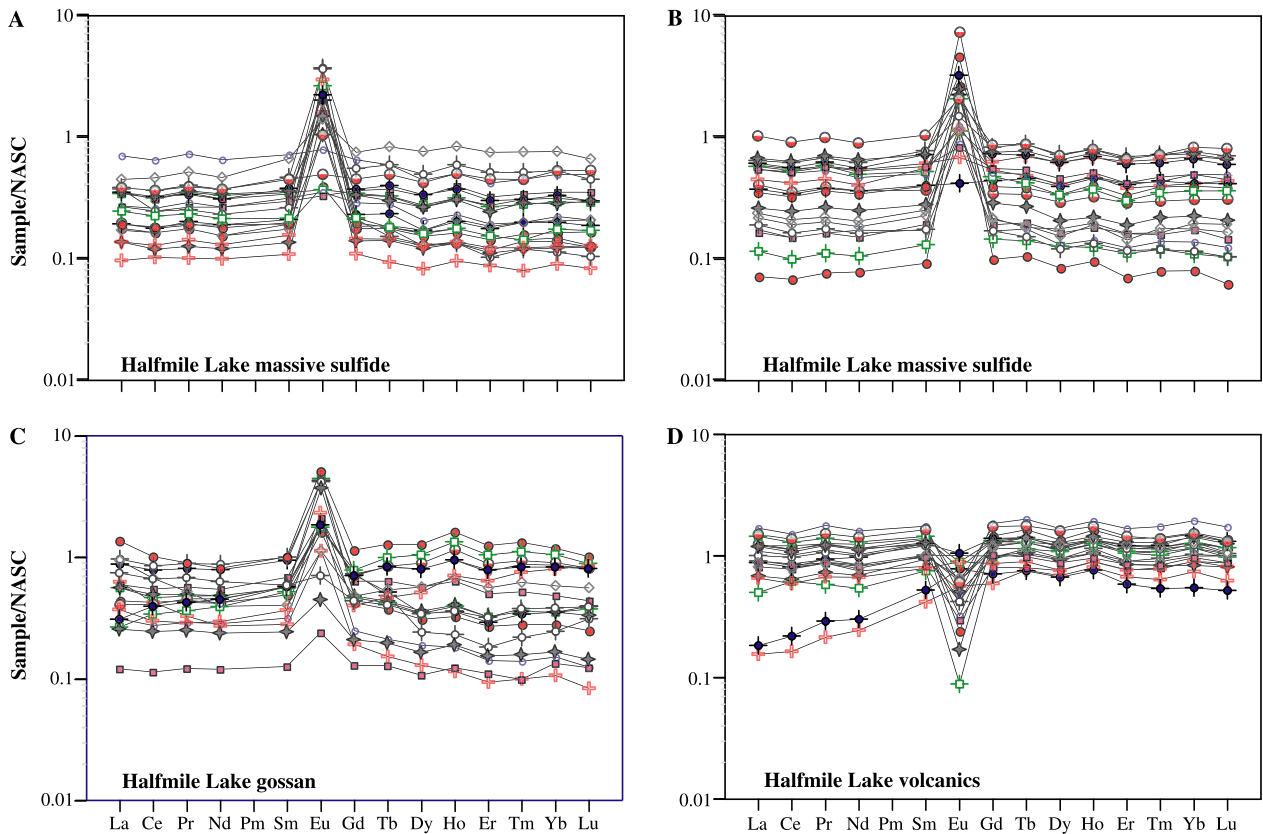


Fig. 3. REE plots of massive sulfides (A and B), gossans (C) and host volcanic lithologies (D) from the Halfmile Lake deposit, normalized to North American Shale Composite (NASC; Gromet et al., 1984). Note that gossan values have not been adjusted for loss/gain.

underlying massive sulfide mineralization (Fig. 3). Halfmile Lake deposit gossans have REE patterns that are generally little fractionated compared to underlying massive sulfide mineralization (Fig. 6), with most MSG overlapping massive sulfide mineralization in light REE (LREE) and heavy REE (HREE) enrichment or depletion (i.e., similar $[La/Sm]_{NASC}$ and $[Gd/Yb]_{NASC}$; Fig. 4D).

Using the method of Boyle (2003) to calculate the percent loss or gain of species during supergene oxidation of massive sulfide mineralization to form gossan, we calculate relative loss and gain for the REE in Halfmile Lake deposit and Restigouche deposit gossans. For the Halfmile Lake deposit, element loss percentages are uniform across the REE (Fig. 7), ranging from -40.6% to -54.7% . Compared to average massive sulfide mineralization at the Halfmile Lake deposit, gossans have flat to slightly HREE-enriched and HREE-depleted profiles. Both small positive and small negative Eu anomalies are present (Fig. 7).

4.4. REE in secondary (reworked) gossan at the Restigouche deposit

Gossans at the Restigouche deposit generally have flat NASC-normalized REE patterns, similar to those at the Halfmile Lake deposit, although Restigouche gossans typ-

ically have minor to large negative Eu anomalies compared to underlying massive sulfide mineralization (Figs. 4 and 5). Although Restigouche deposit gossans have REE patterns that are generally less fractionated compared to underlying massive sulfide mineralization (Fig. 6), they trend to more heavily fractionated HREE compared to underlying sulfides and Halfmile Lake deposit gossans (i.e., higher $[Gd/Yb]_{NASC}$; Fig. 4D). Compared to average massive sulfide at the Restigouche deposit, gossans have flat to very HREE-depleted profiles, and many profiles display a subtle convex-up shape (Fig. 6). Unlike the Halfmile Lake deposit gossan samples, no gossan samples from the Restigouche deposit show positive Eu anomalies compared to average massive sulfide. Restigouche deposit gossans have generally lower $[Eu/Eu^*]_{NASC}$ for given Au, Sn (Fig. 4), Sb, and As (not shown) contents compared to underlying massive sulfide mineralization, and lower $[Eu/Eu^*]_{NASC}$ ratios than Halfmile Lake deposit primary gossan.

