Provenance of exhalites associated with the Lemarchant volcanogenic massive sulphide (VMS) deposit, central Newfoundland, Canada: insights from Nd isotopes and lithogeochemistry

Stefanie Lode1*, Stephen J. Piercey1 & Jonathan Cloutier2

1 Department of Earth Sciences, Memorial University, 300 Prince Philip Drive, St John’s, NL A1B 3X5, Canada
2 Department of Earth Sciences, University of St Andrews, St Andrews KY16 9AL, UK
© 2017 The Author(s). Published by The Geological Society of London. All rights reserved. For permissions: http://www.geolsoc.org.uk/permissions.
*Correspondence: slode@mun.ca

Abstract: Neodymium isotope data on exhalites and tuffs from the Cambrian Lemarchant volcanogenic massive sulphide (VMS) deposit provide insights into the tectonic environment of the Tally Pond group, Canada. New data from exhalites from the Lemarchant area show evolved values of εNd513 = −6.0 to −1.8, whereas the associated volcanic rocks have εNd513 of +0.4 to +1.4. The Lemarchant exhalite εNd compositions overlap the underlying Ganderian Neoproterozoic Sandy Brook Group (εNd = −6.5 to −1.9) and Crippleback Intrusive Suite (εNd = −5.9 to −5.2). The evolved Nd isotopic signatures suggest that the volcanic rocks of the Tally Pond group were formed upon Ganderian arc basement, which itself was possibly built upon, or proximal to, the Gondwanan Amazonian margin. Erosion of older crustal material and Tally Pond group volcanic rocks, together with coeval eruption of the volcanic rocks, released Nd-rich detritus into the water column. Uptake of eroded detrital and scavenged Nd resulted in mixed Nd sources (juvenile and evolved), which are archived in the exhalites. The results of this study are not only of significance for occurrences of exhalites within the Tally Pond group, but also have exploration implications for VMS districts globally.

Received 26 January 2017; revised 22 May 2017; accepted 31 May 2017

The Tally Pond group, central Newfoundland Appalachians, Canada, represents a volcanic belt that hosts abundant volcanogenic massive sulphide (VMS) deposits that are locally genetically associated with exhalites (Fig. 1a and b; Franklin et al. 1981; Lydon 1984; Swinden 1991; Squires & Moore 2004). Exhalites are metalliferous sedimentary rocks and are also described as metalliferous/hydrothermal mudstones, iron formation, tetsukiei (‘iron quartz’), tuffite, vassikis (‘Weißkies’ = ‘white sulphide’), also used for sulphidic black chert; Peter & Goodfellow 1996; Szy et al. 2000; Peter 2003; Hannington 2014). Exhalites represent a hiatus in the volcanic activity where the deposition of hydrothermal products is dominant over the abiogenic background sedimentation and/or deposition of volcaniclastic–epiclastic material (Lydon 1984). The lithogeochemical signatures of exhalites can be utilized to discriminate between predominantly hydrothermally or detritally (i.e. non-hydrothermal) derived material in exhalative rocks (Fig. 2a; Boström et al. 1972; Boström 1973; Peter 2003; Lode et al. 2016). The Lemarchant exhalites are dominated by elevated Fe/Al and Zn–Pb–Cu contents compared with detrital sedimentary rocks, and have shalenormalized negative Ce and positive Eu anomalies, indicative of deposition from high-temperature (>250°C) hydrothermal fluids within an oxygenated water column, rather than being the product of predominantly detrital sedimentation (Fig. 2a and b; Boström & Peterson 1969; Boström et al. 1972; Boström 1973; Sverjensky 1984; de Baar et al. 1988; German & Von Damm 2003; Peter 2003; Lode et al. 2015).

The Tally Pond group, which is part of the Dunnage Zone, Newfoundland, Canada, belongs to the Cambrian (c. 515 Ma) to Permian (c. 273 Ma) Appalachian–Caledonide mountain belt, which hosts numerous VMS deposits, including the past-producing Duck Pond and Boundary mines, and the precious metal-bearing Lemarchant deposit (Fig. 1a and b; Williams 1979; Swinden 1988, 1991; Evans & Kean 2002; Grenne & Slack 2003; Rogers et al. 2007; van Staal & Barr 2011; Piercey et al. 2014; Hollis et al. 2015). The Tally Pond group (c. 513 – 509 Ma) volcanic rocks and related massive sulphide mineralization formed during arc rifting during the construction of the Cambrian to Early Ordovician Penobscot Arc, which is known to be built upon Ganderian Neoproterozoic (c. 563 Ma) arc basement of the Crippleback Intrusive Suite and the coeval Sandy Brook Group (Pollack et al. 2002; Zagorevski et al. 2007; Piercey et al. 2014). In the Neoproterozoic and Early Cambrian Ganderia was located NW of the Gondwanan Amazonian margin (Fyffe et al. 2009; van Staal et al. 2012; Murphy et al. 2014). The Penobscot Arc represented the leading edge of Ganderia in a suprasubduction-zone setting and arc rifting was initiated as a result of slab roll-back along this margin (Jennet & Swinden 1993; Schulz et al. 2008; Murphy et al. 2014). The basement to the Ganderian arc is not exposed; however, detrital zircon and Nd isotopic studies indicate the presence of older crustal rocks that were derived from the Gondwanan Amazonian craton (Nance et al. 2008; Schulz et al. 2008). Rifting of the Penobscot Arc led to the formation of VMS mineralization and associated hydrothermal sedimentary rocks of the Tally Pond group (Rogers et al. 2006; Copeland et al. 2009; Zagorevski et al. 2010; Piercey et al. 2014; Lode et al. 2016). During rifting of the Penobscot Arc there was extension, massive sulphide formation and the genesis of exhalites that formed from the deposition from buoyant hydrothermal plumes from black smokers (Hekinian et al. 1993; Hannington et al. 1995; German & Von Damm 2003).

