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**Role of metalliferous mudstones and detrital shales in the
localization, genesis, and paleo-environment of
volcanogenic massive sulphide deposits of the Tally Pond
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Abstract

The Cambrian Tally Pond volcanic belt in central Newfoundland contains numerous volcanogenic massive sulphide (VMS) deposits and prospects associated with exhalative metalliferous mudstones. Deposits in the belt are bimodal felsic VMS deposits that are both base metal-bearing (e.g., Duck Pond/Boundary), and base- metal and precious metal-bearing (Lemarchant). At the Lemarchant deposit metalliferous mudstones are stratigraphically and genetically associated with mineralization. In the remainder of the Tally Pond belt, detrital shales occur predominantly in the northeastern part of the belt (mostly as unrelated mid-Ordovician structural blocks) in the upper sections of the Cambrian volcanic stratigraphy, but locally also are intercalated with metalliferous mudstones. Their relationships to massive sulphides are less obvious, with many spatially, but not necessarily genetically related to mineralization. Upper Cambrian to Lower Ordovician black shales from Bell Island, which represent pelagic sedimentation not associated with hydrothermal activity and volcanism, are compared to the Tally Pond belt mudstones and shales.

Exhalative mudstones, like those at Lemarchant, have elevated Fe/Al and base-metal values, and have shale-normalized negative Ce and positive Eu anomalies, indicative of deposition from high temperature ($>250^{\circ}\text{C}$) hydrothermal fluids within an oxygenated water column. Mudstones and shales sampled from other Tally Pond prospects have more variable signatures, ranging from hydrothermal (signatures as above) to non-hydrothermal black shales (no positive Eu-anomalies, flat REE-patterns, low Fe/Al and base metal contents), to those that have mixed signatures. Accordingly, mudstones from areas with a Lemarchant-like hydrothermal and vent-proximal character

are more attractive exploration targets than mudstones and shales with predominantly detrital signatures.

Introduction

Exhalative metalliferous mudstones and detrital shales are abundant in the Tally Pond volcanic belt, central Newfoundland Appalachians, and are spatially and/or genetically associated with numerous massive sulphide deposits, prospects, and showings (Swinden 1991; Squires and Moore 2004). The Tally Pond belt volcanic rocks and related massive sulphide mineralization were associated with episodes of rifting during the construction of the Cambrian to Early Ordovician Penobscot arc (Dunning et al. 1991; Rogers et al. 2007; Zagorevski et al. 2010; Piercey et al. 2014). Sedimentary rocks deposited in graben/rift-related basins typically are volcanoclastic and epiclastic (Carey and Sigurdson 1984), and locally contain exhalative metalliferous mudstones. The depositional environment of these sedimentary rocks is controlled by volcanic activity and an active tectonic environment (Carey and Sigurdson 1984), with metalliferous mudstones spatially and genetically associated with volcanism and related massive sulphide deposits (Haymon and Kastner 1981; Gurvich 2006; Hannington 2014). Metalliferous mudstones form from black smoker plume fallout during a hiatus in the volcanic activity, resulting in the deposition of hydrothermal matter (i.e., hydrothermally derived polymetallic sulphides, sulphates, carbonates, as well as Al-poor clays) that dominates over the detrital, abiogenic pelagic background sedimentation (Lydon 1984; German and Von Damm 2003). The hydrothermal matter can be diluted by volcanic and/or sedimentary detritus, resulting in sequences of hydrothermal sedimentary rocks

that are intercalated with and/or overlain by volcanoclastic and epiclastic rocks, as well as black shales (Peter and Goodfellow 2003; Sáez et al. 2011).

Metalliferous mudstones in the Lemarchant area have a hydrothermal-exhalative origin (Copeland et al. 2008; Lode et al. 2015); hence, the term ‘metalliferous mudstone’ is used for Lemarchant-like sulphide-rich mudstones with a known or proposed hydrothermal origin and a genetic association with massive sulphide mineralization. The term ‘detrital shale’ is utilized herein to describe non-exhalative black shales that occur predominantly in the northeastern parts of the Tally Pond volcanic belt. These detrital shales are interpreted to have no genetic relationship to mineralization, but they locally are spatially associated with massive sulphides (Pollock 2004; Squires and Moore 2004). Because volcanogenic massive sulphide (VMS) deposits are small targets for exploration, it is important to identify potential ore-bearing horizons, and delineate metalliferous mudstones from less prospective detrital shales (Franklin et al. 1981; Gibson et al. 2007).