Using the method of Boyle (2003) we calculated the relative loss and gain of the REE in Restigouche deposit gossan during supergene oxidation of massive sulfide mineralization to form gossan. In contrast to the primary gossans at the Halfmile Lake deposit, Restigouche deposit gossan samples show a wider range in relative REE loss, from -40% to -91.6% . Maximum REE loss in Restigouche deposit gossan is Eu (-91.6%) and the HREE show

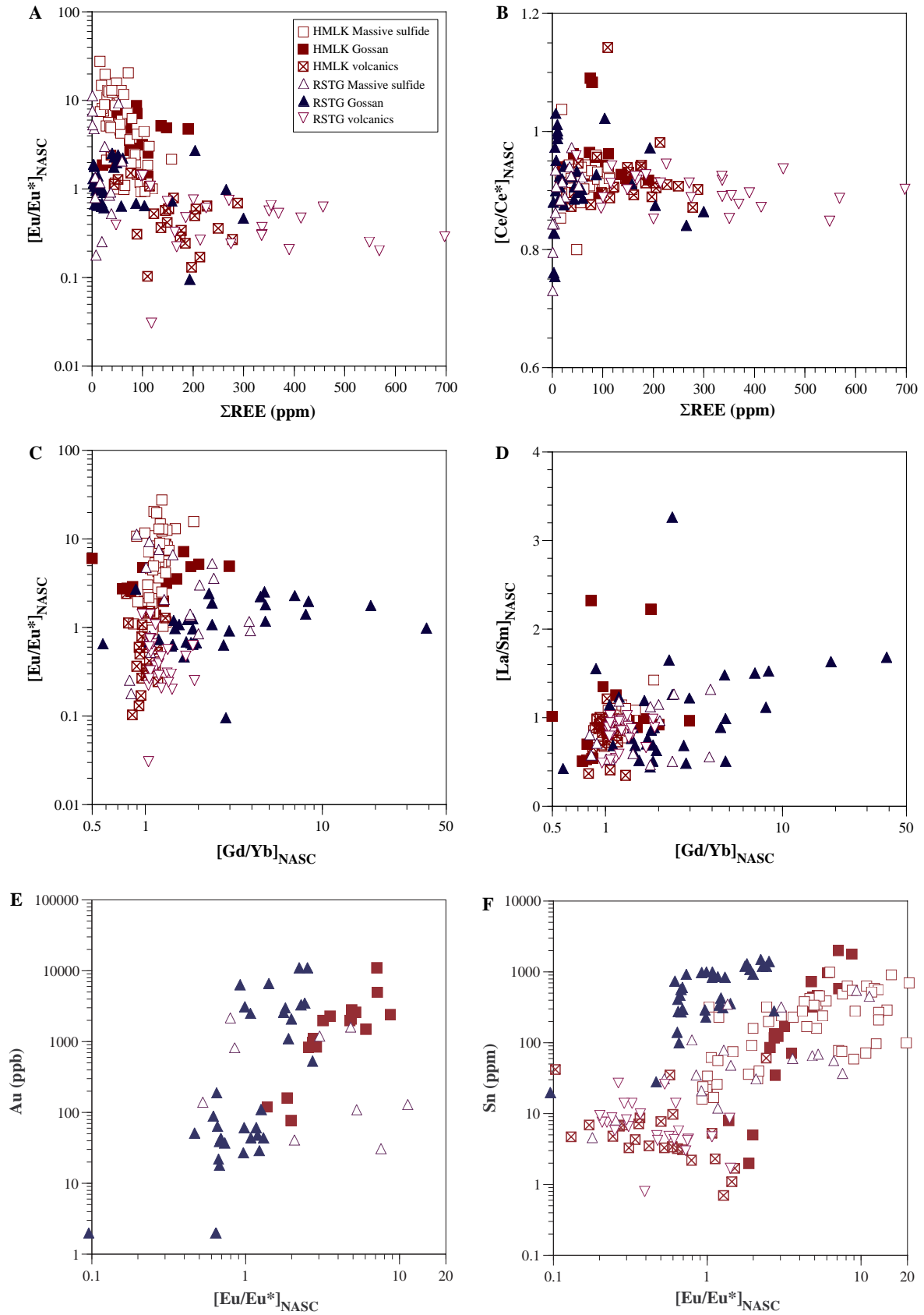


Fig. 4. Plots of (A) $[\text{Eu}/\text{Eu}^*]_{\text{NASC}}$ versus ΣREE , (B) $[\text{Ce}/\text{Ce}^*]_{\text{NASC}}$ versus ΣREE , (C) $[\text{Eu}/\text{Eu}^*]_{\text{NASC}}$ versus $[\text{Gd}/\text{Yb}]_{\text{NASC}}$, (D) $[\text{La}/\text{Sm}]_{\text{NASC}}$ versus $[\text{Gd}/\text{Yb}]_{\text{NASC}}$, (E) $[\text{Eu}/\text{Eu}^*]_{\text{NASC}}$ versus Au, and (F) $[\text{Eu}/\text{Eu}^*]_{\text{NASC}}$ versus Sn for massive sulfides, gossans, felsic, and mafic volcanics from the Halfmile Lake (HMLK) and Restigouche (RSTG) deposits. Note that gossan values have not been adjusted for loss/gain.