These black smokers and associated exhalites occur where hydrothermal fluids are focused along deep synvolcanic faults in extensional settings (e.g. ocean ridges, rifted arcs or back-arc basin spreading centres; Fig. 3; Lydon 1984; Hannington et al. 2005;
Fig. 1. (a) Tectonostratigraphical 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. Notre Dame Subzone VMS: 1, York Harbour; 2 – 8, Baie Verte Belt Deposits; 9 – 12, 46, Springdale Belt Deposits; 13 – 29, Buchans–Roberts Arm Deposits. Exploits Subzone VMS: 30 – 37, Tulks Belt Deposits. Tally Pond Group Deposits: 39, Lemarchant; 40, Duck Pond; 41, Boundary; 42 – 45, Point Leamington Belt Deposits. Modified after Swinden (1991) and Piercey (2007). (b) Geological map of the Tally Pond group. The Tally Pond group comprises the Lemarchant deposit and the Duck Pond and Boundary mines. Figure after Copeland (2009) and Map 2006-01 from Squires & Hinchey (2006) and Lode et al. (2017).
The hydrothermal fluids consist of modified seawater, which is entrained through oceanic or rift-related continental crust, and are variably metal bearing with Fe, Mn, Cu, Pb and Zn, as well as reduced S and Si (Von Damm 1990; German & Von Damm 2003; Galley et al. 2007; Tivey 2007; Huston et al. 2010). The metals and other ligands are generally derived from seawater and leached from host rocks (e.g. metals, Si ± S; Fig. 3; Hannington et al. 2005; Huston et al. 2011). Hydrothermal plume-derived Fe-oxyhydroxides are efficient scavengers of trace metals (e.g. oxyanions such as $\text{HPO}_4^{2-}$, $\text{VO}_4^{2-}$, $\text{CrO}_4^{2-}$ and $\text{AsO}_4^{2-}$) and rare earth elements (REE) plus Y from seawater (Mills & Elderfield 1995; Rudnicki 1995). A rifted arc environment exposes rock units of different ages, and hence varying Nd isotopic signatures, which contribute detrital material to the hydrothermal matter in the exhalative sedimentary rocks as a result of erosional and weathering processes (Keto & Jacobson 1988; Mills & Elderfield 1995). Therefore, exhalites record not only seawater REE (including Nd) but also the diverse provenance components of the detrital sources at the time of formation, even though the detrital matter is only a minor constituent compared with the hydrothermal matter (Mills & Elderfield 1995; Peter 2003; Lode et al. 2015).

By using various isotopic tracers, such as Nd isotopes, it is possible to decipher the potential sources of various components in hydrothermal sedimentary rocks. The Nd isotopic system is specifically useful for understanding the relative roles of evolved versus juvenile crust, and provides further insight into the tectonic environment and provenance of the exhalites, as it is robust and not significantly modified by diagenetic, hydrothermal and metamorphic processes (McCulloch & Wasserburg 1978; McLennan et al. 2003). In addition, the separation of Sm–Nd in Earth’s reservoirs is particularly useful in delineating juvenile versus evolved crust and the time-integrated sources of constituents of Earth materials (McCulloch & Wasserburg 1978; Rollinson 1993; McLennan et al. 2003). The Tally Pond group volcanic rocks have εNd signatures that are typically positive, whereas their basement rocks (i.e. the rifted arc rocks of the Neoproterozoic Crippleback Intrusive Suite and the bimodal volcanic rocks of the Sandy Brook Group) show more evolved εNd values (McLennan et al. 1993; Rogers et al. 2006; Nance et al. 2008; McNicoll et al. 2010; Piercey et al. 2014). Given the level of preservation of stratigraphy of the lithofacies in the Lemarchant deposit, including the exhalites, this deposit is an excellent location to understand the provenance of exhalites in ancient rifted arcs. Correspondingly, the Nd isotopic signatures in the exhalites may be useful in outlining the provenance of these deposits and the potential contributions of local, basement or distal sources in their genesis. Thus, the purpose of this study is to (1) determine the sources of Nd in the exhalites and massive sulphides of the Lemarchant deposit and (2) because the Tally Pond group is formed upon Ganderian and possibly older basement rocks, to evaluate the relative roles of mantle and evolved crustal inputs that contributed to the Lemarchant hydrothermal sedimentary rocks using the Nd isotope compositions of exhalites.
Regional geology

