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

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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 εNd_{513} = −6.0 to −1.8, whereas the associated volcanic rocks have εNd_{513} of +0.4 to +1.4. The Lemarchant exhalite εNd compositions overlap the underlying Ganderian Neoproterozoic Sandy Brook Group (εNd_t = −6.5 to −1.9) and Crippleback Intrusive Suite (εNd_t = −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 of significance not only for occurrences of exhalites within the Tally Pond group, but also have exploration implications for VMS districts globally.

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. 1 A-B; Franklin 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, vasskis ('Weißkies' = 'white sulphide', also used for sulphidic black chert; Peter & Goodfellow 1996; Spry *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 to detrital sedimentary rocks, and have shale-normalized 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-B; Boström & Petersen 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 (~515 Ma) to Permian (~275 Ma) Appalachian-Caledonide mountain belt that hosts numerous VMS deposits, including the past-producing Duck Pond and Boundary mines, and the precious metal-bearing Lemarchant deposit (Fig. 1A-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 (~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 (~563 Ma) arc basement of the Crippleback Intrusive Suite and the coeval Sandy Brook Group (Pollock *et al.* 2002; Zagorevski *et al.* 2007; Piercey *et al.* 2014). In the Neoproterozoic and Early Cambrian Ganderia was located north-west 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 supra-subduction zone setting and arc rifting was initiated due to slab roll-back along this margin (Jenner & 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 volcanogenic massive sulphide (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 sulfide 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 backarc basin spreading centres; Fig. 3; Lydon 1984; Hannington *et al.* 2005; Gibson *et al.* 2007). 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 HPO_4^{2-}, HVO_4^{2-}, CrO_4^{2-}, $HAsO_4^{2-}$) and rare earth elements (REE) plus Y from seawater (Mills & Elderfield 1995; Rudnicki 1995). A rifted arc environment exposes rock units of different ages, hence varying Nd isotopic signatures, which contribute detrital material to the hydrothermal matter in the exhalative sedimentary rocks due to erosional and weathering processes (Keto & Jacobson 1988; Mills & Elderfield 1995). Therefore, exhalites not only record 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 to 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 materials in 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 their provenance and the potential contributions of local versus basement versus 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 (~515 Ma) to Permian (~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): Humber, Dunnage, Gander and Avalon zones (Fig. 1A; Williams 1979; Swinden 1988, 1991). The Dunnage 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 micro-continental blocks during the Early Palaeozoic to Middle Palaeozoic (i.e., Dashwoods, Taconic orogenesis; Ganderia, Salinic orogenesis; and Avalonia, Acadian orogenesis) and related interoceanic arcs and backarcs (Swinden 1991; Zagorevski *et al.* 2010). In the Palaeozoic (Middle Cambrian to Ordovician), these ribbon-shaped micro-continental 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-backarc formation: the Cambrian to Early Ordovician Penobscot 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 comprised 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 group; 4) the Sutherlands Pond group; 5) the Pats Pond group; and 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 ~513 to 453 Ma (Dunning *et al.* 1987; Evans *et al.* 1990; Dunning *et al.* 1991; 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 Ambrose formation (Rogers *et al.* 2006). The latter contains island arc tholeiitic basalts to andesites with εNd_{511} 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_{511} 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 Neoproterozoic 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 Ambrose formations (Fig. 4A; Copeland *et al.* 2009; Fraser *et al.* 2012; Lode *et al.* 2015). These sulphide-rich exhalites extend discontinuously around the massive sulphides for one to four kilometres (Copeland *et al.* 2009; Fraser *et al.* 2012; Lode *et al.* 2015). Three main types of exhalatives 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-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); or 3) interflow exhalites within the hanging wall basaltic rocks (IFE-type; Fig. 4E). Interflow exhalites occur commonly within 15 metres above the massive sulphide mineralization, but are present up to 70 metres 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/organic-rich laminae that are intercalated with siliciclastic, volcaniclastic 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-E). Ba-mineral phases include barite ($BaSO_4$; Fig. 4F), the Ba-rich feldspar celsian ($BaAl_2Si_2O_8$), and a barian K-feldspar with <2wt% Ba (hyalophane or barian adularia $(K,Ba)Al(Si,Al)_3O_8$). 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 $\delta^{34}S$ systematics (ranging from -38.8‰ to +14.4‰, with an average of ~ -12.8‰) indicate that S was predominantly biogenically-derived via microbial/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).

Methodology

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 in Lode *et al.* (2015), including analytical methods and QA/QC for lithogeochemical data. Lithogeochemical data are reproduced here only to compare to Nd isotope results.

Neodymium isotopes

Twelve representative samples in total were selected for Nd isotopic determinations, including ten exhalites from the three main exhalite types and 2 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-H) were selected for analyses, and for comparison to exhalite samples. Samarium and Nd isotopic compositions were measured at Memorial University using a multicollector Finnigan MAT 262 thermal ionization mass spectrometer (TIMS) 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 obtained using conventional two-step column chemical methods (Fisher *et al.* 2011).

Accuracy and precision for the Nd analyses were determined using the standards JNdi-1 and BCR-2 as reference materials following methods described in Fisher *et al.* (2011). The JNdi-1 and BCR-2 standards have following reported values: $^{143}Nd/^{144}Nd$ = 0.512115 and $^{143}Nd/^{144}Nd$ = 0.512633, respectively (Tanaka *et al.* 2000; Raczek *et al.* 2003). Standards were run every 11 samples with each analytical batch. Additionally, blanks were utilized during each analytical run to test 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. Analyses for the Lemarchant samples have an average 0.0013 %RSD for $^{143}Nd/^{144}Nd$ and 0.00055 %RD for $^{143}Nd/^{144}Nd$.