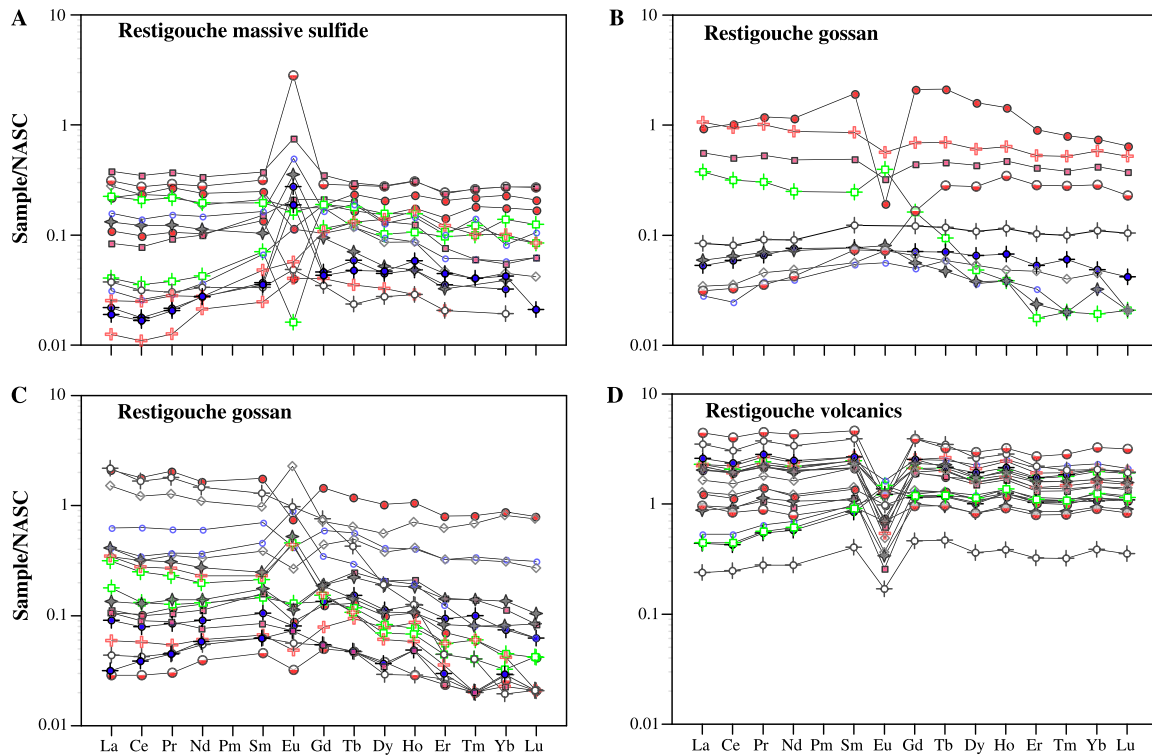


Fig. 5. REE plots of massive sulfides (A), gossans (B and C), and host volcanic lithologies (D) from the Restigouche deposit, normalized to North American Shale Composite (NAS; Gromet et al., 1984). Note that gossan values have not been adjusted for loss/gain.

greater loss (Gd = −79.8%, Lu −90.1%) than the LREE (La = −40%, Sm = −76.8%; Fig. 7). Note the very different calculated percent loss for La compared to the rest of the REE.

4.5. REE in groundwaters

The REE in groundwaters from the Halfmile Lake and Restigouche deposits have been discussed in detail elsewhere (Leybourne et al., 2000b; Leybourne and Cousens, 2005). However, for comparison with massive sulfide mineralization, primary and reworked gossans, REE patterns for three groundwaters from current and past producing mines in the BMC are presented (Fig. 8). Groundwaters from the Heath Steele and Wedge deposits are characterized by elevated REE contents, up to 690,000 ng/L. Mine waters are variable, with $[La/Sm]_{NASC}$ varying from 0.23 to 2.05 with an average of 0.67. The $[Gd/Yb]_{NASC}$ varies from 0.61 to 3.97 with an average of 1.51. Several waters adjacent to the main ore zone at the Heath Steele mine have strong positive Eu anomalies, similar to anomalies for BMC massive sulfide mineralization (Figs. 3, 5, and 8). REE-speciation calculations were performed on the mine waters (Leybourne et al., 2000b). Pertinent features of the speciation calculations include; (1) low pH waters from the Wedge and Heath Steele deposits (field pH values <3) are almost entirely complexed by sulfate ($LnSO_4^+$; where Ln is any REE; Fig. 8), (2) at higher pH, carbonate, Ln^{3+}

and, in some cases, phosphate, complexes dominate (Fig. 8).

5. Discussion

5.1. Formation of primary massive sulfide gossan in the BMC

Based on paleomagnetic studies, Symons et al. (1996) suggested that the BMC gossans began forming between 1.05 and 2.3 Ma. This relatively young age for the BMC gossans is supported by the abundance of jarosite group minerals in these deposits (Table 1), which are unstable under current pH conditions, as well as relatively minor dehydration of goethite to hematite (Boyle, 2003).

