Geology, Mineralogy, and Lithogeochemistry of Metalliferous Mudstones Associated with the Lemarchant Volcanogenic Massive Sulfide Deposit, Tally Pond Belt, Central Newfoundland*

STEFANIE LODE,1,1 STEPHEN J. PIERCEY,1 AND CHRISTINE A. DEVINE2,3

1Department of Earth Sciences, Memorial University, 300 Prince Philip Drive, St. John’s, Newfoundland, Canada A1B 3X5
2Canadian Zinc Corporation, Suite 1710, 650 West Georgia Street, P.O. Box 11644, Vancouver, British Columbia, Canada V6B 4N9
3FugroGeoconsulting, Inc., 6100 Hillcroft (77081), P.O. Box 740010, Houston, Texas 77274

Abstract

The Cambrian Lemarchant Zn-Pb-Cu-(Au-Ag) bimodal felsic volcanogenic massive sulfide (VMS) deposit, Tally Pond group, central Newfoundland, Canada, contains metalliferous mudstones that occur either immediately on top or laterally along strike from massive sulfide mineralization, or as interflow mudstones within hanging-wall basaltic rocks. The mudstones are brown to black, graphite rich, and locally have intercalations of siliciclastic, volcanioclastic and/or amorphous chert layers, and, in some cases, fine lamina of organic matter. The main sulfide phases are pyrite (framboidal and euhedral) and pyrrhotite, with minor chalcopyrite, sphalerite, arsenopyrite, and galena; barite is a common sulfate.

The metalliferous mudstones occur at various stratigraphic levels and have variable inputs of hydrothermal (high Fe/Al and base metal values) and detrital components (lower Fe/Al and base metal values) with positive shale normalized Eu anomalies (Eu/Eu* ≥ 1), negative Ce anomalies (Ce/Ce* ≤ 1), and an average Y/Ho ratio of ∼28.3. These signatures suggest precipitation from reduced, high-temperature hydrothermal vent fluids in an oxygenated water column, coupled with the hydrothermal particles having a short residence time within the hydrothermal plume (i.e., a vent proximal setting). Deposition from an oxygenated water column is also supported by the presence of abundant barite in both the Lemarchant massive sulfides and the metalliferous mudstones, as well as locally preserved marcasite in the mudstones. Redox-sensitive trace elements (As, U, V, Mo, Cr, Ni, and Co) were scavenged as oxyanions onto Fe oxyhydroxides during mudstone formation, and these elevated levels of scavenged redox-sensitive trace elements cause apparent anoxic signatures. Immobile element systematics (La-Th-Zr/10 and Th-La-Sc) indicate that the detrital components of the Lemarchant mudstones were mixtures of both continental and mafic sources, most likely deposited within a pericontinental rifted arc environment. Our research illustrates that the lithogeochemistry of metalliferous mudstones can identify vent proximity and provides insights into the physiochemical conditions of the deposit formation and the ambient environment. These results have implications for similar precious metal-bearing VMS deposits globally.

Introduction

Metalliferous mudstones (also described as exhalites, iron formation, hydrothermal mudstones) that are associated with volcanogenic massive sulfide (VMS) mineralization are interpreted to form from seafloor hydrothermal plume fallout when hot, reduced, and metal-rich vent fluids are discharged and mix with the cold, oxidized, sulfate-rich ambient seawater (Haymon and Kastner, 1981; Gurvich, 2006). Most of the particles emanating from hydrothermal vents (≥90%) are dispersed by the buoyant and neutrally buoyant hydrothermal plume, and subsequently precipitate as metalliferous mudstone, up to several kilometers away from the hydrothermal vent (Hannington et al., 1995; Ohimoto, 1996). As a consequence, only a small fraction (≤10%) of the metals dissolved in the vent fluids are trapped within the host rock and/or the sealing semipermeable layer of metalliferous mudstone (Hekinian et al., 1993). In close proximity to the hydrothermal vent site, polymetalllic (Fe, Cu, Zn, Pb) sulfides and accompanying phases, such as barite, anhydrite, amorphous silica, and Al-poor clays (nontronite), coprecipitate from the buoyant plume within or immediately after exiting the black smoker chimney (Haymon and Kastner, 1981; Hannington, 2009). The mixing of the vent fluids and seawater causes oxidation of the metal sulfides and formation of amorphous iron oxyhydroxide particles and silicagels, which deposit from the neutrally buoyant (or nonbuoyant) plume (Campbell et al., 1984; German and Von Damm, 2003). In consolidated mudstones, as the Lemarchant metalliferous mudstones, the amorphous or only weakly crystalline Fe oxyhydroxides are hydrothermally and diagenetically altered to Fe sulfides (pyrite, pyrrhotite), Fe carbonates (ferroan dolomite, ankerite ± Mg ± Mn), or Fe chlorite, and hence, not preserved in the rock record.

The term “exhalites” was first introduced by Ridler (1971) to describe interbedded volcaniclastic and/or detrital and chemical sedimentary rocks. The temporal and spatial association of metalliferous mudstone (exhalites) with ancient and modern VMS deposits and their use as stratigraphic marker horizons in the location of massive sulfides is well recognized (Franklin et al., 1981; Spry et al., 2000; Peter, 2003). Furthermore, metalliferous mudstones form an impermeable to semipermeable layer capping the massive sulfide lens and therefore, likely increase the preservation probability of massive sulfides (Hannington et al., 1995; Gurvich, 2006).
Additionally, this geologic membrane helps to retain more of the metal-rich hydrothermal fluids within the massive sulfide mound and decreases the amount of metals lost to the hydrothermal plume (Large, 1992; Kharaka and Hanor, 2014).

In addition to capping deposits, metalliferous mudstones provide insight into, and record, processes associated with ore formation, including understanding the relative importance of vent fluid contributions, seawater scavenging of elements by hydrothermal particles, and detrital sedimentation associated with volcanism and sedimentary activity (Hannington et al., 1995; German and Von Damm, 2003). Hydrothermal metalliferous sediments represent a hiatus in this volcanic activity, where the deposition of hydrothermal matter dominates over the abiogenic pelagic background sedimentation (Lydon, 1984). Furthermore, lithogeochemistry of metalliferous mudstones can shed insight into the relative roles of the above processes played in the genesis of these sediments (de Baar et al., 1988; Peter, 2003).

In the Tally Pond massive sulfide belt in the central Newfoundland Appalachians, sulfide-bearing mudstones are abundant and are spatially associated with numerous deposits and prospects (e.g., Swinden, 1991; McNicoll et al., 2010; Fig. 1A, B). However, very few studies have been undertaken to understand their geology and lithogeochemistry, as well as the relationship of the mudstones to VMS genesis and their exploration significance. The Cambrian (~512–509 Ma) Lemarchant Zn-Ph-Cu-(Au-Ag) deposit is an ideal location to study metalliferous mudstones within the Tally Pond belt, because laminated sulfide-rich mudstones are spatially and possibly genetically associated with mineralization (Fig. 1B). Upper Cambrian to Lower Ordovician black shales from Bell Island, eastern Newfoundland, were utilized as an example of detrital mudstones not spatially associated with sulfide mineralization (Fig. 1C). Furthermore, whereas in some cases the Lemarchant mudstones are directly associated with mineralization, they also occur at various distances from mineralization and at various stratigraphic levels. Therefore, they provide the ability to monitor the chemical variation of the hydrothermal fluid that is a component of the mudstones as a function of stratigraphic position and spatial proximity to mineralization.

The spatial association of the Lemarchant metalliferous mudstones to massive sulfides provides the possibility to study what kind of lithogeochemical proxies can be used to (1) confirm and/or identify a hydrothermal origin versus, e.g., shallow basin pyrite-bearing carbonate black shales/mudstones (nonhydrothermal muds/shales); (2) define and better understand the depositional environment in terms of paleoredox conditions of ambient seawater; and (3) study the chemical properties of the fluids, from which the Lemarchant mudstones precipitated. Although the results of this study are of significance to understand how the hydrothermal components of the mudstones spatially associated with the Lemarchant deposit form, they have significance for other metalliferous mudstones/shales within the Tally Pond belt, as well as VMS districts globally, and provide key insight into the evolution of VMS hydrothermal systems in ancient volcanic belts.