The Tally Pond group is located within the Central Mobile Belt, Newfoundland, Canada, which is part of the Cambrian (c. 515 Ma) to Permian (c. 275 Ma) Appalachian mountain belt (Williams 1979; Swinden 1988; Rogers et al. 2007; van Staal & Barr 2011). The Newfoundland Appalachians are divided into four tectonostratigraphical zones (from west to east): the Humber, Dunngan, Gander and Avalon zones (Fig. 1a; Williams 1979; Swinden 1988, 1991). The Dunngan Zone represents the Central Mobile Belt (Williams et al. 1988; Swinden 1991; Rogers et al. 2007). These zones result from and were affected by the successive accretion of three microcontinental blocks during the Early Palaeozoic to Middle Palaeozoic (i.e. Dartmouth, Taconic orogenesis; Ganderia, Salinic orogenesis; and Avalonia, Acadian orogenesis) and related interoceanic arcs and back-arcs (Swinden 1991; Zagorevski et al. 2010). In the Palaeozoic (Middle Cambrian to Ordovician), these ribbon-shaped microcontinental blocks separated from Gondwana and Laurentia, forming peri-Gondwanan and peri-Laurentian terranes, and subsequently accreted to Laurentia, creating the composite Laurentian margin (Rogers et al. 2007; Zagorevski et al. 2010; van Staal & Barr 2011). The Exploits Subzone represents two phases of arc–back-arc formation: the Cambrian to Early Ordovician Penobscoot Arc and the Early to Middle Ordovician Victoria Arc (Zagorevski et al. 2010). The Tally Pond group and its VMS deposits (Duck Pond and Boundary mines; Lemarchant deposit; Fig. 1b) are hosted in the lower Victoria Lake supergroup within the Exploits Subzone, which is composed of Cambrian to Ordovician volcanic and sedimentary rocks (Dunning et al. 1991; Rogers et al. 2007; McNicoll et al. 2010; van Staal & Barr 2011). 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, Long Lake and Tally Pond groups; (4) the Sutherlands Pond group; (5) the Pat Pond group; (6) the Wigwam Pond group; the Tulks, Long Lake and Tally Pond groups are known to host VMS deposits. These six tectonic assemblages yield U–Pb zircon ages ranging from c. 513 to 453 Ma (Dunning et al. 1987, 1991; Evans et al. 1990; Evans & Kean 2002; Zagorevski et al. 2007; McNicoll et al. 2010). Furthermore, the Tally Pond group is informally subdivided into the felsic volcanic rock dominated Bindons Pond formation (also referred to as Boundary Brook formation; Pollock 2004) and the mafic volcanic rock dominated Lake Ambroise formation (Rogers et al. 2006). The latter contains island arc tholeiitic basalts to andesites with εNd(t) 11 Ma of +3.1 (Dunning et al. 1991; Evans & Kean 2002; Rogers et al. 2006), whereas the former contains predominantly transitional to calc-alkalic rhyolitic to dacitic rocks with εNd(t) 11 Ma of +1.8 to +2.6 (Rogers et al. 2006; McNicoll et al. 2010; Piercey et al. 2014). The Cambrian felsic volcanic rocks of the Bindons Pond formation contain inherited zircons with Neo-proterozoic U–Pb ages of 563 Ma (McNicoll et al. 2010).

Deposit geology and lithofacies

The Lemarchant VMS deposit is hosted within the Bindons Pond formation and is capped by a <1 to 20 m thick layer of exhalites occurring at the contact between the bimodal volcanic rocks of the Bindons Pond and Lake Ambroise formations (Fig. 4a; Copeland et al. 2009; Fraser et al. 2012; Lode et al. 2015). These sulphide-rich exhalites extend discontinuously across the massive sulphides for 1–4 km (Copeland et al. 2009; Fraser et al. 2012; Lode et al. 2015). Three main types of exhalites occur at the Lemarchant deposit: (1) exhalites immediately on top of massive sulphide mineralization between the felsic and mafic volcanic rocks (exhalative–massive sulphide (EMS)-type; Fig. 4a–c, g and h); (2) exhalites extending laterally outwards from mineralization, but at the same stratigraphical level and without immediate association with mineralization (felsic–exhalative–mafic (FEM)-type; Fig. 4d); (3) interflow exhalites within the hanging-wall basaltic rocks (IFE-type; Fig. 4e). Interflow exhalites occur commonly within 15 m above the massive sulphide mineralization, but are present up to 70 m stratigraphically above the ore horizon. Crystal lithic vitric (locally vitric crystal) tuff is intercalated with the exhalites and surrounding mafic and felsic volcanic lithologies, and commonly contains chloritized glass shards and locally euhedral apatite phenocrysts (Fig. 4f). Independent of their stratigraphical positions, the exhalites are brown to black, graphite-rich, finely laminated, and contain fine carbonaceous or organic-rich laminae that are intercalated with siliciclastic, volcanoclastic and/or amorphous kidney-shaped chert ± apatite layers (Fig. 4a–c). The main sulphide phases are pyrite (framboidal, massive and euhedral) and pyrrhotite, with minor marcasite, chalcopyrite, sphalerite, arsenopyrite and galena (Fig. 5a–c). Sphalerite commonly displays chalcopyrite disease (Fig. 5a). Contents of chalcopyrite, sphalerite and galena increase proximal to mineralization. The sulphides occur both parallel to bedding and in later stage, stringer-like veins (Fig. 4a–c). Ba-mineral phases include barite (BaSO4; Fig. 4f), the Ba-rich feldspar celsian (BaA12(Si2O8)·O8) and a barian K-feldspar with <2 wt% Ba (hyalophane or barian adularia (K, Ba)Al(Si,Al)3O8). Barite locally forms anhedral (semi)-continuous layers or occurs as bladed crystals in vugs or veins, which are often associated with bladed Ca–Fe–Mg–Mn-carbonates.