Boyle (2003) has characterized the sequence of formation of primary gossan by oxidation of the VMS deposits in the BMC in the following manner. Oxygenated groundwater infiltrates the upper portions of massive sulfide mineralization underlying the gossan zone, resulting in the oxidation of sulfide minerals, dissolution of vein and gangue carbonate minerals (primarily siderite, ferroan dolomite, and calcite), and downward movement of Cu- and SO_4 -rich solutions into lower parts of the profile. Lower in the profile, conditions are reducing, and Cu is removed from solution as secondary Cu-sulfides, which replace primary sulfides, principally chalcopyrite, sphalerite and galena, with covellite, digenite, and chalcocite. During this process Zn and sulfate are largely removed in solution

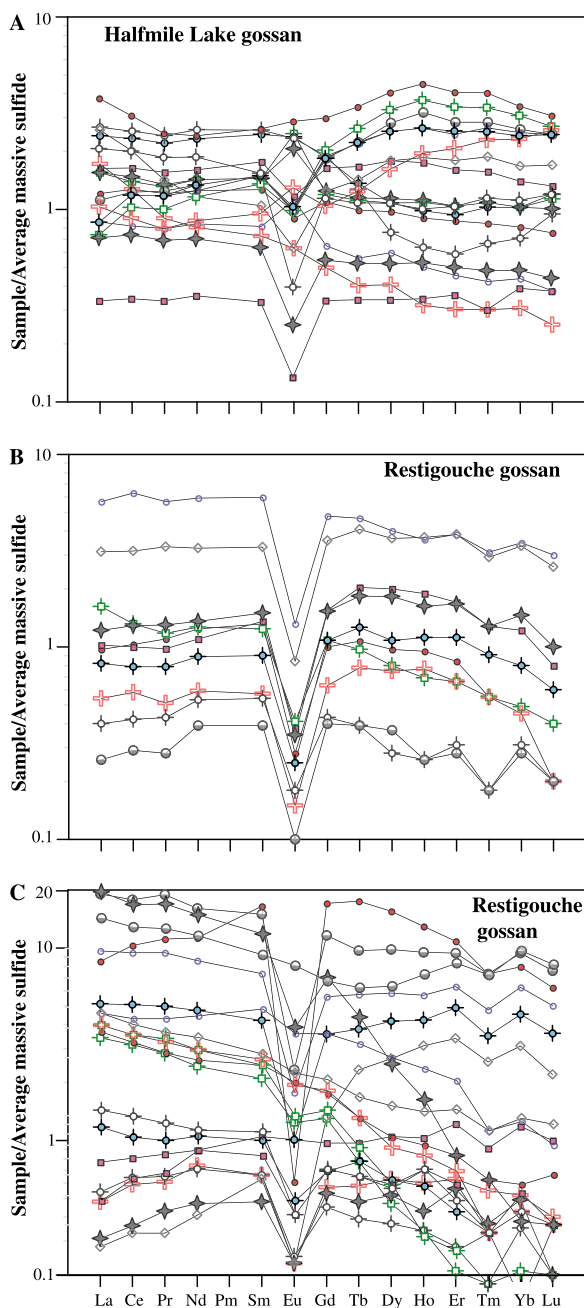


Fig. 6. REE plots of Halfmile Lake (A) and Restigouche (B and C) deposit gossans relative to average massive sulfide from each deposit. Note the difference in Eu anomaly for the two deposits.

(e.g., Fig. 2), whereas Pb commonly forms secondary sulfate minerals such as anglesite and plumbojarosite. Although Pb/Zn ratios increase in the gossans over primary massive sulfide mineralization, Pb is generally lost from the system (Boyle, 2003). For example, at the Murray Brook deposit, Boyle (2003) calculated that about 99% of the Zn, 90% of the Cu, and 36% of the Pb, on average, was lost during the formation of the massive sulfide gossan. In contrast, Au is enriched (+295%), as is As (+65%) and Sb (+50%) (relative to Sn). At the Halfmile Lake deposit, Boyle (2003) calculated losses of 99%,

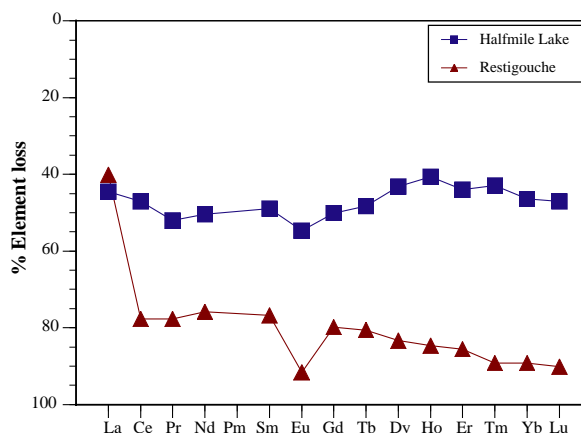


Fig. 7. Percent element loss plot showing relative loss of the REE in average gossan compared to average massive sulfide for the Halfmile Lake and Restigouche deposits. Note the relatively high loss of Eu in the Restigouche gossan compared to average gossan from the Halfmile Lake deposit. See text for calculation of percent loss.

47%, and 75% for Zn, Cu, and Pb, respectively, and gains of 141%, 612%, and 54% for Au, As, and Sb, respectively. However, in the reworked gossan at the Restigouche deposit, losses of 99%, 97%, and 97% for Zn, Cu, and Pb, and losses of 98%, 91%, and 90% for Au, As, and Sb, were calculated (Boyle, 2003).

As weathering proceeds, secondary Cu-sulfide minerals are progressively dissolved, leading to increased porosity (Sato and Mooney, 1960). As a result of this increased porosity, oxygenated groundwater/rock ratios increase, in turn driving greater oxidation of galena and sphalerite, followed by arsenopyrite and pyrite. Oxidation of the Fe (and As) sulfides lowers the pH and produces higher concentrations of the strong oxidizer ferric sulfate, promoting dissolution of remaining sulfides (except cinnabar and cassiterite). Sulfide minerals possess an electrochemical potential values that accentuates these chemical changes (Blain and Brotherton, 1975). Grain contacts with large potential differences promote dissolution of the mineral with the lower potential e.g., pyrite ($\sim +0.18$ V) in contact with sphalerite (~ -0.2 to -0.4 V) enhances the oxidation of sphalerite. Most sulfide minerals undergo preferential weathering in the presence of significant amounts of pyrrhotite (Goodfellow and McCutcheon, 2003; Peter et al., 2003b).