**Regional Geology**

The Lemarchant Zn-Pb-Cu-Ba-(Au-Ag) VMS deposit is one of many VMS deposits within the Central Mobile Belt in central Newfoundland, Canada, that are part of the Cambrian (~515 Ma) to Permian (~275 Ma) Appalachian mountain belt (e.g., Williams, 1979; van Staal, 2007; van Staal and Barr, 2011). The Newfoundland Appalachians are divided into four tectonostratigraphic zones (from west to east): the Humber, Dunnage, Gander, and Avalon zones (Swinden, 1988, 1991; Williams et al., 1988). The Dunnage zone represents the Central Mobile Belt (Williams, 1979; Rogers et al., 2007). These zones result from and were affected by the successive accretion of three microcontinental blocks during the early Paleozoic to the middle Paleozoic (i.e., Dashwoods, Taconic orogenesis; Ganderia, Salinic orogenesis; and Avalonia, Acadian orogenesis) and related interoceanic arcs and back arcs (Swinden, 1991; Zagorevski et al., 2010). These ribbon-shaped microcontinental blocks were located on the leading edges of Gondwana and Laurentia, forming peri-Gondwanan and peri-Laurentian terranes (Rogers et al., 2007; van Staal and Barr, 2011). The Dunnage zone has been subdivided into the peri-Laurentian Notre-Dame subzone to the northwest and the peri-Gondwanan Exploits subzone to the southeast (Fig. 1A; Swinden, 1988, 1991). The suture between the subzones is the Red Indian Line, a ribbon-shaped zone of a tectonic mélange, which contains remnants of Cambro-Ordovician oceanic infant arc and arc terranes that existed within the Iapetus Ocean (Williams, 1979; van Staal and Barr, 2011). Despite deformation and metamorphism, the Central Mobile Belt was only moderately affected by metamorphism (lower greenschist facies) and deformation and internally stratigraphic relationships are well preserved (e.g., Hinchey and McNicoll, 2009; Piercey et al., 2014).

The Lemarchant VMS deposit is hosted in the lower Victoria Lake supergroup within the Exploits subzone, which is comprised of Cambrian-Ordovician volcanic and sedimentary rocks (Dunning et al., 1991; McNicoll et al., 2010). The Victoria Lake supergroup is further subdivided into six assemblages (Zagorevski et al., 2010; Piercey et al., 2014), which are bounded by faults and are from east to west: (1) the Tally Pond group, (2) the Long Lake group, (3) the Tulks group, (4) the Sutherlands Pond group, (5) the Pats Pond group, and (6) the Wigwam Pond group, the Tulks, Long Lake, and Tally

**Fig. 1.** A. Tectonostratigraphic assemblages with the main zones of the Newfoundland Appalachians (Avalon, Gander, Dunnage, and Humber zones) and VMS occurrences within the Notre Dame and Exploits subzones (modified after Swinden 1991; Pierc, 2007). Notre Dame subzone VMS: 1 = York Harbour, 2-15 = BaieVerte belt deposits, 9–12, 40 = Springhaule belt deposits, 13–29 Buchans-Roberts Arm deposits. Exploits subzone VMS: 30–35 = Tulks belt deposits, Tally Pond belt deposits: 30 = Lemarchant, 40 = Duck Pond, 41 = Boundary, 42–45 = Point Leamington belt deposits. B. Geologic setting of the Victoria Lake supergroup, including the Tally Pond and Tulks volcanic belts. The Tally Pond group hosts the Lemarchant deposit and the Duck Pond and Boundary mines. Diagram after Piercey et al. (2014). CLIS = Crippleback intrusive suite, TPB = Tally Pond belt. C. Overview map of the location of Bell Island. Sampled outcrops from Lance Cove, the Beach, and Powersteps.
Silurian and/or Devonian

Bottwood Group
- Undivided
- Rogerson Lake Conglomerate

Notre Dame Subzone

Ordovician igneous complexes
- Red Indian Lake Group (~464 Ma)
- Harbour Round and Healy Bay formations
- Skidder Formation

Buchans Group (~473 Ma)
- Lloyds River Complex (~473 Ma)
- Annieopsquotch-Star Lake Ophiolite (~480 Ma)

Neoproterozoic

Crippleback Intrusive Suite (~584 Ma)

Sandy Brook Group (~564 Ma)
Pond groups are known to host VMS deposits. These six tectonic assemblages yield U-Pb zircon ages ranging from ~513 to 453 Ma (Dunning et al., 1987; Evans et al., 1990; Dunning et al., 1991; Evans and Kean, 2002; Zagorevski et al., 2007; McNicoll et al., 2010). The operating Duck Pond and Boundary mines as well as the Lemarchant deposit are located within the Tally Pond group (Fig. 1B; e.g., Squires and Moore, 2004). The Tally Pond group (U-Pb zircon ages ranging from ~513–509 Ma) is divided into the felsic volcanic rock-dominated Bindons Pond formation (also referred to as Boundary Brook formation) and the mafic volcanic rock-dominated Lake Ambrose formation. The latter contains island-arc tholeiitic basalts (Dunning et al., 1991; Evans and Kean, 2002), whereas the former contains predominantly transitional to calc-alkalic rhyolitic rocks (Rogers et al., 2006; Piercey et al., 2014). VMS-style hydrothermal alteration and mineralization occurs in several areas within rocks of the Bindons Pond formation (Squires et al., 1991; Piercey et al., 2014). Collectively, the Tally Pond group is interpreted to represent an arc to rifted-arc environment (e.g., Rogers et al., 2006).

**Deposit Geology**

The Lemarchant deposit occurs along the contact between footwall felsic volcanic rocks of the Bindons Pond formation and hanging-wall mafic volcanic rocks and metalliferous mudstones of the Lake Ambrose formation. Both formations are crosscut by gray- to beige-bleached amygdulite-rich mafic dikes. The contact between the formations is complex and commonly marked by complex intermingling of felsic and mafic volcanic rocks, with a thin (<1- to 20-m) layer of argillite, siltstone, or pyritic mudstone. This metalliferous mudstone layer is discontinuous with a short lateral extent of 1 to 4 km, but similar metalliferous sediments are also found proximal to other VMS occurrences within the Tally Pond volcanic belt (Copeland et al., 2009; Fraser et al., 2012).

The Lemarchant deposit is associated with ~4,000-× 700-m hydrothermal alteration zone (Fig. 2B, C), with intense quartz, sericite, chlorite, and Ba enrichment, plus anomalous disseminated and stringer-type pyrite, base metal sulfides with lesser amounts of pyrrhotite (Fraser et al., 2012). The mineralization occurs as semimassive to massive sulfide within the Lemarchant Main zone (sections 101N–104N), and in a smaller mineralized sequence, the 24 zone (Fig. 2A; Copeland et al., 2009; Fraser et al., 2012). The indicated resources for the Lemarchant Main zone currently are 1.24 Mt at 5.38% Zn, 0.55% Cu, 1.19% Pb, 1.01 g/t Au, and 59.17 g/t Ag, with inferred resources of 1.34 Mt at 3.70% Zn, 0.41% Cu, 0.86% Pb, 1.00 g/t Au, and 50.41 g/t Ag (Fig. 2A-C; Fraser et al., 2012). An additional mineralized zone, the Northwest zone (Fig. 2A, C), was discovered in early 2013, and has a strike length of 100 m, and remains open to the north and south (http://www.canadianzinc.com/images/Docs/News_Releases/CZNNR20131221.pdf). The Northwest zone currently does not have a defined resource.