The purpose of this study is to apply geological and lithogeochemical proxies to:

- 1) identify and test a hydrothermal-exhalative origin of metalliferous mudstones occurring in the Tally Pond volcanic belt; 2) to better understand the relationships of the Lemarchant and other metalliferous mudstones and detrital shales to massive sulphide mineralization; and to 3) define the depositional environment of the metalliferous mudstones and detrital shales in terms of provenance, geochemistry of contributing fluids, the paleoredox conditions of ambient seawater, and the rift basin characteristics at the time of formation. The results of this study have significance and exploration implications for the metalliferous mudstones and detrital shales and associated VMS

deposits within the Tally Pond belt, but also mudstone/shale-associated VMS districts globally.

Regional Geology

The Tally Pond volcanic belt 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 and Barr 2011). The Newfoundland Appalachians are divided into four tectonostratigraphic zones (from west to east): Humber, Dunnage, Gander, and Avalon zones (Fig 1A; Williams, 1979; Swinden and Kean, 1988; Swinden, 1991). 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 and Kean, 1988; Swinden 1991). The suture between the subzones is called the Red Indian Line, and represents a ribbon-shaped zone of tectonic *mélange*, which contains remnants of Cambro-Ordovician oceanic juvenile arc and arc terranes that existed within the Iapetus Ocean (Williams 1979; Zagorevski et al. 2010; van Staal and 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). Despite deformation and metamorphism, the Central Mobile Belt was only moderately affected by metamorphism (lower greenschist-facies) and deformation and thus, internal stratigraphic relationships are well preserved (e.g., Hinchey and McNicoll 2009; Zagorevski et al. 2010; van Staal and Barr 2011; Piercey et al. 2014). Massive sulphide formation is known to be associated with the evolution and rifting of the Cambrian to Ordovician Penobscot arc (Swinden et al. 1989; Rogers et al. 2007;

Zagorevski et al. 2010). The Duck Pond and Boundary mines, as well as the Lemarchant deposit, and numerous other prospects and showings also occur within the Tally Pond volcanic belt (Fig. 1B) (Dunning et al. 1991; Evans and Kean 2002; Rogers et al. 2007; McNicoll et al. 2010).

The Tally Pond volcanic belt and its deposits 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 and Barr, 2011). The Tally Pond group (U-Pb zircon ages ranging from ~513 to 509 Ma; zircons obtained from rhyolites and felsic volcanoclastic rocks) is informally 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 (Rogers et al. 2006; Copeland et al. 2009). The latter contains island arc tholeiitic basalts to andesites (Dunning et al. 1991; Evans and Kean 2002; Rogers et al. 2006), whereas the former contains predominantly transitional to calc-alkalic rhyolitic to dacitic rocks (Rogers et al., 2006; Piercey et al., 2014). The bimodal volcanic sequence of the Tally Pond group is unconformably overlain by a thick unit of graphitic carbon-rich argillaceous shales, as well as volcanoclastic, epiclastic, and turbiditic rocks of the Wigwam Pond group/Noel Paul's Brook group (Squires et al. 1991; Evans and Kean 2002; Squires and Moore 2004; Rogers et al. 2006). These volcanoclastic sedimentary rocks and detrital shales occur either as sequences with undisturbed lamination and bedding, or as strongly reworked and sheared unit; the latter is also known as 'black shale mélange' (Pollock 2004; Copeland 2009a). The contact between the volcanic and volcanoclastic sedimentary rocks

is considered as tectonic and is marked by a thrust fault, e.g., the Trout Brook Fault (Fig. 1B; Squires et al. 1991; Pollock 2004; Squires and Moore 2004). This black shale mélange contains pebble- to boulder-sized fragments of rhyolite and felsic volcanoclastic rocks, which locally are mineralized, and is commonly intruded by andesitic to mafic volcanic dykes/sills (Pollock 2004; Copeland 2009). Rare fossil data in the detrital black shales indicates Middle Ordovician (Sandbian to Katian/Caradocian) (Zagorevski et al., 2010), but locally they are intercalated with volcanic rocks of the Cambrian Bindons Pond and Lake Ambrose formations, as well as with metalliferous mudstone (Copeland, 2009). The metalliferous mudstones as well as the detrital shales are overall carbonaceous (i.e., rich in finely disseminated graphitic carbon), locally with subhedral hydrothermal graphite, or have preserved organic matter (e.g., microbial/algal mat fragments)(Beyssac and Rumble 2014; Rumble 2014; Lode et al. 2015). Metalliferous mudstones occur predominantly at the contact of the Bindons Pond and the Lake Ambrose formations, and are commonly associated with massive sulphide deposits (e.g., the Lemarchant VMS deposit)(Copeland et al. 2008; Lode et al. 2015). Collectively, the tectonic environment in which the felsic and mafic volcanic rocks, as well as the metalliferous mudstones, of the Tally Pond group are formed is interpreted as an arc to rifted arc (Rogers et al. 2006; McNicoll et al. 2010; Zagorevski et al. 2010; Piercey et al. 2014).