The results herein are presented using the epsilon notation (εNd) and calculated for a formation age of 513 Ma, the U-Pb age of the host stratigraphy as reported by Dunning *et al.* (1991); data are presented in Table 1 and Figures 4B, 5A-B, and Figure 8. εNd_{513} was calculated by $\varepsilon Nd_t = (^{143}Nd/^{144}Nd_{rock,t} / {}^{143}Nd/^{144}Nd_{CHUR,t}) \times 10^4$ after Rollinson (1993) and $f^{Sm/Nd} = [(^{147}Sm/^{144}Nd_{sample,t}) / (^{147}Sm/^{144}Nd_{CHUR,t}) - 1]$ after McLennan *et al.* (1990). Chondrite uniform reservoir (CHUR) values utilized in this study are $^{143}Nd/^{144}Nd$ of 0.512638 and a $^{147}Sm/^{144}Nd$ of 0.1967 (Hamilton *et al.* 1983; Rollinson 1993). Depleted mantle model ages (T_{DM}) were calculated using depleted mantle values of $^{144}Nd/^{144}Nd$ = 0.513163 and $^{147}Sm/^{144}Nd$ = 0.2137, and a decay constant of $\lambda = 6.54 \times 10^{-12}$ (Goldstein *et al.* 1984).

Results

Neodymium isotopic systematics. The Lemarchant exhalites (n = 10) have εNd_{513} = −6.0 to −1.8 and T_{DM} = 1.63 to 3.05 Ga (Table 1). Overall, the three types of Lemarchant exhalites (EMS = proximal; FEM = distal; IFE = interflow) have similar εNd_{513} values; however, the EMS-type have slightly lower εNd_{513} values and range from −5.6 to −4.1 with an average of −4.8; the FEM-type are less evolved and range from εNd_{513} = −4.0 to −3.2 with an average of −3.7; and the IFE-type has the widest range of εNd_{513} = −6.0 to −1.8 and average of −3.9 (Table 1; Fig. 6B, 7A-B). The Lemarchant tuff samples (n = 2) have εNd_{513} = −5.7 to −4.7 with an average of −5.2 and T_{DM} = 1.75 to 1.81 Ga. In εNd versus Th/Sc space the Lemarchant exhalites and tuff have Th/Sc ratios of 0.06 to 1.93 and fall between the arc andesite fields, with samples that have greater Th/Sc containing lower εNd 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 εNd_{513} = +0.4 and a T_{DM} = 1.47 Ga, and εNd_{513} = +1.4 and a T_{DM} = 1.74 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 $f^{Sm/Nd}$ reflects the fractional deviation of $^{147}Sm/^{144}Nd$ from CHUR in parts per 10^4 because of light rare earth element enrichment (i.e., lower Sm/Nd) during igneous differentiation processes (McLennan *et al.* 2003). Accordingly, in $f^{Sm/Nd}$-εNd space (Fig. 7B) the Lemarchant exhalite and tuff samples have more evolved εNd_{513} values than the Lemarchant volcanic rocks, and are comparable to values reported by Rogers *et al.* (2006) for the Neoproterozoic Crippleback quartz monzonite and Sandy Brook Group rhyolite. However, the Lemarchant exhalite and tuff samples have $f^{Sm/Nd}$ higher than the Neoproterozoic Crippleback quartz-monzonite and Sandy Brook Group rhyolite and trend towards those of 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-B). The T_{DM} = 1.63 to 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 to 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 by Winchester and Floyd (1977) and Pearce (1996) in Figure 8. This plot enables 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 the more felsic rocks trending towards dacite boundary, and the more mafic rocks trending towards the basalt boundary (Fig. 8). Because of the limited sample number 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 Penobscot 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 Ganderia, led to the formation of the Ellsworth belt (~509-505 Ma) of coastal Maine and New Brunswick representing the separation of Ganderia 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 $\varepsilon Nd_{500\ Ma}$ values ranging from +5.6 to +8.6, but also calc-alkaline rhyolite (R-1 Rhyolite) that yielded $\varepsilon Nd_{500\ Ma}$ ~0 (Schulz *et al.* 2008). The latter 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 ($\varepsilon Nd_{511\ Ma}$ = +3; Rogers *et al.* 2006 and this study), whereas Bindons Pond formation rhyolites and dacites have less juvenile values (εNd_{511Ma} = +1.8 and +2.6) (Rogers *et al.* 2006; Zagorevski *et al.* 2010). There is a noticeable difference in $\varepsilon Nd_{513\ Ma}$ values between the sedimentary and volcanic rocks of the Lemarchant deposit, however. In general, the exhalites and tuffs have lower εNd_{513} values ranging from −6.0 to −1.8 (Fig. 7A-B), like the Sandy Brook Group rhyolite $\varepsilon Nd_{513\ Ma}$ = −6.5 to −1.9, and the Crippleback Intrusive Suite $\varepsilon Nd_{513\ Ma}$ = −5.9 to −5.2 (Rogers *et al.* 2006). Mafic volcanic rocks are common in the Sandy Brook Group; however, no Nd isotopic data are published thus no comparison can be made to 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 $\varepsilon Nd_{570\ Ma}$ 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, interflow), have negative εNd_t 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/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 oxyanions (e.g., HPO_4^{2-}, HVO_4^{2-}, CrO_4^{2-}, $HAsO_4^{2-}$), trace elements, and rare earth elements (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 indicate that continental Nd is the predominant source of REE in modern seawater resulting in different Nd values within the main water masses/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, 10). The Nd in the Lemarchant exhalites was derived predominantly from scavenging and detrital matter, which explains their evolved Nd signatures; signatures that are not present in the more juvenile Tally Pond group volcanic rocks. Moreover, the Lemarchant exhalites have similar $\varepsilon Nd_{513\ Ma}$ values throughout the sections of the Lemarchant Main Zone, the Northwest and 24 zones, and the North Target (Fig. 6A-B), albeit proximal Lemarchant exhalites (EMS-type) have more evolved εNd_{513} values than the more distal exhalites (FEM-type; Figs. 6A-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 and erosion of the more juvenile Cambrian Tally Pond group volcanic rocks (Fig. 9A-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 that derive their Pb 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). Especially more vent distal exhalites showed more radiogenic detritally Pb contributions, which were characterised 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 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 palaeogeographic 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; Rogers *et al.* 2007; McNicoll *et al.* 2010; Zagorevski *et al.* 2010). Similar, Neoproterozoic (~553 Ma) inherited zircon ages are also known from rocks of the Pats Pond group (~487 Ma), which are found regionally proximal to the Tally Pond group albeit younger, and these rocks also have Mesoproterozoic (0.9-1.2 Ga) xenocrystic zircons (Zagorevski *et al.* 2007, Zagorevski *et al.* 2010). This indicates that the bimodal Pats Pond group was built near or upon Ganderian basement as the Tally Pond group (Zagorevski *et al.* 2010). Plutonic and gneissic boulders, as well as sedimentary rocks in the Ellsworth Formation of coastal Maine and New Brunswick, rocks penecontemporaneous with the Tally Pond group, contained small populations of Mesoproterozoic, Palaeoproterozoic, and Archean zircons up to 3.23 Ga, but with a dominant population between 1.07 to 1.61 Ga (Hibbard *et al.* 2007; Schulz *et al.* 2008; Fyffe *et al.* 2009; van Staal *et al.* 2012). These inherited zircon patterns present in the Victoria Lake supergroup and Ellsworth terrane are consistent with these rocks being built atop Ganderian basement, and are also consistent with Ganderia having originated along the Gondwanan Amazonian margin (Fyffe *et al.* 2009; van Staal *et al.* 2012). The Mesoproterozoic to Archean T_{DM} model ages and Nd isotopic data of the Lemarchant exhalites (1.63 to 3.05 Ga) together with the detrital zircon populations and the Nd signatures of the Tally Pond group volcanic rocks, as well as of the Crippleback Intrusive Suite and Sandy Brook Group, are also consistent with an Amazonian provenance for Ganderia, and also suggests that the Tally Pond group evolved along this margin (Fig. 8; Zagorevski *et al.* 2007; Pollock *et al.* 2011; van Staal & Barr 2011; van Staal *et al.* 2012).