The Lemarchant Main zone (Fig. 2B) is 1.7 to 30.4 m thick and consists of a barite-rich outer zone that grades into a Pb-Zn sulfide-rich zone, and an interior zone with Zn-Cu sulfides, which grades into stringer mineralization at depth, typical of bimodal felsic/Kuroko-style mineralization (Copeland et al., 2009; Fraser et al., 2012; Gill and Piercey, 2014). The deposit contains typical VMS sulfides (pyrite, sphalerite, galena, and chalcopyrite) but also abundant sulfosalts (e.g., tetrahedrite-tennantite), bornite, stromeyerite, electrum, bladed barite, and calcite; as well as minerals that contain enrichments in epithermal suite elements (e.g., Au, Ag, As, Hg, Sb, Bi; Gill and Piercey, 2014). The sulfosalts-rich mineralogy, barite-calcite textures, and anomalous element suite in the ores have led to the interpretation that the Lemarchant deposit was a shallow-water VMS deposit with both VMS and epithermal features (Gill and Piercey, 2014).

The massive sulfides at Lemarchant are stratigraphically overlain by metalliferous mudstones that contain many of the above minerals. The contact between the massive sulfides and the mudstones consists of a 5- to 40-cm-wide zone of Fe-rich red to purple sphalerite that grades downdip in the drill hole into white- to honey brown-colored sphalerite-dominated massive sulfides. Electrum ± Hg ± Sb also occurs in the mudstones. Due to an offset along the Lemarchant fault at a gentle to moderate angle, a repetition of the mineralized strata and mudstone occurrences is likely (Copeland et al., 2009). The Lemarchant fault locally cuts off mineralization (Figs. 3, 4) and displaces the ore horizon and the mudstones. Some of the mudstones also display a foliation that is orientated parallel to the sedimentary lamination with occasional cleavage traces that crosscut bedding.

**Mudstone Stratigraphy and Lithofacies**

The mudstones occur either immediately stratigraphically above the massive sulfides in the Bindons Pond formation, or form a layer capping volcanic rocks within the same formation (Figs. 3, 4). They laterally extend in the same stratigraphic level up to 200 m away from the mineralization in the Lemarchant Main zone, but they are also spatially associated with the Northwest zone, the 24 zone, and the North Target, as well as areas west of the South Target zone (Fig. 2A). The extent of mudstones in the last three areas is difficult to determine due to the limited number of drill holes. The interflow mudstones within Lake Ambrose formation basalts occur up to 50 m above massive sulfide mineralization in stratigraphic sections that are tectonically undisturbed. Mudstones within the felsic volcanic rocks below the ore horizon are rare, and only seen in one drill hole with a thickness of ~1 m. Synsedimentary folding and faulting has locally increased the thickness of the mudstone, but most have true thicknesses of 1 to 20 m (Figs. 5A, 6B).

The contacts between the mudstones and surrounding units (e.g., massive sulfide and basalt) range from conformable (Fig. 5A, B) to tectonized (Figs. 3, 4). At the contact between the mudstones and mafic volcanic rocks (flows and sills; Fig. 5C) peperitic textures are locally present, whereby mafic rocks chaotically mingled with mudstones, interpreted as formed by magma-wet sediment interactions, indicating contemporaneous volcanism and sedimentation (Skilling et al., 2002). Another common feature is the intermingling of the mudstones with felsic volcanic and/or volcaniclastic sedimentary material (Fig. 5D), which is interpreted to represent mass wasting (e.g., Flüchtbauer et al., 1988).

Mudstones of various stratigraphic positions are generally brown to black, graphite rich, finely laminated, and contain fine carbonaceous/organic matter-rich laminae that are
intertwined with siliciclastic, volcanioclastic and/or amorphous kidney-shaped chert layers (Fig. 5A). The sulfides occur both parallel to the bedding in the organic-rich layers, but also in later stage, stringer-like veins. Crosscutting veins intercept the original bedding, indicating diageneric/tectonic remobilization and/or formation by intrastratal shrinkage (synaeresis) cracks (e.g., Füchtbauer et al., 1988).

The main sulfides in the mudstones are pyrite and pyrrhotite, with minor chalcopyrite, sphalerite, arsenopyrite, marcasite, and galena, as well as rare cubanite and gersdorffite. Sphalerite commonly displays chalcopyrite disease, whereas pyrite exists as framboids and euhedral grains. The framboids occur either as scattered single spheres or in semimassive layers (Figs. 6A, 7A). Based on the textural robustness (i.e., withstanding certain amounts of reworking) and δ34S isotope studies ranging from −38 to +12‰ (Lode et al., 2014), the organic-rich laminae are potentially microbial mats (Fig. 7F). Framboid layers are locally crosscut by veins that are filled with later stage polynmetal sulfides, including euhedral pyrite, interstitial chalcopyrite, sphalerite, and galena (Fig. 6B-D). These later stage veins are locally enriched in precious metals in the form of electrum ±Hg ± Sb, acanthite, pyrargyrite, and stephanite (Fig. 6D-F). Marcasite occurs as tabular crystals or blades in euhedral or massive pyrite, or as semiomissive layers of marcasite clusters.

Mudstones spatially associated with the massive sulfides, and interflow mudstones in the hanging-wall mafic volcanic rocks, commonly have a high abundance of barium-bearing minerals, including barite, celsian, hyalophane, and witherite. Barite generally forms anhedral semicontinuous layers or occurs as bladed crystal vug inllfs, whereas the Ba feldspars (celsian and hyalophane) are later stage minerals with euhedral crystals overgrowing earlier phases such as pyrite framboids (Fig. 7A-E). Barite also forms in crack-and-seal-type veins, crosscutting the mudstones and Pb-Zn-Cu sulfides (Fig. 7E). Carbonates, quartz, sericite, Fe-Mg chlorite, and apatite are common gangue minerals in mudstones, with accessory monazite, Y xenotime, and rutile. Carbonates are generally Fe bearing (e.g., ferroan dolomite and ankerite ± Mg ± minor Mn), but calcite and dolomite are also locally present (Figs. 6D, 7B, C, F).

Lithochemistry

Sampling, methods, and quality control and assurance

Mudstone types collected from drill core include those that (1) occur in contact with or are within 5 m of massive sulfides and represent the main stratigraphic marker between the felsic and mafic volcanic rocks (Bindons Pond and Lake Ambrose formations, respectively); (2) do not have an obvious spatial and possibly genetic relation with mineralization, but occur along the same stratigraphic contact between the Bindons Pond and Lake Ambrose formations; (3) occur within the Bindons Pond felsic volcanic rocks; and (4) occur as interflow mudstones in the hanging-wall Lake Ambrose basalts. Tuff is intercalated with all types of mudstones, and if the tuff had a sufficient thickness it was sampled for whole-rock geochemistry as well.

Samples for whole-rock lithogeochemical studies were analyzed for major and minor elements by lithium metaborate/tetraborate fusion followed by HNO3 dissolution and analysis by inductively coupled plasma (atomic)-emission spectroscopy (ICP-ES). Carbon (C) and sulfur (S) were obtained by infrared spectroscopy, and mercury (Hg) was obtained by the cold vapor flow injection mercury system (Hg-FIMS). All of the former analyses were acquired at Activation Laboratories Ltd. (Actlabs) in Ancaster, Canada. Additional trace elements, including rare earth elements (REE), high field strength elements (HFS), trace metals, and many low field strength elements (LFS) were analyzed in the Department of Earth Sciences at Memorial University, using screw-top Teflon® bomb (Savillex®) microacid dissolution with a finish by inductively coupled plasma-mass spectrometry (ICP-MS).

The multiacid (HNO3, HF, HCl, H3BO3, and H2O2) whole-rock dissolution process was a modified version of Jenner et al. (1990) and Longerich et al. (1990) to account for the high amounts of carbonate material in the samples; the procedures are described in detail in Appendix 1.