5.2. REE fractionation and mobility during primary gossan formation

In the primary massive sulfide mineralization the REE likely occur primarily in the gangue minerals, consistent with the inverse correlation between REE abundance and sulfur content for Halfmile Lake deposit and Restigouche deposit massive sulfide samples. Studies of modern hydrothermal fluids have shown that high temperature black-smoker fluids, inferred to be analogs for fluids that formed

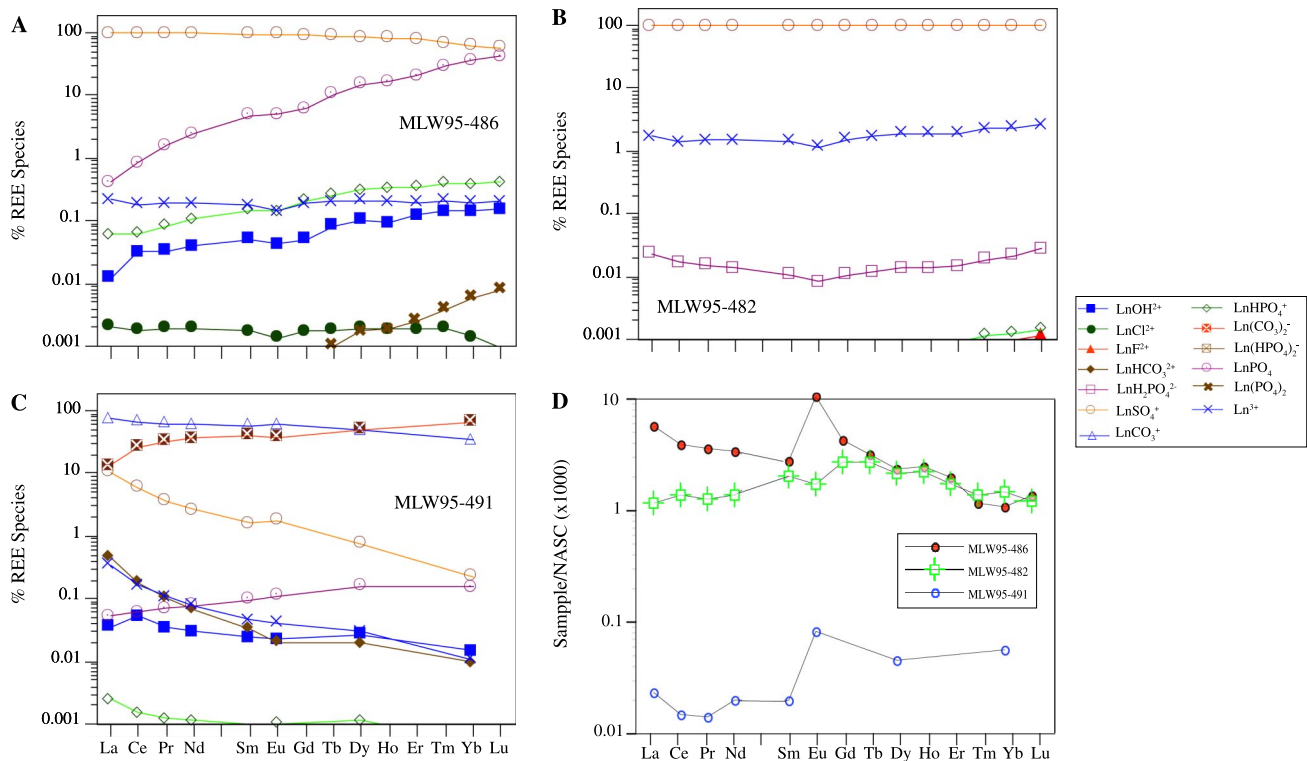


Fig. 8. Speciation of REE for selected groundwaters from the Heath Steele and Wedge deposits. (A) Low pH groundwater from the Heath Steele mine, (B) low pH groundwater from the Wedge deposit, (C) neutral pH groundwater from the Heath Steele mine. Speciation details and data from (Leybourne et al., 2000b). Speciation calculations were based on calculated contents of the major inorganic free (uncomplexed) ligands (OH^- , F^- , Cl^- , HCO_3^- , CO_3^{2-} , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , SO_4^{2-}), as determined by PHREEQC, using the WATEQ4F thermodynamic database (Ball and Nordstrom, 1991; Parkhurst, 1995). Stability constants for the REE species were taken from Millero (1992) except those for carbonate species, which were taken from Lee and Byrne (1993) and phosphate, which were taken from Byrne and Liu (1996). (D) NASC-normalized REE plots for the groundwaters shown above.

the massive sulfide mineralization in the BMC, are characterized by generally flat REE patterns and strong positive Eu anomalies compared to NASC (Klinkhammer et al., 1983; German et al., 1990; Klinkhammer et al., 1994; Bau and Dulski, 1999).

Previous work has shown that the BMC gossans formed during the Late Tertiary under conditions of a falling water table (Boyle, 1995; Symons et al., 1996). As described above, oxidation of massive sulfide minerals (especially Fe-sulfides) resulted in low pH conditions, as shown by the occurrence of jarosite group minerals in the gossans (jarosite, plumbojarosite, and argentojarosite). By analogy with low pH waters we have collected interacting with the Heath Steele and Wedge deposits (Fig. 8), we expect (and model) that under these oxidizing low pH conditions the REE would be primarily speciated as sulfate complexes (Fig. 8). Under these conditions, there would be little fractionation of the REE from La to Lu, consistent with the generally similar shapes of REE profiles for massive sulfide mineralization and concurrent massive sulfide gossans.