Altogether, the Nd and Pb isotopic data support that older crustal basement plays a role in hydrothermal activity in the Tally Pond group, either through direct leaching (Pb), detrital (Pb+Nd), or via adsorption/deposition from the water column (Nd). Furthermore, trace element signatures of the Tally Pond group volcanic rocks and provenance-related immobile element systematics of the exhalites are consistent with a formation in a volcanic arc environment, such as a graben/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/caldera setting record diverse provenance components that are useful for palaeogeographic 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 (~513-509 Ma) felsic, intermediate, and mafic volcanic rocks and was underlain by Neoproterozoic (~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/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 to both ambient seawater and as detrital materials. Exhalative sedimentary rocks in the Lemarchant deposit contain both Nd scavenged from seawater and from detritus and they collectively record Nd additions from both Neoproterozoic Ganderian basement and intrabasinal 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 εNd signatures, the abundance of exhalites with more evolved εNd 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 suggests 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.

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Figure Captions

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 and Hinchey (2006) and Lode *et al.* (2017).

Fig. 2. (**a**) Fe-Ti/Al-Fe-Mn discrimination diagram indicating a hydrothermal origin for the Lemarchant exhalites. According to their higher Al-contents, tuff samples plot predominantly towards the right-hand side of the diagram, partially outside of the hydrothermal field. Diagram after Boström (1973). (**b**) REE plus Y geospider plots of Lemarchant proximal, distal, and interflow exhalites of various stratigraphical levels. All samples are normalized to the post-Archean Australian shale (PAAS) of McLennan (1989).

Fig. 3. Schematic illustration of the main aspects of hydrothermal circulation in extensional tectonic environments. In the recharge zone seawater is entrained through

crustal and progressively heated during downward migration. Water-rock interactions lead to loss of Mg^{2+}, SO_4^{2-}, and OH^- and H_2S is generated. These reactions produce H^+ and create acidic fluids that leach metals out of rocks. In the reaction zone the highest temperatures are reached and the hydrothermal fluids gain their geochemical signatures. The hot fluids rise buoyantly up along synvolcanic faults and are expelled via the hydrothermal plume into the ambient seawater. Figure modified after German and Von Damm (2003) and Gibson *et al.* (2007).

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.