Precision and accuracy of the analyses were determined using duplicates and reference materials following methods described in Jenner (1996) and Piercey (2014). The reference materials utilized in the study included three different organic- and/or sulfide-rich shales (SCO-1, SDO-1, and SGR-1b) and one iron formation (FeR-1). These standards were run every 20 samples and with each analytical batch. In addition, blanks were utilized during each analytical run to test for contamination; none was detected. Precision was determined using the percent relative standard deviation (%RSD) on the replicate analyses of the reference materials, and accuracy was determined using percent relative difference (%RD) from accepted values. The detailed QA/QC protocol is given in Appendix 1.

Results

Alteration—major element systematics: The major elements have variable mobility with the alkali elements, exhibiting considerable mobility during hydrothermal alteration and diageneric processes (Nesbitt and Young, 1982; Nesbitt, 2003). Hydrothermal and diageneric alteration starts during and immediately after the precipitation of the metalliferous mudstones due to ongoing hydrothermal activity. The alkali elements and Fe-Mg are often compared to the immobile Al2O3 in A-CN-K and A-CNK-FM molar diagrams (Fig. 8A, B; Nesbitt, 2003), which broadly mirror the chemical index of alteration (CIA; Nesbitt and Young, 1982). The CIA describes the degree of alteration and is calculated using the equation CIA = 100 × [Al2O3/(Al2O3 + CaO + Na2O + K2O)]. Unaltered samples have a CIA ~50, whereas strongly altered samples yield CIA values of up to 100 (Nesbitt and Young, 1982). Most of the Lemarchant samples (95th percentile) have CIA values around ~84, comparable with the average shale values of 70 to 80 (e.g., Nesbitt, 2003). The elevated values (max CIA = ~94) are consistent with significant alteration, and authigenic and diageneric clay mineral content. A smaller group of samples with higher amounts of carbonate have CIA values <25 (Appendix Table A1). In A-CN-K space, most mudstones lie within the sericite (illite/muscovite) and carbonate-dolomite portion of the diagram, and less so along the chlorite-smectite trend (Fig. 8A). Exceptions to the former are mudstones in the hanging-wall mafic volcanic rocks,
which have less calcite-dolomite alteration. The Bell Island black shales fall within the average shale field (Fig. 8A). In A-CNKF-M space mudstones plot near the FM part of the diagram proximal to the sulfide-oxide apex, chlorite-smectite and calcite-dolomite; tuff displays trends toward muscovite/illite and feldspars. Also trending toward muscovite/illite, with only minor carbonate contribution, are the Bell Island black shales (Fig. 8B).

A positive correlation between Al$_2$O$_3$ and TiO$_2$ ($r^2 = 0.848$; Fig. 8C) in the Lemarchant mudstones and tuff indicates that both were likely immobile during postdepositional processes, such as diagenesis and alteration (Barrett and MacLean, 1994a). Some of the interflow mudstones, tuff, and other mudstone samples deviate from the correlation line and plot toward lower Al$_2$O$_3$/TiO$_2$ ratios, potentially reflecting more mafic detritus.

**Hydrothermal versus detrital element signatures:** Samples from Lemarchant and Bell Island have been plotted in Boström-type diagrams in Figure 9A and B (Boström et al., 1972; Boström, 1973). Samples from various stratigraphic levels in the Lemarchant deposit have hydrothermal signatures with Fe/Ti versus Al/(Al + Fe + Mn) systematic, which suggest the hydrothermal component is between 40 and 80% (Fig. 9A), and lie predominantly in the hydrothermal field of Figure 9B, with the exception of volcanic tuff samples. In general, there are very little differences between samples that occur...
Fig. 2 (Cont.)
Metalliferous mudstones occur in close association with mineralization, at or close to the contact between the felsic and mafic hanging-wall volcanic rocks, and also as interflow mudstones.

---

**Fig. 3.** Lithostratigraphic columns at section 102 + 50N, from 101 + 75E to 102 + 15E, intercepting the Lemarchant Main zone. The lithofacies, including the mudstones, are shown in true thickness. The selected drill holes are shown in Figure 2A.
METALLIFEROUS MUDSTONES, LEMARCHANT VMS DEPOSIT, CENTRAL NEWFOUNDLAND

Fig. 4. Lithostratigraphic columns at section 102N to 102 + 12.5N, from 100 + 39E to 102E, intercepting the Lemarchant Main zone in holes LM11-68 and LM07-14. Shearing associated with felsic dikes partially cut-off the main sulfide lens, LM08-32. Drill hole LM08-34 is located ~150 m west of the main sulfide lens and does not intercept mineralization. Metalliferous mudstones occur at the contact between felsic and mafic volcanic rocks and can be correlated to the other drill holes (LM11-64, LM11-63, LM11-52, LM10-43, LM08-32, LM11-68, and LM07-14) shown in Figures 3 and 4, since the main sulfide lens dips to the east. Hence, mudstones are expected to occur in shallower levels farther west. In drill hole LM07-14 interflow mudstones were also intercepted within mafic volcanic rocks of the lower mafic block. The various lithofacies, including the mudstones, are shown in true thickness. The locations of the drill holes are shown in Figure 2A.
Fig. 5. A. Dark brown to black graphite- and sulfide-rich metalliferous mudstone immediately above massive sulfides (lower right corner) of the Lemarchant Main zone. The mudstones show planar lamination, roughly parallel to massive sulfide mineralization. Mass wasting and reworking of muds occur in a section above the massive sulfides with incorporated felsic volcaniclastic rocks (lower left corner), followed by a section with bedding subparallel to the core due to reworking and folding (middle row). Sulfide-rich layers alternate with graphite-rich layers. Lamination is interrupted by synsedimentary faulting (drill hole LM08-33, section 103N; top to the left). B. Laminated sulfide-rich mudstone is conformably overlain by flow-banded hanging-wall basalts (drill hole LM08-32, section 102N; top to the left). C. Synvolcanic peperitic texture: hydrothermal mud intermingled with beige-gray-bleached mafic dikes (drill hole LM11-49, section 108N). D. Mass-wasting sediment: gray felsic lapilli-tuff reworked into dark brown metalliferous sediment (drill hole LM11-56, section 104N).
FIG. 6. A. Backscattered electron image of layered framboidal-rich mudstone. Nonsulfidic matrix consists mostly of quartz, chlorite ± carbonaceous material (drill hole LM08-24 text, section 105N, CNF20963; top is toward the upper left). B. Possible synsedimentary slump structure in framboidal-rich mudstone. Void space within slump structure filled with later stage polymetallic sulfides and ferroan dolomite ± Mg ± Mn (drill hole LM11-59, section 103 + 25N, CNF30959). C. Reflected light microscope image from a thin section of layers of laminated framboidal-rich mudstone that is crosscut by a vein filled with later stage polymetallic sulfides (euhedral pyrite, interstitial chalcopyrite and sphalerite), and minor electrum (drill hole LM13-76, section 100 + 50N, CNF25062b). D. Reflected light image from a polished epoxy puck with electrum (light yellow) in sample shown in 7C, associated with chalcopyrite (cpy, yellow) and galena (gal, gray), occurring interstitially between euhedral pyrite (py, dominant mineral) with ankerite (ank), Fe-Mg chlorite (Fe-Mg chlor), and quartz (qtz) gangue (black) (drill hole LM13-76, section 100 + 50N, CNF25062b). E. SEM-BSE image of interstitial Hg-bearing electrum and galena (gal) between euhedral arsenopyrite (aspy) in a pyrrhotite (po) layer, with minor pyrite (py) (drill hole LM13-77, section 100 + 50N, CNF25064). F. Reflected light image of chalcopyrite (cpy), galena (gal), and pyrargyrite with quartz (qtz) gangue (drill hole LM11-69, section 103 + 50N, CNF30994).
Fig. 7. A. SEM-BSE image of euhedral celsian (Ba feldspar) overgrowing pyrite frambooids (drill hole LM10-43, section 102N, CNF20978). B. SEM-BSE image of euhedral overgrowths of celsian (cels, Ba feldspar) on pyrite (py), and barite (bar), apatite (apat), ferroan dolomite (Fe-dol), and quartz (qtz) as gangue (drill hole LM11-59, section 103 + 25N, CNF30959). C. SEM-BSE image of a vein filled with bladed barite (bar) and calcite (calc), and euhedral celsian (cels) rhombs in the pyrite-framboid-rich mudstone (drill hole LM13-79, section 101 + 25N, CNF25071). D. SEM-BSE image of massive barite (bar) with kaolinite (kaol) in a mudstone with chalcopyrite (cpy), pyrite (py), and galena (gal) (drill hole LM07-17, section 104N, CNF30953). E. SEM-BSE image from a thin section showing a barite vein crosscutting chalcopyrite-pyrite-sphalerite-celsian-rich mudstone (drill hole LM07-13, section 101N, CNF30955). F. Reflected-light image with chalcopyrite (cpy), euhedral pyrite (py), and a framboidal pyrite layer (possibly microbial mat) with Fe-Mg chlorite (Fe-Mg chlor) and ferroan dolomite (Fe-dol) gangue (drill hole LM07-16, section 104N, CNF30951).
within 5 m of mineralization and those that are hosted within various rocks distal to mineralization (Fig. 9A, B). One exception is a nearly pure sulfide-rich sample consisting almost solely of layered sulfides (pyrite, Fe sphalerite, minor galena), which falls within the same field as Red Sea metalliferous sediments (Fig. 9A). In comparison, the Bell Island black shales predominately consist of detrital matter and, accordingly, fall within the nonhydrothermal sediment fields (Fig. 9A, B). To account for the high contents of Ba and Hg in the Lemarchant hydrothermal system, a plot with Ba/Al versus (Zn + Hg)/Al was utilized, where Ba, Zn, and Hg represent hydrothermally derived components of the mineralization, and Al the detrital constituents. In this plot, proximal sediments show trends toward high Ba/Al and (Zn + Hg)/Al ratios, whereas detrital sedimentary rocks have low ratios (Fig. 9C).