All types of the Lemarchant exhalites (proximal, distal and interflow) have variable contributions of hydrothermal (high Fe/Al and base metal values; Fig. 2a) and detrital components (lower Fe/Al and base metal values). Furthermore, they display positive shale-normalized Eu anomalies and positive Ce anomalies (Fig. 2b). These signatures suggest precipitation from reduced, high-temperature (>250°C) hydrothermal vent fluids in an oxygenated water column in a hydrothermal vent proximal setting (Lode et al. 2015, 2016). Deposition into an oxygenated water column in a vent proximal environment is also supported by the presence of barite in both the exhalites and associated massive sulphides, as well as the S-isotopic signatures of sulphides within the exhalites (Lode et al. 2017). The δ34S systematics (ranging from −38.8 to +14.4‰, with an average of c. −12.8‰) indicate that S was predominantly biogenically derived via microbial or biogenic sulphate reduction of seawater sulphate, microbial sulphide oxidation and microbial disproportionation of intermediate S compounds, but also from inorganic thermochemical sulphate reduction (Fig. 5a–d). The latter is more pronounced in sulphides from the proximal EMS-type Lemarchant exhalites (Fig. 5d; Lode et al. 2017). Combined detailed lithogeochemical, mineralogical, and S- and Pb-isotopic studies and the stratigraphical context of these sulphide-rich mudstones, and intimate association with massive sulphides, suggests that they are hydrothermal in origin and formed from black smoker plume fallout and true exhalites rather than detrital sedimentary rocks (Lode et al. 2015, 2016, 2017).

Methods

Sampling, methods, and quality control and quality assurance (QA/QC)

Samples were collected during stratigraphical mapping and drill core logging of the Lemarchant deposit from drill holes that have exhalites and include the Lemarchant Main Zone, the Northwest and 24 zones, as well as the North and South targets (Fig. 6a). Samples were taken from representative exhalite types (EMS, FEM and IFE), tuff, and surrounding mafic and felsic volcanic units. The whole-rock lithogeochemical data were previously evaluated and presented by Lode et al. (2015), including analytical methods and
Nd isotopic provenance of Lemarchant exhalites

**Fig. 4.** Core photographs of the main Lemarchant exhalite types and associated felsic and mafic volcanic rocks of the Bindons Pond and Lake Ambrose formations, respectively, and scanning electron microscope (SEM) image in back-scattered electron (BSE) mode of tuff intercalated with exhalite. (a) Finely laminated sulphide-rich EMS-type exhalite with cross-cutting stringer type veins and overlying massive sulphide mineralization. Section 101N, LM11-65, exhalite sample CNF30983, 160.7 m. (b) Proximal EMS-type exhalite associated with the Lemarchant Main Zone. Section 102 + 50N, LM10-43, CNF20976, 202.3 m. (c) Proximal EMS-type exhalite with intercalated chert–apatite layers. Section 101N, LM07-13, CNF30954, 164.7 m. (d) FEM-type exhalite associated with the Northwest Zone. Section 106N, LM08-28, CNF20986, 240.6 m. (e) Sulphide-rich interflow exhalite. Section 101 + 25N, LM13-79, CNF25072, 169.0 m. (f) Euhedral apatite (Ap) phenocrysts in an aphanitic quartz (Qz), feldspar, and chlorite-rich matrix of a vitric crystal tuff that is intercalated with FEM-type exhalite. Other phases are chlorite (Chl) in a vein, pyrite (Py) and barite (Brt). Section 104 + 51N, LM08-19, CNF30957a, 98.89 m. (g) Felsic to intermediate volcanic rock of the Bindons Pond formation located in the North target. Section 108N, LM11-49, 144.6 m. (h) Mafic to intermediate volcanic rock of the Lake Ambrose formation located in the North target. Section 108N, LM11-49, 422.9 m.
QA/QC for lithogeochemical data. Lithogeochemical data are reproduced here only to compare with Nd isotope results.

**Neodymium isotopes**

Twelve representative samples in total were selected for Nd isotopic determinations, including 10 exhalites from the three main exhalite types and two tuffs that are intercalated with the exhalites (Fig. 4a–f). These samples were chosen to cover both the horizontal and vertical distributions of all exhalite types and tuff occurring in the Lemarchant area. Additionally, one least altered sample of the felsic and mafic volcanic rocks (Fig. 4g and h) was selected for analyses, and for comparison with exhalite samples. Samarium and Nd isotopic compositions were measured at Memorial University by thermal ionization mass spectrometry (TIMS) using a multicollector Finnigan MAT 262 system in static and dynamic acquiring modes. Samples for Nd analyses were prepared using the methods of Fisher et al. (2011) from whole-rock powders using a multi-acid (HF, HNO$_3$ and HCl) dissolution–evaporation process. Separation of Sm and Nd was achieved using conventional two-step column chemical methods (Fisher et al. 2011).