Fig. 5. (**a**) Detailed photomicrograph (RL = reflected light). EMS-type exhalite, sample. with euhedral pyrite (Py), sphalerite (Sp) with chalcopyrite-disease, galena (Gn), and chalcopyrite (Ccp) S-isotopic spot analyses. Section 101+25N, LM13-79, CNF25071b, 186.6 m. (**b**) Photomicrograph (RL) of framboid-rich EMS-type exhalite with a sulphide-rich vein parallel lamination. Vein sulphides consist of euhedral pyrite (Py), interstitial chalcopyrite (Ccp), and pyrrhotite (Po) and were analysed for S-isotopes. Section 105N, LM08-24ext, CNF20983, 432.8 m. (**c**). Photomicrograph (RL) of a FEM-type exhalite, with euhedral and massive pyrite (Py), galena (Gn) inclusions, and associated interstitial chalcopyrite (Ccp) and S isotopic results of spot analyses. Section 103+25N, LM11-59, CNF30998, 194.2 m. (**d**) $\delta^{34}S$ data ranges of pyrite (Py) including marcasite, pyrrhotite (Po), arsenopyrite (Apy), chalcopyrite (Ccp), and galena (Gn) with distribution shape and 95th percentile (hatched line), as well as the average (solid line). Green bar on right-hand side indicates range of $\delta^{34}S$ values that have only biogenically-derived S sources, based on two-component mixing modelling presented in Lode *et al.* (2017). Grey arrows display $\delta^{34}S$ ranges that have mixed sources. Data are subdivided into the three exhalite types: EMS, FEM, and IFE. EMS-type exhalites have more contribution of S derived from thermochemical sulphate reduction than IFE-type exhalites. FEM-type show intermediate ranges.

Fig. 6. (**a**) Spatial distribution of εNd for the EMS-, FEM-, and IFE-type exhalites and tuff, as well as the Lemarchant felsic and mafic volcanic rock from this study. Sample data do not show any spatial variations throughout the sections and/or with depth in the stratigraphy in the Lemarchant area. 2σ error bars calculated after algorithm from Ickert (2013). (**b**) Resource map of the massive sulphides of the Lemarchant Main, 24 Zone, and Northwest Zone. Massive sulphides are projected to the surface. Modified from the resource map of Canadian Zinc Corporation.

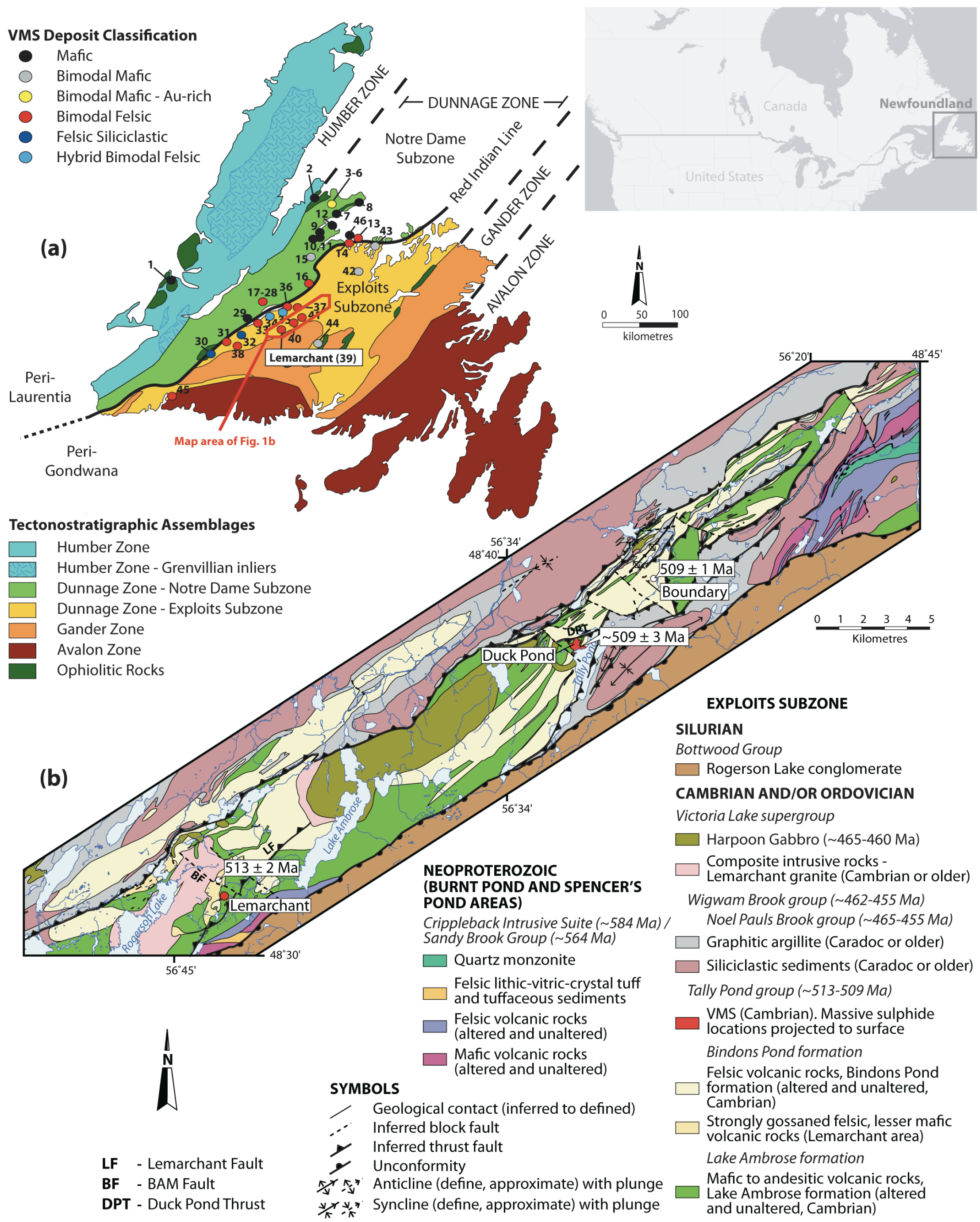
Fig. 7. (**a**) Diagram of εNd versus Th/Sc ratio for the three main types of Lemarchant exhalites (EMS, FEM, and IFE) and tuff. Also plotted are data from Rogers *et al.* (2006) for felsic and mafic volcanic rocks of the Tally Pond group and the Crippleback/Sandy Brook Group crustal basement rocks. Mid Ocean Ridge Basalt (MORB) field from data from Gale *et al.* (2014). Arc andesite field from data from Hawkeswoth *et al.* (1979). All data re-calculated for εNd_{513}. Diagram modified after McLennan *et al.* (1993). (**b**) Plot of $f^{Sm/Nd}$ versus εNd for the EMS-, FEM-, and IFE-type exhalites and tuff, as well as the Lemarchant felsic and mafic volcanic rock from this study. Also plotted are data from Rogers (2004) and Rogers *et al.* (2006) for felsic and mafic volcanic rocks of the Tally Pond group, a felsic volcanic rock samples from the unmineralized Upper Block at Duck Pond and a sample from the Mineralized Block at Duck Pond from data from McNicoll *et al.* (2010), and the Crippleback/Sandy Brook Group crustal basement rocks. Diagram modified after McLennan *et al.* (1993).