Limited LREE or HREE fractionation suggests that the REE were complexed mainly by sulfate during gossan formation, consistent with low pH waters in contact with in situ (Heath Steele) and tailings (Wedge) sulfides in the BMC (Fig. 8). Stability constants for LnSO_4^+ and $\text{Ln}(\text{SO}_4)_2^-$ are relatively uniform from La to Lu, so that lit-

tle or no fractionation of the REE would be expected where they are dominantly complexed by sulfate (Wood, 1990). The lack of negative Ce anomalies is also consistent with low pH conditions during gossan formation as Ce^{4+} is unstable below $\sim\text{pH}$ 4 and 5 (Brookins, 1989). In contrast, lateritic profiles commonly display negative Ce anomalies in the upper most-weathered portions and positive Ce anomalies reflecting Ce^{4+} accumulation in the upper saprolite beneath the ferruginous horizons (Braun et al., 1998). Comparison of the low pH waters collected from the Heath Steele and Wedge deposits is consistent with the interpretation that oxidizing, low pH fluids result in little fractionation of the REE owing to strong sulfate complexation. Waters at neutral pH commonly display middle REE enrichment (Johannesson et al., 1996b), and alkaline waters commonly display strong HREE fractionation with strong LREE depletion as a result of complexation of the HREE by CO_3^{2-} (Johannesson and Lyons, 1994). Some studies have shown preferential enrichment of the middle REE (MREE) in acidic waters owing to acid leaching of Fe- and Mn-oxides and oxyhydroxides that are MREE-enriched (Johannesson and Lyons, 1995; Johannesson and Zhou, 1999). Weathering of massive sulfide mineralization at low pH would not produce MREE-enrichment, as there is no mechanism to preferentially enrich the MREE in the host rock. In addition, REE in other acidic environments

have been modeled as being speciated by both sulfate and as free Ln^{3+} , whereas modeling of the low pH waters in the BMC (Wedge and Heath Steele deposits) suggest complexation almost exclusively by sulfate (Fig. 8). Thus, although MREE enrichment may occur owing to preferential adsorption onto Fe-oxides during gossanization, the activity of free sulfate was sufficiently high such that the REE were essentially 100% in solution as sulfate complexes, so that no preferential adsorption took place.

Gammons et al. (2003) studied the REE contents of an acidic mine pit lake in Butte, Montana (pH = 2.3–2.6). Here, REE contents are elevated and although pit waters show LREE depletion, suggesting MREE-enrichment, there is no corresponding HREE depletion. Gammons et al. (2003) suggested that if sufficiently low water–rock ratios are inferred, the preferential loss of the LREE can be modeled as a function of adsorption/coprecipitation with ferric precipitates. Thus, the lack of significant (or consistent) fractionation of the REE during primary gossan formation in the BMC suggests combined integrated high water–rock ratios and elevated free sulfate activity, consistent with the formation scheme described by Boyle (2003).

5.3. Chemical reworking of massive sulfide gossan

Boyle (2003) briefly discussed the physical and chemical evidence for chemical reworking of the gossan at the Restigouche deposit. Physical evidence includes: (1) lack of jarosite group minerals in the reworked gossans, whereas jarosite minerals are common constituents of all other massive sulfide gossans in the BMC, (2) occurrence of massive aggregates of crystalline anglesite on fracture surfaces and infilling pore spaces in gossan at the Restigouche deposit, (3) lack of preservation of primary sulfide structures and textures, unlike other massive sulfide gossans in the BMC, (4) presence of late-stage botryoidal goethite, and (5) greater porosity compared to the other MSG's in the BMC. Chemical evidence for reworking includes overall loss of species such as Au, As, and Sb at the Restigouche deposit, whereas, in the other massive sulfide gossans these elements typically show a mass enrichment as a result of primary massive sulfide gossan formation (Boyle, 2003). The Restigouche gossans are unlikely to be groundwater-transported Fe-oxide deposits (hydromorphic gossan in the parlance of Boyle, 2003) because of the generally elevated Pb contents; hydromorphic gossans do not have high Pb owing to its relative immobility, even during the low pH conditions of gossan formation. In addition, the foundational work of Dan Boyle on the gossans in the BMC indicates that the most immobile element during gossan formation was Sn, hence the basis of using this element to determine chemical losses and gains during supergene weathering. Because it is so immobile, Sn is also not present in abundance in hydromorphic gossans in the BMC. At the Restigouche deposit, Sn varies from 94 to 1200 ppm, with a mean of 599 ppm and a geometric mean of

481 ppm (Boyle, 2003). These numbers compare well to the Halfmile Lake deposit, with values of 118–2010, mean = 665 ppm, and geometric = 468 ppm, especially given that average Sn contents of the massive sulfides in the BMC appear to increase with increasing tonnage of the Zn–Pb portions of these deposits (Boyle, unpublished data).