Accuracy and precision for the Nd analyses were determined using the standards JNd1-1 and BCR-2 as reference materials following methods described by Fisher et al. (2011). The JNd1-1 and BCR-2
Results

Neodymium isotopic systematics

The Lemarchant exhalites ($n = 10$) have $\varepsilon_{Nd}^{513 \text{ Ma}} = -6.0$ to $-1.8$ and $T_{DM} = 1.63 - 3.05 \text{ Ga}$ (Table 1). Overall, the three types of Lemarchant exhalites (EMS, proximal; FEM, distal; IFE, interflow) have similar $\varepsilon_{Nd}^{513 \text{ Ma}}$ values, however, the EMS-type have greater Th/Sc containing lower $\varepsilon_{Nd}^{513 \text{ Ma}}$ values similar to upper crust values (Fig. 7b) the FEM-type are less evolved and range from $-4.0$ to $-3.2$ with an average of $-3.7$; and the IFE-type has the widest range of $\varepsilon_{Nd}^{513 \text{ Ma}} = -6.0$ to $-1.8$ and average of $-3.9$ (Table 1; Figs 6b and 7a, b). The Lemarchant tuff samples ($n = 2$) have $\varepsilon_{Nd}^{513 \text{ Ma}} = -5.7$ to $-4.7$ with an average of $-5.2$ and $T_{DM} = 1.75 - 1.81 \text{ Ga}$. In $\varepsilon_{Nd}$ v. Th/Sc space the Lemarchant exhalites and tuff have Th/Sc ratios of 0.06 - 1.93 and fall between the arc andesite and old crust fields, with samples that have greater Th/Sc containing lower $\varepsilon_{Nd}$ values similar to upper crust values (Fig. 7a). These more evolved samples also trend towards the field of the 563 Ma Crippleback Intrusive Suite and Sandy Brook Group basement rocks (recalculated here at 513 Ma for comparison; Fig. 7a). The Lemarchant felsic and mafic volcanic rock measured in this study have $\varepsilon_{Nd}^{513 \text{ Ma}} = +0.4$ and a $T_{DM} = 1.47 \text{ Ga}$, and $\varepsilon_{Nd}^{513 \text{ Ma}} = +1.4$ and a $T_{DM} = 1.74 \text{ Ga}$, respectively, and plot in the field for arc rocks (Table 1; Fig. 7b). These values for the Lemarchant volcanic rocks are similar to values reported by Rogers et al. (2006) and McNicoll et al. (2010) for felsic and mafic volcanic rocks of the Tally Pond volcanic belt, including samples from the ‘Upper Block’ and the ‘Mineralized Block’ of the Duck Pond deposit (Fig. 7b).

The $\nu_{Sm-Nd}$ reflects the fractional deviation of $^{147}\text{Sm}^{144}\text{Nd}$ from CHUR in parts per 10$^4$ because of light REE enrichment (i.e. lower Sm/Nd) during igneous differentiation processes (McLennan et al. 2003). Accordingly, in $\nu_{Sm-Nd}$ v. $\varepsilon_{Nd}$ space (Fig. 7b) the $\varepsilon_{Nd}^{513 \text{ Ma}}$ values for the Lemarchant exhalite and tuff samples are more evolved than those for the Lemarchant volcanic rocks, and are comparable with values reported by Rogers et al. (2006) for the Neoproterozoic Crippleback quartz monzonite and Sandy Brook Group rhyolite. However, the $\nu_{Sm-Nd}$ values for the Lemarchant exhalite and tuff samples are higher than those for the Neoproterozoic Crippleback quartz-monzonite and Sandy Brook Group rhyolite and trend towards those of the Tally Pond group.
Table 1. Sm-Nd isotope data for Lemarchant exhalites and bimodal volcanic rocks

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drill hole</th>
<th>Section (N)</th>
<th>TDM (Ma)</th>
<th>εNd</th>
<th>143Nd/144Nd</th>
<th>147Sm/144Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z21 – East</td>
<td>LM1-94x</td>
<td>10060</td>
<td>0.109000</td>
<td>0.511672</td>
<td>0.512161</td>
<td>0.126400</td>
</tr>
<tr>
<td>Z21 – East</td>
<td>LM1-72</td>
<td>10060</td>
<td>0.120500</td>
<td>0.511685</td>
<td>0.512477</td>
<td>0.142800</td>
</tr>
<tr>
<td>Z21 – East</td>
<td>LM1-70</td>
<td>10060</td>
<td>0.120500</td>
<td>0.511685</td>
<td>0.512600</td>
<td>0.164400</td>
</tr>
</tbody>
</table>

εNd, εNd505 Ma, εNd511 Ma = +1.4 and +0.4, respectively, which are comparable with values that were previously reported for the Tally Pond group volcanic rocks (Fig. 7b; McLennan et al. 2003). The εNd values of the Lemarchant exhalite and tuff samples do not show any spatial variations throughout the zones of the deposit and/or with depth in the stratigraphy in the Lemarchant area (Fig. 6a and b). The TDM values of 1.63 – 3.05 Ga of the Lemarchant exhalites are older than reported values for the coeval felsic volcanic rocks of the ‘Upper Block’ and ‘Mineralized Block’ at Duck Pond of 1.06 and 1.35 Ga, and 0.95 Ga, respectively (McNicoll et al. 2010), and those of the Crippleback Intrusive Suite (1.26 and 1.35 Ga) and the Sandy Brook Group (1.15 – 1.34 Ga; Rogers et al. 2006; this study).