Fig. 8. Zr/Ti versus Nb/Y plot for volcanic rocks after Winchester and Floyd (1977) and Pearce (1996) for the Lemarchant felsic and mafic volcanic rocks from this study and from data from Rogers (2004) and Rogers *et al.* (2006). Additionally, data fields for felsic, intermediate, and mafic volcanic rocks was added (Cloutier *et al.*, 2017). Data from Rogers (2004) and Rogers *et al.* (2006) was also used to plot the Crippleback Lake/Sandy Brook Group crustal basement rocks.

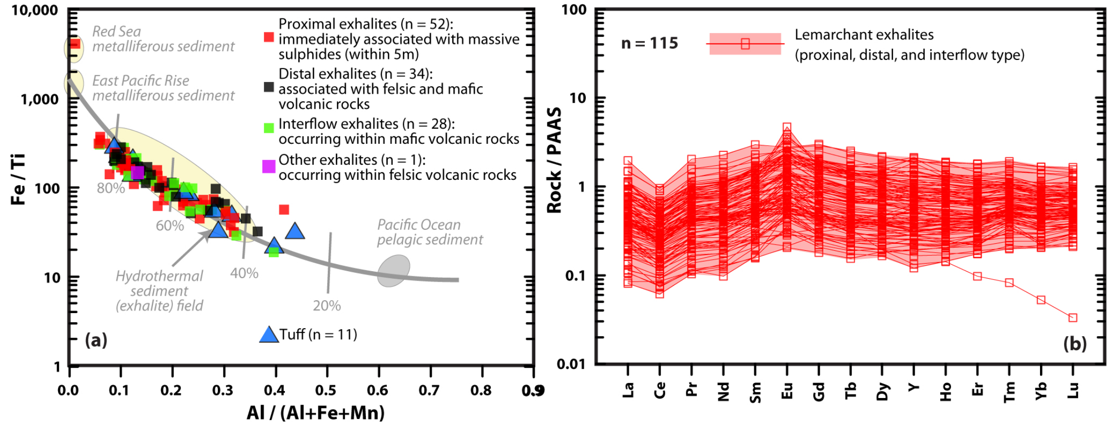
Fig. 9. Model displaying the Cambrian Tally Pond group with juvenile Nd signatures that is built upon the Ganderian and Gondwanan Amazonian rifted crustal basement with evolved Nd signatures. (**a**) Early stages of arc rifting with felsic volcanism and formation of massive sulphides and genetically 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.

Fig. 10. Diagram of εNd versus age for Tally Pond group exhalite and volcanic rock samples from this study and from Rogers (2004), Rogers *et al.* (2006), and McNicoll *et al.* (2010). The field for Ganderian Neoproterozoic rocks is from Rogers *et al.* (2006). Fields for the Mesoproterozoic Amazonian crust, the Transamazonian crust, and the West African Craton are from Satkoski *et al.* (2010) and references therein. Depleted mantle evolution curve is from dePaolo (1981). CHUR = Chondrite uniform reservoir.