Differences in behavior of Au during gossan formation and chemical reworking may also be explained by appealing to Eh–pH conditions. Widler and Seward (2002) showed experimentally that Au is strongly adsorbed (essentially 100%) to Fe-sulfide surfaces at low pH (generally ≤ 5.5 at 25 °C for pyrite and ≤ 4 for pyrrhotite and mackinawite $[(\text{Fe},\text{Ni})\text{S}_{0.9}]$), whereas as pH increases above 5, Au sorption decreases. Thus, the preferential enrichment of Au during primary gossan formation may relate, at least in part, to adsorption of Au onto secondary sulfides formed during supergene weathering. However, if pH conditions were closer to neutral during chemical reworking, Au might more readily be removed from the system as a result of being less strongly adsorbed. In addition, given the presence of primary sulfide mineralization below the reworked gossan, Au mobility at near neutral conditions and further sulfide oxidation would also be enhanced by complexation with thiosulfate (Benedetti and Boulègue, 1991). The Halfmile Lake deposit gossan has a preferential increase in Au relative to Pb. In contrast, the Restigouche deposit gossan has similar to lower Au values than massive sulfide mineralization, relative to Pb abundances. Loss of Au during chemical reworking is most likely to have occurred via Au-thiosulfate complexing, implying neutral to alkaline, oxidizing conditions. Although Cl^- may have been present given the presence of saline waters below the Restigouche deposit (Leybourne and Goodfellow, 2003), the presence of sulfide minerals in close proximity to the gossan suggests that thiosulfate is a more probable complexing agent for Au (and Sb) during chemical reworking.

5.4. Origin of Eu depletion in Restigouche deposit gossan

There are two possible explanations for the presence of positive Eu anomalies in the Halfmile Lake deposit gossans and its absence from those at the Restigouche deposit: (1) the gossans analyzed were formed from massive sulfide mineralization that did not possess positive Eu anomalies, and (2) Eu has been preferentially removed compared to the rest of the REE during chemical reworking of the Restigouche deposit gossan.

The first explanation is consistent with the fact that the Brunswick #6 deposit also possesses a reworked gossan, although the gossan retain a positive Eu anomaly (Boyle, unpublished data). However, consideration of the Au, As, and Sb data (tabulated in Boyle, 2003) suggests that gossan at the Brunswick #6 deposit was not as extensively reworked as gossan at the Restigouche deposit. Thus, although the first explanation is possible, and the apparent loss of Eu in the Restigouche deposit gossan is a sampling

artifact, as discussed below, the geochemical data are more consistent with a model in which Eu was preferentially removed from the Restigouche deposit gossan during chemical reworking.

The second explanation is attractive given that at the Halfmile Lake deposit, gossans retain the positive Eu anomaly of massive sulfide mineralization, whereas, Restigouche deposit gossans generally do not (Figs. 3 and 5). At the Restigouche deposit, loss of jarosite minerals and Au (and related species) suggests near neutral conditions existed during chemical reworking/modification, compared to pH values <3.0 for the Halfmile Lake deposit gossan. The presence of crystalline anglesite in association with botryoidal goethite after reworking is explained by pH values greater than 3.0, following breakdown of plumbojarosite via the reaction (Boyle, 2003):



If conditions during this chemical reworking were reducing, Eu^{2+} could be preferentially mobilized, whereas the other REE, including Ce, in the 3+ state were preferentially retained in the gossan.

Additional geochemical evidence in support of preferential loss of Eu during chemical reworking is the relationship between the Eu anomaly and key gossan-related elements. Boyle (2003) suggested that during gossan formation in the BMC, Au, Sb, and As are generally moderately to strongly enriched in the gossans relative to Sn. This preferential Au enrichment has made the gossans attractive for exploration, including mining of the Murray Brook deposit for Au by cyanide vat-leach from 1989 to 1992 (Rennick and Burton, 1992; Boyle, 1995; Leybourne et al., 2000a). For the Restigouche deposit gossans, there are statistically significant correlations between the magnitude of the Eu anomaly and As, Sb (not shown), and Au values (Fig. 6), suggesting that loss of Au, As, and Sb occurred concurrently with preferential loss of Eu.

Aubert et al. (2001) presented REE data for soil waters, stream waters, and suspended sediments derived from weathered granite. Granite-normalized REE patterns for these media show small positive Eu anomalies (Eu/Eu^* up to 1.8), consistent with preferential mobility of Eu compared to the other REE. In contrast, low pH (2.8–4.0) acid-sulfate springs from Yellowstone show essentially flat host-rock normalized REE patterns, although Eu is also preferentially enriched, suggesting dissolution of feldspar (Lewis et al., 1997).

Based on the work of Sverjensky (1984), at typical surface conditions, Eu^{2+} is only stable at very low redox conditions and alkaline pH. At elevated temperature (>250 °C) essentially all of the europium present would be in the reduced state (Sverjensky, 1984; Douville et al., 1999). At 100 °C, Eu^{2+} could be stable in the presence of sulfate and Fe^{3+} for a narrow range of Eh and pH conditions (Sverjensky, 1984). Assuming that primary gossan initially formed at the Restigouche deposit displayed similar REE

changes as at other gossans in the BMC (essentially uniform mass loss of all the REE, with little or no fractionation), but that Eu was preferentially lost during chemical reworking of the Restigouche deposit gossan, we can place some constraints on the Eh–pH conditions of reworking. pH conditions were presumably sufficiently acidic that there was no formation of secondary carbonates. In addition, during gossan reworking Fe appears to have been oxidized (botryoidal goethite), sulfur present at least in part as sulfate (formation of anglesite), yet Eu appears to have been in the 2+ state. There does not appear to be any equilibrium conditions at 25 °C in which Eu^{2+} , Fe^{3+} and SO_4^{2-} are all stable. Conditions during reworking were also not oxidizing enough to result in oxidation of Ce^{3+} to Ce^{4+} , as shown by the lack of development of negative Ce anomalies in the reworked gossan. It is possible that fluctuations in water table levels or cycling of elements across a redox boundary may explain all of the geochemical characteristics of the reworked Restigouche deposit gossans.