The Lemarchant mudstones have $\Sigma_{Fe^{total}} + Fe_2O_3(Fe_{total})$ that ranges from 13 to 55 and 2 to 42 wt % S, with mudstones that are closely associated with the massive sulfides having higher Fe and S values (avg $Fe_{total}$ of 34.5 wt % and average S of 24.4 wt %). The Fe is hosted within Fe sulfides, carbonates, oxide, and chlorite. Tuffs generally range from 13.8 to 30.8 wt % $Fe_{total}$ and 4.6 to 12.9 wt % S, with two exceptions (39.7 and 51.2 wt % $Fe_{total}$ and 26.5–24.2 wt % S), which are sulfide and/or barite rich proximal to massive sulfides (Fig. 10A). The mudstones also have elevated Zn, Pb, Co, and Cu, and this is particularly so for samples within 5 m of mineralization (Fig. 10B, C).

**Hydrothermal versus hydrogenous element systematics:** Samples proximal to massive sulfides also have elevated Ba (up to 130,200 ppm) and Hg (up to 17,700 ppb; Fig. 10D). One tuff sample intercalated with a proximal mudstone has a Ba content of 165,700 ppm and 543 ppb Hg. In contrast, the other tuff samples only have up to 135 ppb Hg, and the more distal mudstones up to 811 ppb. These systematics are similarly reflected by Sb and As concentrations (Fig. 10E, F), where proximal mudstones have up to 415 ppm Sb and 9,545 ppm As, whereas tuff and more distal mudstones tend to have lower values of 329 ppm Sb and 3306 ppm As, with one distal mudstone exception that has an As value of 13,671 ppm. Therefore, Zn-Pb-Cu-Co-Ba-Hg enrichments are associated with mudstones proximal to mineralization and are lower in distal mudstones.

**Fig. 8.** A. Ternary A-CN-K diagram. A = Al$_2$O$_3$, CN = CaO + Na$_2$O, and K = K$_2$O. B. Ternary A-CNK-FM diagram. A = Al$_2$O$_3$, CNK = CaO + Na$_2$O + K$_2$O, and FM = (FeO + Fe$_2$O$_3$) + MgO. C. Al$_2$O$_3$ vs. TiO$_2$. (A) and (B) are after Nesbitt (2003), (C) is after Barrett and MacLean (1994b).
Rare earth element and Y (REY) signatures: The rare earth element and Y (REY) signatures of the hydrothermal mudstones and tuff from the Lemarchant deposit are shown in Figure 11A to E, and from Bell Island in Figure 11F, and normalized to post-Archean Australian shale using the data of McLennan (1989). Mudstone within 5 m of mineralization has LREE-depleted normalized profiles with relatively flat HREE signatures (Fig. 11A). They have negative Ce anomalies (Ce/Ce* <1) and positive Eu anomalies (Eu/Eu* = 1.1–3.5), and four samples with almost no or slightly negative Eu anomalies (Eu/Eu* around 0.9). Ce/Ce* and Eu/Eu* were calculated using the equations after McLennan (1989) where Ce/Ce* = (Cesample/79.6)/√((LaSample/38.2)*(PrSample/8.83)) and Eu/Eu* = (EuSample/1.08)/√((SmSample/5.55)*(GdSample/4.66)), respectively. A smaller group of proximal mudstones also have a slightly positive Y anomaly (Fig. 11A), whereas a sulfide-rich sample is depleted in HREEs (Fig. 11A). Mudstones that occur at the footwall-hanging wall interface, but are not associated with massive sulfide mineralization, and those that are in the hanging-wall basaltic rocks, are broadly similar to proximal samples but have less strongly pronounced Eu anomalies (Eu/Eu* = 0.9–2.6; Fig. 11B, C). Tuffs intercalated with mudstones also have flat HREE patterns, a negative Ce anomaly, but either no, or only a minor positive Eu anomaly (Eu/Eu* = 0.9–1.4). One tuff that occurs in close proximity and stratigraphically above massive sulfides has a Eu/Eu* = 2.2 (Fig. 11D). The one sample within felsic volcanic rocks (Fig. 11E) has a similar REE pattern to the mudstones shown in Figure 11B. The Bell Island black shales have relatively flat REE patterns, without any significant Ce or Eu anomalies (Fig. 11F).

Unlike samples from the Duck Pond deposit (Piercey et al., 2012), the Lemarchant mudstones and tuff have no significant Y anomalies but have average Y/Ho ratios of ~28.3 that are near the chondritic ratio of 27 (Fig. 12A; Bau, 1996; Slack et al., 2007). In the Y/Ho-Ce/Ce* plot, the Lemarchant mudstone and tuff samples are scattered around the chondritic Y/Ho ratio of 27, with some samples tending toward lower Ce/Ce* values and higher Y/Ho ratios (trend toward the seawater value of Y/Ho >44; Fig. 11B). Three samples are outliers and plot outside the field of the majority of the Lemarchant samples (Fig. 11B).

Hydrothermal versus hydrogeneous element systematics: Redox-sensitive elements can be used to determine the paleoredox conditions of the ambient seawater during the
METALLIFEROUS MUDSTONES, LEMARCHANT VMS DEPOSIT, CENTRAL NEWFOUNDLAND

Fig. 10. Selected base metal, transition element, and hydrothermal element plots A. Total S vs. Fe$_2$O$_3$(total). B. Zn vs. Pb. C. Co vs. Cu. D. Ba vs. Hg (after Piercey et al., 2012). E. Ba vs. As. F. As vs. Sb.
Metalliferous mudstones within mafic volcanic flows

Metalliferous mudstones associated with massive sulfides (within 5 m) n = 34

Metalliferous mudstones associated with felsic and mafic volcanic rocks

Bell Island blackshales n = 5

Fig. 11. REE plus Y geospider plots of Lemarchant mudstones and tuff of various stratigraphic levels. A. Mudstones that are closely associated with massive sulfides (within 5 m). B. Mudstones at the contact between felsic and mafic volcanic rocks. C. Interflow mudstones within the hanging-wall mafic volcanic rocks. D. Tuff samples that are intercalated with mudstones from various stratigraphic levels. E. Mudstone occurring within felsic volcanic rocks. F. Bell Island samples. All samples are normalized to the post-Archean Australian shale (PAAS) of McLennan (1989).
time of deposition of the hydrothermal sediments (Emerson and Huested, 1991; Jones et al., 2006). These redox-sensitive trace elements (U, V, Mo, Cr, and Co) have variable oxidation states and their solubility is dependent on this oxidation state and the pH of the ambient water, and, for some elements (e.g., Ni), the presence or absence of organic matter (Tribovillard et al., 2006). In Figure 13A and B, the Lemarchant mudstones fall within the anoxic field, whereas the Bell Island black shales plot in the oxic field. However, plots of these redox-sensitive elements have to be taken with care in hydrothermal sedimentary environments, when abundant Fe oxyhydroxides are present.