Lode, Stefanie Fig. 1



Lode, Stefanie Fig. 2



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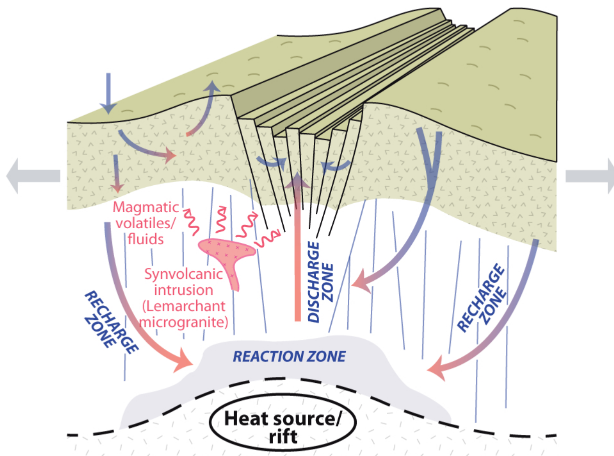
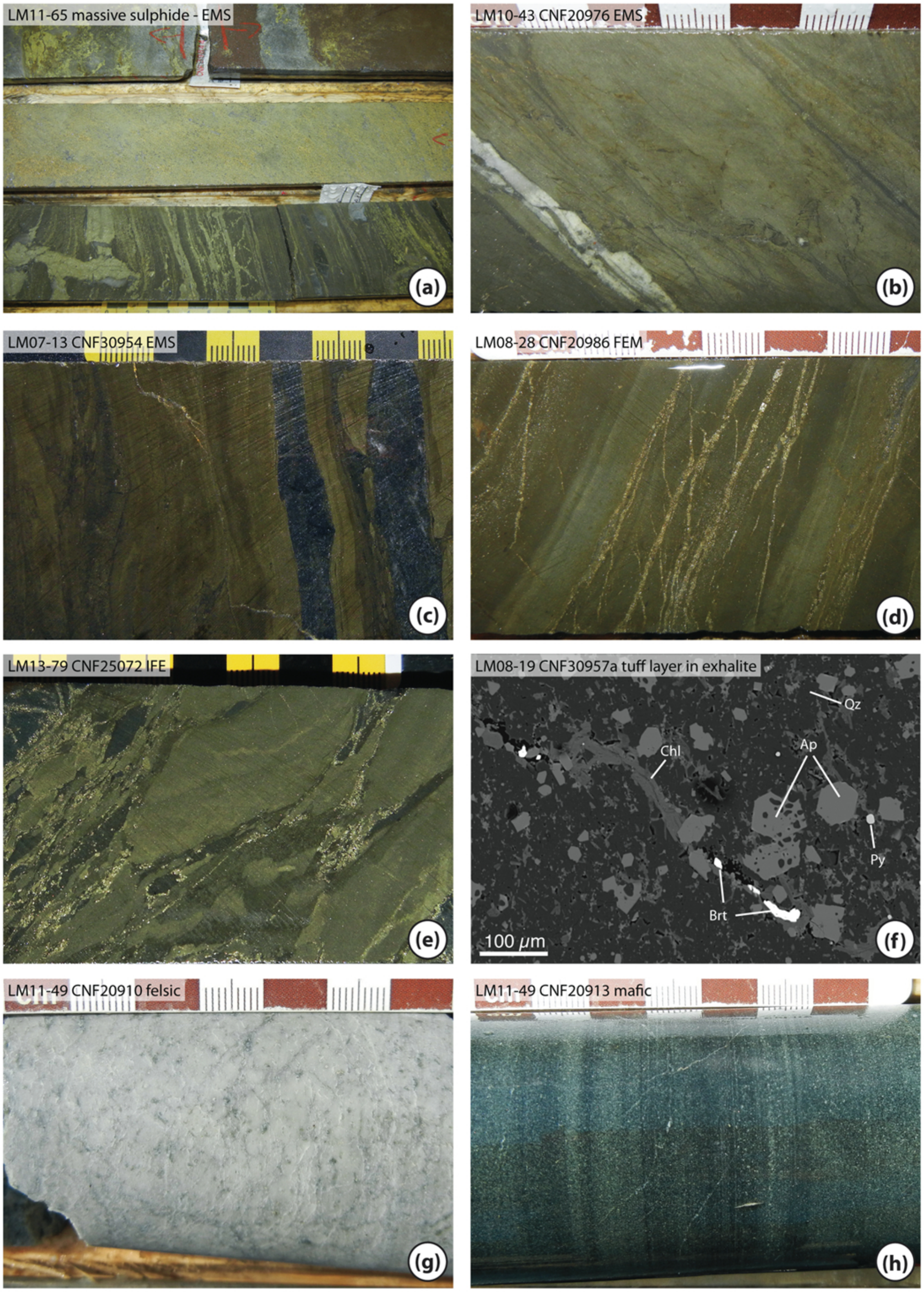
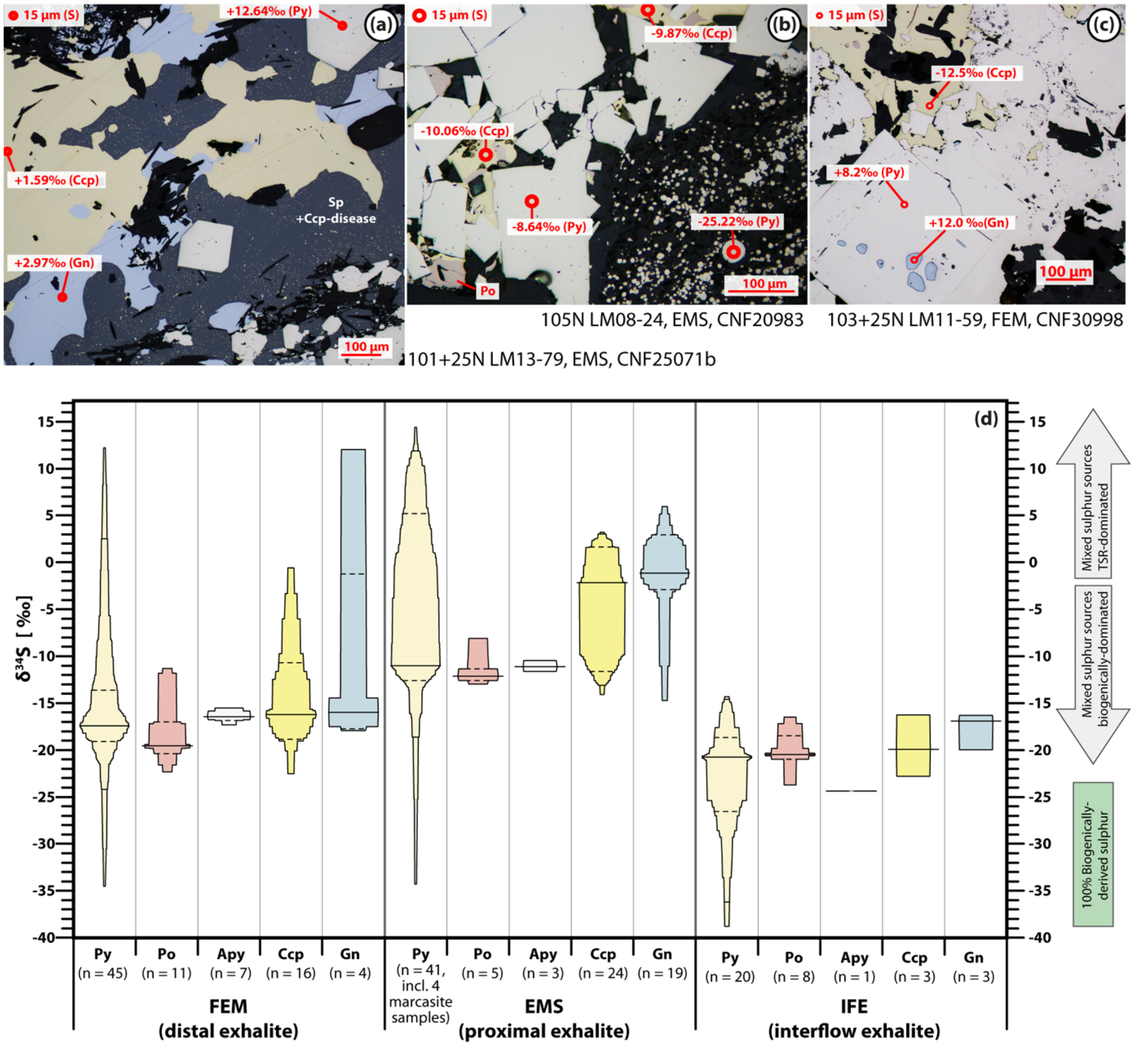
Lode, Stefanie Fig. 3