**Immobile element systematics**

Volcanic rocks of the Tally Pond group that are associated with the hydrothermal sedimentary rocks and volcanic and igneous rocks of the Sandy Brook Group and Crippleback Intrusive Suites are shown on the immobile element Zr/Ti-Nb/Y classification diagram of Winchester & Floyd (1977) and Pearce (1996) in Figure 8. This plot allows us to discriminate and identify rock types, independently from the degree of alteration (Winchester & Floyd 1977; Pearce 1996). The volcanic rocks from the Lemarchant deposit are subalkaline basaltic andesites, with more felsic rocks trending towards the dacite boundary, and the more mafic rocks trending towards the basalt boundary (Fig. 8). Because of the limited number of samples for volcanic rocks from this study, fields from Cloutier et al. (2017) were added for felsic, intermediate and mafic volcanic rocks from the Lemarchant deposit (Fig. 8). Additionally, samples for Tally Pond group felsic and mafic volcanic rocks, the Sandy Brook Group rhyolite and basalt and Crippleback quartz monzonite of Rogers (2004) and Rogers et al. (2006) were also added for comparison. Chemically, the volcanic rocks of Lemarchant show a wide distribution, with felsic-dominated rhyolite–dacites of the Bindons Pond formation as well as intermediate andesite–basaltic andesites and mafic rocks of the Lake Ambrose formation (Cloutier et al. 2017), which is consistent with potential source rocks for the detrital constituent in the hydrothermal sedimentary rocks and regional models for the Tally Pond group (e.g. Rogers et al. 2007; Piercey et al. 2014).

**Discussion**

### Provenance, tectonic setting and the role of crustal input

The Tally Pond group represents the oldest magmatism of the Penobscol Arc and was developed during phases of arc rifting at the leading edge of the Ganderian margin (Rogers et al. 2006; Zagorevski et al. 2010; Piercey et al. 2014). Penecontemporaneously, further rifting on the trailing edge of Gondwana led to the formation of the Ellsworth belt (c. 509 – 505 Ma) of coastal Maine and New Brunswick, representing the separation of Gondwana from the Gondwanan Amazonian margin (Fyffe et al. 2009; van Staal et al. 2012). The volcanic rocks of the Ellsworth terrane comprise tholeiitic basalts and rhyolites with εNd505 Ma = +5.6 to +8.6, but also calc-alkaline rhyolite (R-1 Rhyolite) that yielded εNd505 Ma c. 0 (Schulz et al. 2008). The latter values of c. 0 are similar to the εNd values of felsic and mafic volcanic rock samples from the Tally Pond group (Bindons Pond and Lake Ambrose formations) of this study (εNd = +1.4 and +0.4, respectively), which are comparable with values that were previously reported for the Tally Pond group volcanic rocks (Fig. 7b; Rogers et al. 2006; Zagorevski et al. 2010). This illustrates that the Lake Ambrose formation basalts have predominantly juvenile signatures (εNd511 Ma = +1.3; Rogers et al. 2006; this study), whereas Bindons Pond formation rhyolites and dacites have less juvenile values (εNd511 Ma = +1.8 and +2.0) (Rogers et al. 2006; Zagorevski et al. 2010). There is a noticeable difference in
Nd isotopic provenance of Lemarchant exhalites

\[ \varepsilon_{\text{Nd}} \]

values between the sedimentary and volcanic rocks of the Lemarchant deposit, however. In general, the exhalites and tuffs have lower \( \varepsilon_{\text{Nd}} \) values ranging from \(-6.0\) to \(-1.8\) (Fig. 7a and b), like the Sandy Brook Group rhyolite \( \varepsilon_{\text{Nd}} = -6.5 \) to \(-1.9\) and the Crippleback Intrusive Suite \( \varepsilon_{\text{Nd}} = -5.9 \) to \(-5.2\) (Rogers et al. 2006). Mafic volcanic rocks are common in the Sandy Brook Group; however, no Nd isotopic data have been published, thus no comparison can be made with data from this study. Kerr et al. (1995) presented data for Late Precambrian mafic rocks of the Valentine Lake Pluton, which is correlative to the Crippleback Intrusive Suite, and may also represent a correlative mafic unit to the Sandy Brook Group mafic rocks (Kerr et al. 1995). The Valentine Lake Pluton mafic rocks yielded an \( \varepsilon_{\text{Nd}} \) of \(+0.5\) (Kerr et al. 1995). Given the similarities to Tally Pond mafic rocks, it is not possible to clearly distinguish the Late Precambrian mafic rocks from the Cambrian mafic volcanic rocks of the Tally Pond group. Considering that the exhalites, regardless of the exhalite type (proximal, distal or interflow), have negative \( \varepsilon_{\text{Nd}} \) values, contributions from mafic sources from either the Tally Pond group or underlying Sandy Brook Group appear minimal and negligible.