Lemarchant mudstones and tuff have higher P2O5 values (lower Fe2O3/P2O5 ratios) and exhibit a weak correlation with higher Y/Ho ratios, whereas samples with higher Fe2O3 values plot around the chondritic Y/Ho value of ~27 (avg = 28.3, Fig. 14A). Nevertheless, this Ba versus Y/Ho plot additionally illustrates that mudstones closely associated with mineralization have higher Ba (and Hg) concentrations than more distal mudstones or tuff (Figs. 10D, 14B).

**Immobile elements and sediment provenance:** Homogenization of the detritus in sedimentary basins results in basin muds having immobile trace element patterns that reflect their source rocks (Bhatia and Crook, 1986; Nesbitt and Markovics, 1997). Ratios of immobile elements like the HFSE (e.g., Zr), the REE (e.g., La), and the compatible elements (e.g., Sc) are not significantly influenced by chemical weathering, diagenesis, hydrothermal alteration, or low-grade metamorphism and, therefore, can be used for provenance studies of sedimentary rocks, and to reconstruct the tectonic environment of deposition for sedimentary rocks (Taylor and McLennan, 1985; Kolata et al., 1996; McLennan et al., 2003).

In plots of Th-Sc-Zr/10 (Fig. 15A) and La-Th-Sc (Fig. 15B), interflow mudstones and some samples of tuff overlap fields for intraoceanic and continental-arc environments, consistent with proposed tectonic models for the Tally Pond group (Dunning et al., 1991; McNicoll et al., 2010; Piercey et al., 2014). In Figure 15B, several samples trend toward the La apex, particularly so for mudstones associated with massive sulfides and/or felsic volcanic rocks, and suggests potential La scavenging from seawater (e.g., Bau, 1991, 1993). The ternary Th-Sc-Zr/10 plot also shows that the Lemarchant source rocks are zirconium depleted, as previously reported by Squires and Moore (2004) and McNicoll et al. (2010) for the bimodal volcanic rocks of the Tally Pond belt (Fig. 15A). This Zr depletion is also noticeable in Figure 15C, which indicates an upper crustal character of source rocks for mudstones associated with massive sulfides and/or felsic volcanic rocks and trends toward more andesitic to MORB-like source rock for interflow muds and some tuff.

*Fig. 12. A. Y/Ho vs. Ce/Ce* scatter plot of the Lemarchant metalliferous mudstones. Samples scatter around the chondritic/plume-derived value of ~27, with only minor amounts of sample trending toward the seawater value of >44. B. Diagram to determine whether Ce anomalies are true anomalies or caused by positive La anomalies. Accordingly, the positive Ce anomalies in the Lemarchant samples are true Ce anomalies. Ce/Ce* and Pr/Pr* values are calculated based on McLennan (1989) and the equation Pr/Pr* = (Prsample/8.83)/SQRT((Cesample/79.6)*(Ndample/3.39)); Diagrams are after Bau (1996), Webb and Kamber (2000), and Slack et al. (2007).*
Discussion

Sediment provenance—evaluating hydrothermal, hydrogenous, and detrital components

The chemistry of metalliferous sedimentary rocks associated with the Lemarchant VMS deposit reflects the varying contribution of elements from (1) hydrothermal exhalation, (2) detrital sedimentation, and 3) those scavenged from seawater by hydrothermal particles (e.g., Boström and Peterson, 1966; German and Elderfield, 1990; German and Von Damm, 2003). Boström and Peterson (1966) illustrated that the relative contribution of hydrothermal and detrital components in sediments can be quantified by comparing the relative enrichments in base and transition metals, such as Fe, Mn, Cu, Ni, and Pb (exhalative), relative to Al (detrital). They also illustrated that elements, such as, Ba, Zn, W, Ca, Hg, As, and S, are associated with exhalative activity and also are enriched in these sediments (Boström and Peterson, 1966, 1969). Sulfide-rich mudstones

Fig. 13. Diagrams of redox-sensitive trace elements. A. Ni/Co vs. V/Cr. B. U-Th vs. V/Cr. Diagrams after Algeo and Tribovillard (2009).

Fig. 14. Various element plots testing hydrothermally versus hydrogenuously derived components. A. Y/Ho vs. Fe₂O₃/P₂O₅. B. Y/Ho vs. Ba.
at Lemarchant contain elevated base metal and transition element contents, particularly so in those that are spatially associated with massive sulfides and, thus, consist predominantly of hydrothermal components (Figs. 9A-C, 10A-F). This is the case regardless of stratigraphic position and most mudstones have between 40 to 80% hydrothermal input (Fig. 9A, B). The elevated base and transition metal contents (Fe, Cu, Zn, Pb) reflect derivation from hydrothermal fluids as precipitated polymetallic sulfide (Jones et al., 2006) and are consistent with the sulfide mineralogy of the mudstones (Figs. 5, 6).

In addition to base metals, the samples show enrichment in metalloids. The enrichment in Ba is typical of many VMS deposits (Lydon, 1984; Large, 1992; Huston et al., 2010) and is likely due to the formation of barite with Ba being derived from the thermochemical breakdown of feldspars in the hydrothermal reaction zone (Hamington et al., 2005; Griffith and Paytan, 2012). Reduced hydrothermal fluids transport the Ba\textsuperscript{2+}, which reacts with sulfate in the water column resulting in barite precipitates at or near the seafloor (Ohmoto and Goldhaber, 1997; Huston and Logan, 2004; Griffith and Paytan, 2012). The presence of barite in samples found in mudstones proximal to mineralization strongly favors a hydrothermal origin and a vent proximal location of deposition (Fig. 7). But, barite also occurs north of the Lemarchant Main zone.
in section 10SN, where currently no mineralization is known, suggesting potential for mineralization in this location as well (Fig. 2A). In addition to barite, however, other Ba minerals such as hyalophane and celsian (Fig. 7A-E), and witherite are present. The celsian typically overgrowth pyrite framboïds to form euhedral crystals (rhombs, blades) and occurs in pyrite-chalcopyrite-rich mudstones (Fig. 7A, B), commonly associated with massive semicrystalline barite layers, as bladed barite in veins, or as crack-seal-type barite veins that crosscut the mudstones and sulfides (Fig. 7C-E). The crack-seal textures suggest that later stage fluids must have remobilized the vent. In contrast to the vent-proximal mudstones, the basaltic interflow mudstones, or mudstones that have no close association to the mineralization show lower Ba levels, which indicates a more distal depositional environment.

Besides polynuclear sulfides and barite, the Lemarchant mineralization and mudstones have elevated levels of Au, Ag, Hg, Sb, and As, which are mirrored by the presence of electron Hg As (Fig. 6D-F), as well as acanthite, pyrrargyrite, stephanite, bladed barite, and carbonates. The presence of precious metals, elevated Hg-Sb-As, and bladed barite and carbonates are consistent not only with hydrothermal input, but specifically magmatic-hydrothermal (epithermal) input (e.g., Hannington and Scott, 1989), and are also found proximal to mineralization (and other areas, as for example, section 100+00N to 101+00N, south of the Lemarchant Man zone).