Lode, Stefanie Fig. 4



Lode, Stefanie Fig. 5



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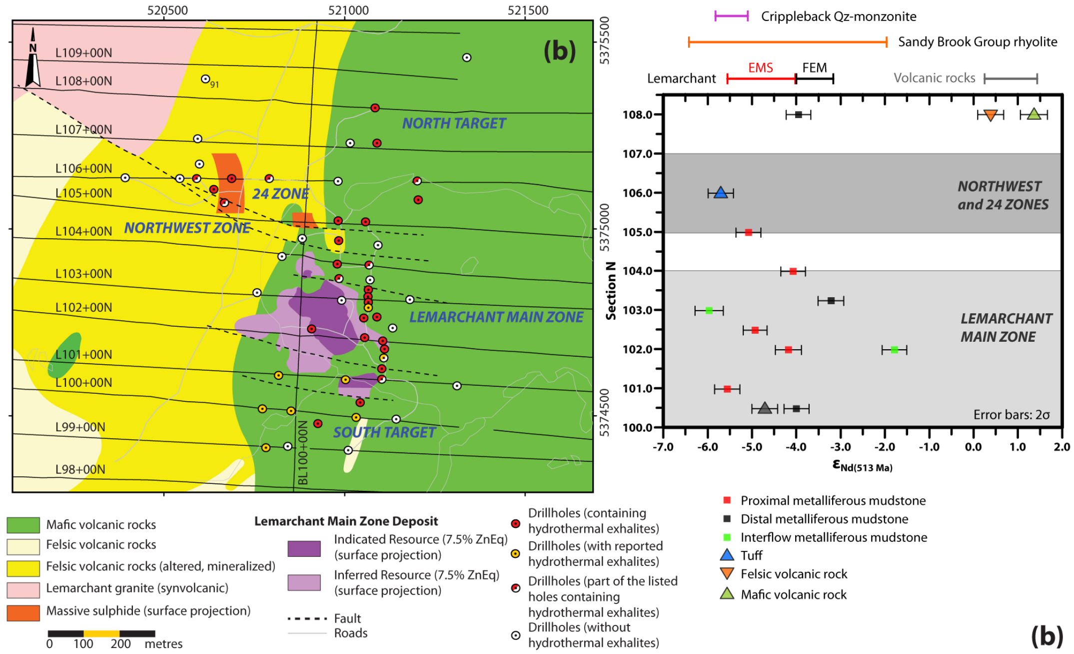
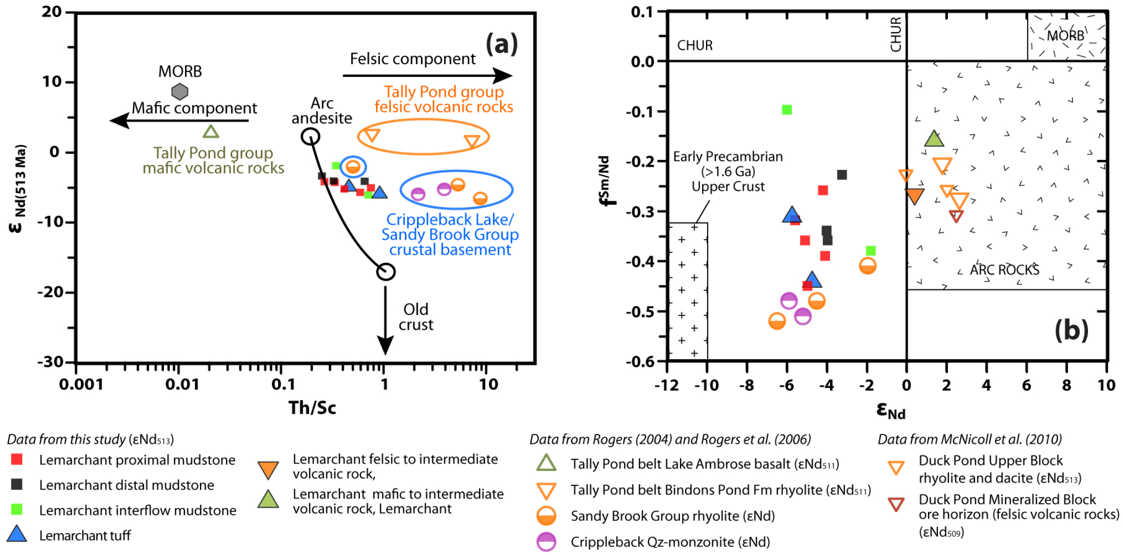
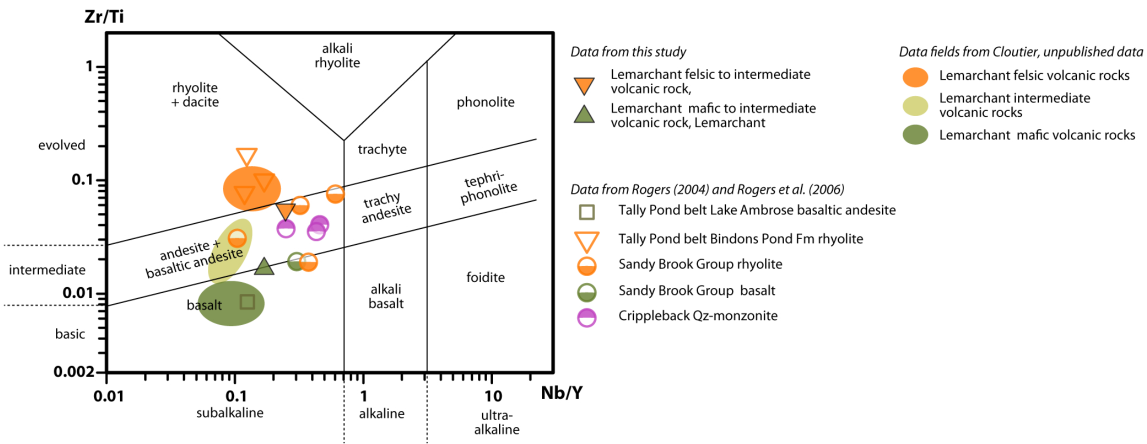
Lode, Stefanie Fig. 6



Lode, Stefanie Fig. 7



Lode, Stefanie Fig. 8



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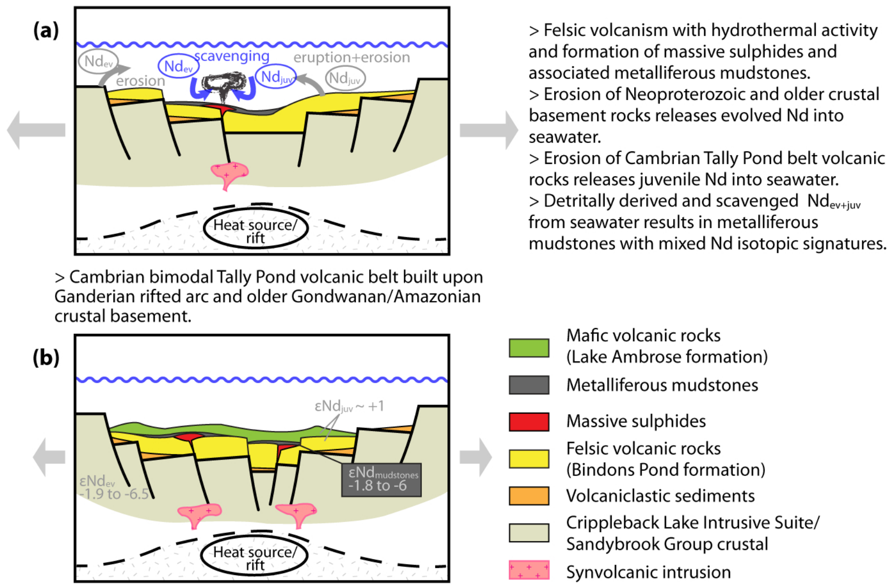
Lode, Stefanie Fig. 9



Lode, Stefanie Fig. 10