There are a number of potential Nd sources in hydrothermal sedimentary rocks (exhalites), including seawater-derived or
-scavenged, detrital and hydrothermally derived components (Goldstein et al. 1984; Mills et al. 1993; Mills & Elderfield 1995). Scavenging of REE from seawater occurs during mixing of the hydrothermal fluids with seawater, where oxynions (e.g. HPO$_4^{2-}$, HVO$_4^{2-}$, CrO$_4^{2-}$, HASO$_4^{2-}$), trace elements and REE (including Nd) are scavenged from seawater onto Fe-oxyhydroxides and subsequently deposited around the hydrothermal vent site (de Baar et al. 1988; Rudnicki 1995; German & Von Damm 2003; Peter 2003). Nd isotopic signatures measured from modern seawater show a wide range that indicates that continental Nd is the predominant source of REE in modern seawater, resulting in different Nd values within the main water masses or oceans (Goldstein et al. 1984; Bertram & Elderfield 1993; Tachikawa et al. 2003). Thus, exposure of crustal basement during arc rifting would bring crustally derived evolved Nd into the ambient seawater, together with Nd derived from the broadly contemporaneously eruptions and erosion of the more juvenile Cambrian Tally Pond group volcanic rocks. Both sources of Nd would allow for scavenging of Nd that is dissolved in the water column via adsorption, or via a particulate Nd shuttle as detrital grains (e.g. detrital monazite; Wood & Williams-Jones 1994; Mills & Elderfield 1995; Rudnicki 1995; Chavagnac et al. 2005). In contrast, hydrothermal Nd is a minimal component in hydrothermal sediment, mostly because REE are in extremely low concentrations in seafloor hydrothermal fluids and initial hydrothermal Nd signatures in the hydrothermal sediment are often rapidly overprinted by Nd scavenged from seawater (Elderfield et al. 1988; Mills et al. 1993; Mills & Elderfield 1995).

Considering these processes and potential Nd sources, it is noticeable that even though the Lemarchant hydrothermal sediments predominantly consist of hydrothermally derived matter (e.g. Zn–Pb–Cu–Fe–S), their Nd budget contains only minor hydrothermally derived Nd. The dilution of hydrothermal fluids by seawater, scavenging processes and contributions of detrital matter generally annihilates the initial hydrothermal Nd signatures in hydrothermal sediments (Mills & Elderfield 1995). In rifted arc basins, typical of that hosting the Lemarchant deposit (e.g. Cloutier et al. 2017), the provenance of Nd is generally restricted and often local (i.e. Tally Pond group volcanic rocks, Crippleback Intrusive Suite and Sandy Brook Group basement rocks), such that erosion of these rocks results in locally derived detrital Nd in the hydrothermal sedimentary rocks, as well as dissolved Nd in the water column (Figs 9a, b and 10). The Nd in the Lemarchant exhalites was derived predominantly from scavenging and detrital matter, which explains the evolved Nd signatures of these rocks; signatures that are not present in the more juvenile Tally Pond group volcanic rocks. Moreover, the Lemarchant exhalites have similar εNd$_{513 Ma}$ values throughout the sections of the Lemarchant Main Zone, the Northwest and 24 zones, and the North Target (Fig. 6a and b), albeit proximal Lemarchant exhalites (EMS-type) have more evolved εNd$_{513 Ma}$ values than the more distal exhalites (FEM-type; Fig. 6a and b). It is suggested that the more evolved Nd signatures of the proximal exhalites represent early stages of arc-rifting, which were dominated by erosion of the rifted Neoproterozoic Ganderian (see below) and possibly older crustal basement, whereas the more distal exhalites reflect greater contributions from the continuously erupting more juvenile Cambrian Tally Pond group volcanic rocks and their erosion (Fig. 9a and b).

Significant input from crustal material is further supported by the Pb isotopic data of the Lemarchant deposit and other massive sulphide occurrences in the Tally Pond group (Swinden & Thorpe 1984; Pollock & Wilton 2001; Gill 2015; Lode et al. 2017). Volcanogenic massive sulphides and associated hydrothermal sediments have Pb sources derived predominantly from leaching of basement rocks, which may include different reservoirs (Franklin et al. 1981; Swinden & Thorpe 1984; Tosdal et al. 1999; Ayuso et al. 2003). Lead isotopic data measured in situ on galena hosted within sulphides in the hydrothermal sediments using secondary ion mass spectrometry (SIMS) suggested hydrothermally and detritally derived Pb sources (Lode et al. 2017). In particular, the more vent distal exhalites showed more radiogenic detritally derived Pb contributions, which were characterized by more radiogenic $^{206}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb ratios (Mills & Elderfield 1995; Lode et al. 2017). These data are also consistent with derivation of Pb from juvenile to evolved sources and suggest that such crust was present beneath the Tally Pond group.