Anoxia versus scavenging

Fine-grained sedimentary rocks, such as black shales and hydrothermal mudstones are useful indicators of paleooceanographic conditions and basin redox. Furthermore, these units can locally shield massive sulfides from anoxic environment, thereby increasing their preservation potential (e.g., Goodfellow and McCutcheon, 2003; Peter, 2003; Sáez et al., 2011). Redox-sensitive trace elements, including the transition elements/oxyanions concentrations in shales/mudstones, are particularly useful for discriminating paleo-redox conditions in ancient environments (e.g., Tribovillard et al., 2006; Algeo and Tribovillard, 2009). The redox sensitive trace elements (As, U, V, Mo, Cr, Ni, and Co) are enriched in the Lemarchant mudstones and plot in the fields for depositation under anoxic bottom-water conditions (Fig. 13A, B). Paradoxically, the presence of abundant barite coupled with negative Ce anomalies in the samples, some with high Y/Ho, suggest deposition from an oxygenated water column (de Baar et al., 1988). The presence of marcasite additionally supports an oxygenated environment (Schieber, 2011). In most cases marcasite partially replaces pyrite and it is suggested that marcasite formed paragenetically late, after the higher temperature hydrothermal system ceased, because marcasite has higher growth rates and dominates over pyrite at lower temperatures and acidic conditions (pH <5; Schieber, 2011). Pyrite associated with the euhedral marcasite shows corrosion textures likely due to partial reoxidation (Schoonen and Barnes, 1991).

A basinal environment with hydrothermal activity is a unique setting associated with Fe oxyhydroxide particles that form during turbulent mixing of hydrothermal fluids with seawater. Oxyanions, such as HPO$_4^{2-}$, HVO$_4^{2-}$, CrO$_4^{2-}$, HS$_2$O$_8^{2-}$, and HPO$_4^{3-}$, are scavenged from seawater onto the exhaled Fe oxyhydroxide particles (Rudnicki, 1995). Accordingly, it is expected that more distally precipitated hydrothermal sediments show higher contents of these oxyanions. The high abundance of Fe oxyhydroxide particles in the buoyant and nonbuoyant hydrothermal plume also allows for increased scavenging of U, Mo, Ni, and Co from seawater (e.g., German and Von Damm, 2003); compared to basin environments with nonhydrothermal black shale deposition (Morford et al., 2005). Nonhydrothermal environments do not have the excessive scavenging rates of redox-sensitive elements onto Fe oxyhydroxide particles but are able to retain and enrich redox-sensitive elements within the sediment when reduced conditions prevail (Morford et al., 2005; Tribovillard et al., 2006). The Bell Island black shales and silicic mudstones fall within the oxic field in Figure 13 A-B, and deposition in an oxic environment is also supported by the presence of abundant ichnofauna in the Bell Island sedimentary rocks (Harazim et al., 2013).

Enrichments in the aforementioned oxyanions in the hydrothermal sediments are therefore not a function of the anoxic character of the basin, but rather the efficiency of scavenging these elements from seawater by upwelling hydrothermal particles in the hydrothermal plume. This ultimately results in hydrothermal sediments with an apparent (but not true) anoxic signature (e.g., Piercey et al., 2012, Fig. 13A, B). Furthermore, the longer the residence time of the hydrothermal particles in the plume, the more scavenging from seawater occurs, which will increase the apparent anoxic signature (Rudnicki, 1995; Peter et al., 2003; Fig. 16). Therefore, sediments deposited in a vent proximal environment have a more strongly pronounced hydrothermal signature, whereas sediments that precipitated in more distal environments have oxyanionic features more indicative of deposition under anoxic conditions. These same sediments, however, will also have a greater seawater REE signature with a more pronounced Ce anomaly, a feature of oxic seawater, and therefore the combination of seawater-like REE signatures and oxyanion enrichment can be used to distinguish apparent from real anoxic depositional conditions in hydrothermal sediments.

Physiochemical conditions of hydrothermal sediment formation: Insight from rare earth elements and Y (REY)

The REY in hydrothermal fluids, and by association hydrothermal sediments, provide significant insight into the physiochemical conditions of VMS formation. Unlike the other REEs, which occur in the trivalent state only, Eu and Ce have two redox states (di- and trivalent, and tri- and tetravalent, respectively) that are affected by the temperature and Eh-pH conditions of the hydrothermal fluids (Michard et al., 1983; Sverjensky, 1984; Bau, 1993). Europium is particular useful and its behavior in hydrothermal fluids is dependent on whether it is in its divalent or trivalent form. Furthermore, the Eu$^{2+}$/Eu$^{4+}$ redox equilibrium is strongly temperature-dependent, and under high-temperature (>$250^\circ$C), acidic and reducing conditions as in VMS hydrothermal fluids, divalent Eu is the predominant species in solution, and/or bound in related complexes (Sverjensky, 1984; Bau, 1999; Peter, 2003). Consequently, hydrothermal fluids and precipitates that are derived from high-temperature fluids have positive Eu$^{2+}$ anomalies (German and Von Damm, 2003; Peter et al., 2003), and given that all samples from the Lemarchant...
deposit, regardless of location or stratigraphic position, have positive Eu anomalies (Fig. 11A-C, E), it suggests deposition from fluids with temperatures greater than 250°C. In contrast, detrital sediments have no positive Eu anomalies (Peter and Goodfellow, 2003), a pattern that is reflected in the Bell Island black shales (Fig. 11F). Therefore, increased mixing of hydrothermal and detrital sediments can result in a masking of a positive Eu anomaly due to input of abundant detrital material (Peter and Goodfellow, 2003). Given that all samples have positive Eu anomalies, it suggests that the latter, dilution of the anomaly by detritus, was minimal and that the Eu/Eu* values represent the hydrothermal conditions of deposition for the mudstones.

Although Eu can provide insight into the thermal conditions of the fluids, Ce provides a proxy for the prevailing redox conditions during the precipitation of metalliferous sediments (McLennan, 1989; Peter, 2003). In oxidized ambient seawater, Ce³⁺ oxidizes to the less soluble Ce⁴⁺ after being scavenged onto Fe-Mn oxyhydroxides (German and Elderfield, 1990, Bau and Koschinsky, 2009), causing fractionation of the Ce⁴⁺ from the REE³⁺ (Peter et al., 2003; Bau and Koschinsky, 2009; Hannington, 2009) and resulting in a negative Ce anomaly of the surrounding seawater. These negative Ce anomalies are also present in pelagic clays (Elderfield and Greaves, 1981) and in currently formed hydrothermal sediments (Mills and Elderfield, 1995). Fe oxyhydroxides within metalliferous hydrothermal sediments gain their REEs from the hydrothermal vent fluids, and from seawater. The presence of the negative Ce anomalies in the hydrothermal sediments is inherited from mixing of the vent fluids with Ce-depleted oxygenated seawater (German and Elderfield, 1990; Hannington, 2009). No negative Ce anomalies are expected in reduced vent fluids, as Ce³⁺ will not oxidize to Ce⁴⁺ in such fluids (Mills et al., 2001; Peter and Goodfellow, 2003; Humphris and Bach, 2005), or when the shale sample is similar in composition to the shale used for normalization of the samples (e.g., post-Archean Australian shales). An absence of negative Ce anomalies can further be caused by large amounts of detrital input to the hydrothermal component (Peter and Goodfellow, 2003). Given that all of the mudstones from the Lemarchant deposit have weakly to strongly negative Ce anomalies argues very strongly that they have not been affected by significant detrital material and were deposited into an oxygenated water column.

Support for mixing with oxygenated seawater is also reinforced by the Y/Ho systematics of the hydrothermal metalliferous mudstones. Yttrium is typically enriched relative to Ho in oxygenated seawater relative to hydrothermal vent fluids (e.g., Bau, 1996; Bau and Dulski, 1999). Correspondingly, hydrothermal particles that have spent considerable residence time in an oxygenated water column will scavenge Y from the column and inherit a high Y/Ho ratio.