There is a second possible explanation to account for the preferential loss of Eu during chemical reworking of the gossan at the Halfmile Lake deposit. Europium may reside in a different mineral phase than the other REE. Thus, during primary gossan formation Eu is only partially oxidized to Eu^{3+} , so that much of the Eu budget is still in the reduced form similar to the original hydrothermal fluid. For example, Peter et al. (2003a) suggested that for hydrothermal sediments in the BMC (iron formations), Eu showed a different elemental association compared to the other REE, with Eu much more closely associated with a hydrothermal source. These workers performed multidimensional scaling analysis (MDS) and showed that all the REE (except Eu) are closely associated with SiO_2 , K_2O , Ga, Sc, Nb, Al_2O_3 , and TiO_2 (“detrital” components), whereas, Eu is chemically associated with Pb, Sb, In, As, Ag, S, Cu, and Zn (“hydrothermal” components). Peter et al. (2003a) suggest that Eu^{2+} was scavenged by, or coprecipitated with, hydrothermal oxides and sulfides during hydrothermal venting at the BMC paleoseafloor. Thus, it is possible that during reworking of the Restigouche deposit, Eu was preferentially lost from the gossan relative to the rest of the REE because it was hosted in a readily reworked (weathered) phase owing to being in a largely reduced state. One possible host mineral for Eu would be the jarosite mineral group, which are typical in primary BMC gossan, but which are absent to rare in the reworked gossan at the Restigouche and Brunswick #6 deposits (Boyle, 2003). Unfortunately, there has been insufficient work done on substitution of the REE in jarosite group minerals. However, Eu^{2+} has a similar ionic radius to Pb^{2+} (131 versus 133 pm, respectively) compared to Sm^{3+} , Eu^{3+} , and Gd^{3+} (109.8, 108.7, and 107.8 pm, respectively), raising the possibility that Eu^{2+} substitutes for Pb in plumbojarosite and beudantite.

The presence of subtle REE fractionation in the Restigouche deposit gossan compared to the Halfmile Lake

deposit gossan can also be used to elucidate conditions during gossan reworking. The former appears to have a slight MREE enrichment in many sulfide-normalized samples (Fig. 6). Near neutral, oxidizing conditions would limit the formation of sulfate complexes (Fig. 8C), allowing development of MREE-enrichment through preferential loss from Fe-oxides. Although in some acidic waters MREE enrichment is commonly observed (Johannesson and Lyons, 1995; Johannesson and Zhou, 1999), in many low pH waters there is no fractionation across the REE (Gimeno Serrano et al., 2000; Gammons et al., 2003; Verplanck et al., 2004; Gammons et al., 2005b). Verplanck et al. (2004) studied the partitioning of REE between ferric oxides and acid waters from pH 1.6 to 6.1 and found that significant HREE fractionation only occurred above pH 5.1. These experimental results and recent field results in anthropogenic and natural acid-impacted streams (Gammons et al., 2005a,b) are consistent with our contention that the REE in gossan at the Halfmile Lake deposit are unfractionated from massive sulfide mineralization owing to the low pH conditions present during gossan formation. In contrast, more neutral conditions inferred to have been present during reworking of the Restigouche gossan permitted minor REE fractionation. In particular, note that the %loss for the REE in the Restigouche gossan is lowest for La, consistent with the observations of Bau (1999), who showed increasing fractionation of La from the other LREE in the presence of Fe-oxyhydroxide with increasing pH from 3.63 to 6.21.

6. Conclusions

Using the mineralogical and geochemical compositions of primary and secondary gossans, we can infer the redox and pH conditions of formation of primary and reworked gossans. Primary massive sulfide gossans in the Bathurst Mining Camp (BMC), New Brunswick, Canada, are characterized by relative enrichments of Au, Sb, and As, formation of jarosite group minerals (jarosite, plumbojarosite, and argentojarosite) and little or no fractionation in the rare earth elements (REE), including preservation of large positive primary Eu anomalies. The chemical and mineralogical characteristics of these primary gossans (as exemplified by gossan at the Halfmile Lake deposit) imply low pH (<3) and relatively oxidizing conditions during gossan formation, such as would be experienced during oxidation of a volcanogenic massive sulfide body (with dominant sulfide minerals of pyrite, pyrrhotite, sphalerite, galena and chalcopyrite) with a falling water table. The lack of light REE or heavy REE fractionation and preservation of positive Eu anomalies characteristic of the original (465 Ma) hydrothermal fluid is consistent with relatively high integrated water-rock ratios during massive sulfide oxidation, and removal of the REE predominantly as sulfate complexes (LnSO_4^+ , $\text{Ln}(\text{SO}_4)_2^-$). Low pH groundwaters recovered from past producing mines in the BMC display REE pat-

terns consistent with those inferred to have occurred during gossan formation.

In contrast to the Halfmile Lake deposit, gossans at the Restigouche deposit display mineralogical and chemical evidence for having been chemically reworked since primary gossan formation. Evidence for chemical reworking includes loss of primary massive sulfide textures, replacement of plumbojarosite with anglesite, almost wholesale removal of jarosite minerals, loss of Au, Sb, and As and apparent preferential removal of Eu, resulting in loss of positive Eu anomalies for most samples. Based on geochemical modeling, conditions inferred for the chemical reworking of the Restigouche deposit (secondary-MSG) include near neutral conditions and either relatively oxidizing or cycling between reduced and oxidized, depending on the inferred model for preferential removal of Eu relative to the other REE.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2005.11.003](https://doi.org/10.1016/j.gca.2005.11.003)

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