The Nd and Pb isotopic data from Lemarchant exhalites also provide insight into the crustal architecture and potential palaeo-geographical relationships of the Lemarchant deposit and Tally Pond group within the Iapetus Ocean. For example, inherited zircons (563 Ma) in the Cambrian felsic volcanic rocks of the Tally Pond group are consistent with them having erupted from or interacted with Neoproterozoic Ganderian basement rocks (Crippleback Intrusive Suite and the coeval bimodal Sandy Brook Group; Rogers et al. 2006, 2007; McNicoll et al. 2010; Zagorevski et al. 2010). Similar, Neoproterozoic (c. 553 Ma) inherited zircon ages are also known from rocks of the Pats Pond group (c. 487 Ma), which are found regionally proximal to the Tally Pond group.

Fig. 9. Model displaying the Cambrian Tally Pond group with juvenile Nd signatures, which is built upon the Ganderian and Gondwanan Amazonian rifted crustal basement with evolved Nd signatures. (a) Early stages of arc rifting with felsic volcanism and formation of massive sulphides and genetically associated exhalites. Scavenged and detrital juvenile and evolved Nd is archived in the exhalites, resulting in mixed signatures. (b) Final stages of arc rifting and emplacement of mafic volcanic rocks that form the hanging wall to the Lemarchant VMS deposit.
systematics of the exhalites are consistent with a formation in a volcanic arc environment, such as a graben or caldera in a rifted continental arc, or an arc proximal to continental crust along the Gondwanan margin (Rogers et al. 2006; Zagorevski et al. 2010; Piercey et al. 2014). Therefore, exhalites that precipitate in a rifted arc basin or caldera setting record diverse provenance components that are useful for palaeogeographical reconstructions and provide a mechanism to elucidate the source of metals that contributed to the formation of spatially and genetically associated massive sulphides.

Conclusions

It is proposed that the volcanogenic massive sulphides of the Lemarchant deposit and related exhalites formed from fluids that ascended along deep synvolcanic faults in a rifted arc basin that contained Cambrian (c. 513 – 509 Ma) felsic, intermediate and mafic volcanic rocks and was underlain by Neoproterozoic (c. 565 Ma) mafic and felsic volcanic rocks (Sandy Brook Group), and associated intrusive rocks (Crippleback Lake Intrusive Suite). The eruption and erosion of the Tally Pond group volcanic rocks within this rift-related graben or caldera environment resulted in the addition of juvenile Nd to the basin and water column that was recorded in the exhalites that are found near massive sulphide mineralization. Furthermore, the uplift associated with arc rifting led to the erosion of the Ganderian arc rocks of the Crippleback Intrusive Suite and the coeval Sandy Brook Group, resulting in the addition of evolved crustal Nd both to ambient seawater and as detrital materials. Exhalative sedimentary rocks in the Lemarchant deposit contain Nd scavenged from seawater and from detritus, and they collectively record Nd additions from both Neoproterozoic Ganderian basement and intrasubductional Tally Pond group volcanic sources. These results are also consistent with previous detrital zircon and Nd isotopic studies that suggest that unexposed older crustal basement of the Gondwanan Amazonian margin existed beneath the Ganderian arc rocks and contributed detrital Nd to the Tally Pond group and Lemarchant exhalites specifically. As the precipitating exhalites record the mixed sources, with evolved and juvenile Nd signatures, the abundance of exhalites with more evolved Nd systematics suggests that the predominant source of Nd was eroded older crustal material. However, results herein and published previously suggest that this Amazonian basement signature is not recorded significantly in the volcanic rocks of the Tally Pond group. Overall, the Nd isotopic compositions, as well as the lithogeochemical data, of the Lemarchant exhalites suggest that the Lemarchant deposit exhalites record a formation within a rifted arc environment built upon Ganderian (exposed) and Gondwanan Amazonian (unexposed) crustal basement, consistent with existing models for the Tally Pond group.

Acknowledgements

Kind support was provided by D. and C. Fost, M. Vande Guchte, A. Marcotte and G. Squires from Paragon Minerals Corporation (a 100%-owned subsidiary of Canadian Zinc Corporation). The authors would further like to thank K. Hiscock, P. King, S. Strong and A. Westhues, as well as L. Beranek and G. Dunning for the helpful reviews, and I. Nobre Silva for general discussions, help and support. Furthermore, the authors are grateful for the thoughtful comments and suggestions of the reviewer N. Rogers and an anonymous reviewer, and the subject editor A. F. Bird.

Funding

Research was funded by the Canadian Mining Research Organization (CAMIRO, Project 08E04) and grants of the Natural Sciences and Engineering Research Council of Canada (NSERC): NSERC Discovery Grant – 249095-2011; NSERC IRC Grant – 408433-09; NSERC CRD Grant – CAMIRO Project – 387592-09; and a grant of the Research and Development Corporation of Newfoundland and Labrador (RDC) RDC IRIF for IRC – 5003.121.001 to S.J.P. Research was also funded by the NSERC-Altius Industrial Research Chair in Mineral Deposits, funded by NSERC, Altius Resources Inc.

Scientific editing by Anna Bird