![Diagram](image-url)
Due to the general similarity of the REY patterns between the mudstones of various stratigraphic levels (Fig. 11A-C, E), it is suggested here that they were all derived from the same hydrothermal fluids. There are, however, slight variations, particularly in the Y systematics and size of the Eu anomalies. In particular, interflow mudstones and those more distal to mineralization have higher Y, Y/Ho, and slightly smaller positive Eu anomalies (Fig. 11B, C). Increased Y values from seawater seem to be weakly correlated with stronger negative Ce anomalies (Fig. 12A), indicating more REY scavenging from seawater due to longer residence times of the hydrothermal particles in the plume. Correspondingly, the utilization of Eu anomalies and lower Y/Ho ratios may be useful in delineating mudstones more proximal to mineralization than those distal from mineralization in similar geologic environments.

**Sediment provenance—basin setting and tectonics**

Provenance-related immobile element systematics of all four types of Lemarchant metalliferous mudstones and tuff have continental to oceanic island-arc signatures (Fig. 15A-C). This is strongly controlled, however, by local host rocks in the Lemarchant deposit. For example, the oceanic island-arc signatures are found predominantly in interflow mudstones within Lake Ambrose formation basalt and in some tuff samples, whereas those hosted primarily by Bindons Pond rhyolite have more continental island-arc signatures. These systematics are expected for sediments deposited in a graben/caldera basin in a rifted continental arc, or an arc proximal to continental crust, which is the suggested tectonic model for the Tally Pond belt (Rogers et al., 2006; McNicoll et al., 2010; Zagorevski et al., 2010; Piercey et al., 2014). The occurrence of mudstones with hydrothermal signatures within hanging-wall mafic volcanic rocks of the Lake Ambrose formation further indicates that the Lemarchant hydrothermal system and exhalation was still active during the emplacement of the basaltic lava flows.

A rifted arc environment is also consistent with much of the mineralogy, compositions, and paragenesis of the phases in the hydrothermal metalliferous sediments. It is proposed that the deposit likely formed at moderate to shallow water (>1,200 m) depth in a rift/caldera setting, which is atypical for most VMS deposits (Hannington et al., 2005; de Ronde et al., 2012). Due to this relatively shallow depth, and a suggested temperature of formation of >250°C, the boiling curve for seawater can be intercepted and shifted from the one-phase field (VMS-style mineralization) to the two-phase (liquid and vapor) field (magmatic-epithermal input due to boiling), when depth and pressure of the depositional system decrease and/or temperature increases (Fig. 17). Hence, the Lemarchant hydrothermal system records both normal seafloor hydrothermal activity and magmatic-epithermal fluid contributions (e.g., Gill and Piercey, 2014). Given that the mudstones are crosscut by younger sulfide and barite (Figs. 6B, C, 7C-E), it is proposed that they represent the first hydrothermal activity in the Lemarchant deposit. Mudstone deposition was followed by precipitation of barite and Zn-Pb sulfides, which themselves were cut by galena, electrum, and sulfosalts, and subsequently replaced or crosscut by Cu sulfides. This type of activity could reasonably be assumed to represent an earlier lower temperature Zn-Pb sulfide-forming event with barite precipitation, followed by fluid boiling leading to the epithermal suite minerals and electrum, and a final stage with a higher temperature Cu-rich fluid that overprinted the latter. A similar situation was described previously for the Lemarchant deposit by Copeland et al. (2009) and Gill and Piercey (2014). The late high-temperature Cu sulfide-forming event was followed by an event characterized by crack-and-seal-type barite veins that crosscut the Pb-Zn and Cu sulfides (Fig. 7E).

This type of model can also be accommodated by the tectonic regime of the region. In particular, early-stage Zn-Pb
epithelial activity could have occurred early in the basin's history during initial arc rifting. This shallower water environment would allow the hydrothermal fluids to intersect the depth to boiling curve and form epithelial suite enrichments due to phase separation (e.g., Hannington, 2009). With continued extension, the hydrothermal system would have subsided and allowed the system to get hotter (i.e., >300°C), enabled the fluids to carry Cu, and led to the formation of higher temperature Cu-Zn stringer mineralization and interstitial chalcopyrite typical of VMS deposits. This later stage chalcopyrite phase is recorded within the mudstones as well as in the massive sulfides at Lemarchant (Gill and Piercy, 2014). However, chalcopyrite predominantly occurs as stringer type, and not as massive sulfide ore. This suggests that temperatures between >300° to 350°C were not sustained over a long period of time. At temperatures >350°C hydrothermal fluids are undersaturated in metals, and leaching of chalcopyrite will occur (Large, 1992), a feature, which is not observed at Lemarchant. Accordingly, the Lemarchant mineral assemblages provide some evidence of water depth, the presence of positive Eu anomalies (T >250°C), and the lack of massive chalcopyrite ore (T <325°C), as well as evidence for boiling and an epithelial element suite, suggests that the deposit formed between 250° and 325° (Fig. 17). This broadly coincides with measurements of modern arc-related hydrothermal systems (Hannington et al., 2005), which are similar to the environment of formation of the Lemarchant deposit.

Conclusions

The Lemarchant deposit provides an understanding of the relationship of hydrothermal metalliferous mudstones to mineralization in bimodal felsic environments. Exploration criteria to delineate potentially productive from less prospective mudstones from this study include: (1) the hydrothermal mudstones have elevated Fe and base metals, and plot within the hydrothermal fields in Boström-type plots; (2) an enrichment in base metal sulfides, barite, and epithelial suite elements, namely Hg-Sb-As, that is unique to the Lemarchant deposit in the Tally Pond belt, but similar to other VMS epithelial hybrids in comparable settings, and which enables potentially prospective mudstones using a Ba-Hg diagram to be identified; and (3) REY systematics that are indicative of deposition from high-temperature fluids (i.e., Eu/Eu* >1), and that are rock buffered (i.e., Y/Ho ~27 and not like seawater with Y/Ho >44), with or without evidence for mixing with oxygenated seawater (Ce/Ce* <1). Additionally, due to processes occurring within the hydrothermal plume, i.e., mixing of hydrothermal fluids with seawater and scavenging of hydrogenous elements, metalliferous sediments can record paleoredox conditions at the time of precipitation. Redox-sensitive proxies, such as occurrences of barite and marcasite, and the presence of positive Ce anomalies, are indicative of deposition of the metalliferous Lemarchant exhalates from an oxygenated water column. Even though V-Cr-Ni-Co-Mo-U characteristics suggest an anoxic depositional environment, enhanced scavenging of oxysanions onto Fe oxyhydroxides possibly creates this apparent anoxic environment.

These geochemical and mineralogical signatures are useful for the Tally Pond belt and likely similar environments globally. The results herein, however, require further testing and this can only be achieved via increased drill hole density and two- and three-dimensional sampling coupled with a sound understanding of the basin geology and architecture.

Acknowledgments

This research was funded by the Canadian Mining Research Organization (CAMIRO) and an NSERC CRD grant. Kind support was provided by Christine Devine, Dianne and Charlie Fost, Michael Vande Gucht, Alexandra Marcotte, and Bryan Sparrow from Paragon Minerals Corporation (now Canadian Zinc Corporation). Research was also funded by the NSERC-Altius Industrial Research Chair in Mineral Deposits, funded by NSERC, Altius Resources Inc., and the Development Corporation of Newfoundland and Labrador. Furthermore, the help and support from the technical staff, Lakmali Hewa, Keir Hiscock, and Pam King, as well as the Piercy research group, and especially from Michael Buschette, Jonathan Cloutier, Shannon Gill, Shannon Guffey, Dario Harazim, Hannah Mills, Inês Nobre Silva, and Jean-Luc Pilote, are greatly appreciated. Additionally, we thank John Hinchee from the Geological Survey of Newfoundland for his help and support. Also very much appreciated are the reviews and recommendations of Economic Geology reviewers, Paul Spry and Nils Jansson, which greatly improved the manuscript.

REFERENCES


Ridler, R.H., 1971, Analysis of Archean volcanic basins in the Canadian Shield using the exhalite concept: Bulletin of the Canadian Institute of Mining and Metallurgy, v. 64.