**Massive Sulphide Mineralization Associated with Hydrothermal Mudstones
and Graphitic Black Shales**

Twelve deposits, prospects, and showings occurring in the Tally Pond volcanic belt contain metalliferous mudstones and detrital black shales with variable relationships

to VMS mineralization (Table 1; Fig. 1B). Upper Cambrian to Lower Ordovician detrital black shales from Bell Island, eastern Newfoundland, were utilized for comparison and are not spatially and/or genetically associated with massive sulphide mineralization (Fig. 1C).

Lemarchant deposit

The Cambrian Lemarchant Zn-Pb-Cu-Ba-(Au-Ag) VMS deposit has metalliferous mudstones both immediately associated with and distal from mineralization (Fig. 1B). The mineralization is defined in the Lemarchant Main Zone with the Northwest and 24 zones as additional potential resources (Fig. 2). A quartz-feldspar-phyric tuff in the general vicinity of the Lemarchant deposit yielded a U-Pb zircon age of 513 ± 2 Ma (Dunning 1991; Squires and Moore 2014).

The main metalliferous mudstone horizon at Lemarchant occurs in all mineralized zones (the Main Zone, the 24 Zone, and the Northwest Zone), located immediately above the massive sulphides stratigraphically in the Bindons Pond formation at the contact with the hanging wall mafic volcanic rocks of the Lake Ambrose formation (Fig. 2). The mudstone horizon extends laterally west of the Lemarchant Main Zone, at the same stratigraphic level, but not in immediate contact with massive sulphides, up to 200 m away from the mineralization. Metalliferous mudstones also occur as interflow mudstones within Lake Ambrose formation basalt, up to 50 m above the massive sulphide mineralization. Locally, barite-rich metalliferous mudstones occur in areas of the North and South targets (Lode et al. 2015). Due to an offset along the gently west-dipping Lemarchant Fault, a repetition of the mineralized strata and mudstone occurrences is likely (Squires and Moore 2004; Copeland et al. 2009).

175 *Cookstown showing*

176 The Cookstown showing (Fig. 1B) was discovered in 2005 by Rubicon Minerals
177 during a short trenching program that targeted EM conductors and weak historic till
178 anomalies. Trenching exposed sulphide-rich, detrital shales associated with felsic and
179 mafic volcanic rocks (Collins 1989; Sparkes 2005; Copeland 2009b). The detrital shales
180 occur within a bimodal succession of volcanic and volcanoclastic rocks, where felsic
181 volcanic rocks of the Bindons Pond formation are intercalated with mafic volcanic rocks
182 of the Lake Ambrose formation. This bimodal sequence is intruded by synvolcanic mafic
183 dykes/sills and feldspar-phyric felsic dykes (Fig. 3A).

184 *Higher Levels prospect*

185 The base metal mineralization of the Higher Levels prospect (Fig. 1B) consists of
186 pyrite, chalcopyrite, sphalerite, minor pyrrhotite, and galena, hosted in laminated
187 metalliferous mudstones that are intercalated with detrital shales. These sedimentary
188 rocks occur within mafic volcanic flows of the Lake Ambrose formation that overly the
189 felsic volcanic rocks of the Bindons Pond formation (Squires and Moore 2004). The
190 stratigraphy is folded with sedimentary rocks present in the core of a syncline (Fig. 3B;
191 Squires and Moore 2004). Both, the felsic and mafic volcanic rocks locally have VMS-
192 style alteration and stringer mineralization (Squires and Moore 2004).

193 *Beaver Lake prospect*

194 The Beaver Lake prospect (Fig. 1B) is a three-kilometer long VMS-style sericite-
195 chlorite-silica alteration zone in felsic volcanic rocks that was found via anomalous base
196 metal values in till samples (Copeland 2009a). In 2011, Paragon Minerals Corporation
197 (now Canadian Zinc Corporation) drilled three holes (BL11-01, BL11-02, and BL11-03)

intercepting a felsic-dominated bimodal sequence (felsic volcanic rocks of the Bindons Pond formation and mafic volcanic rocks of the Lake Ambrose formation), locally with stringer mineralization and VMS-style alteration. The volcanic rocks and mineralization are intercalated with metalliferous mudstones and detrital shales (Fig. 3C).

Duck West showing

The Duck West showing is hosted by VMS-style altered felsic volcanic rocks (Fig. 1B). The stratigraphy of the felsic volcanic rocks of the Duck West alteration zone correlates with the 'Mineralized Block' that hosts the Duck Pond massive sulphide deposit (Figs. 4-5; Squires and Moore 2004; Copeland 2009a). They consist of massive to jigsaw-fit quartz-chlorite-sericite altered felsic volcanic rocks that are intercalated with locally reworked detrital shales and mineralized tuff.

Duck Pond deposit

The Duck Pond deposit (Fig. 1B) and was discovered by Noranda in 1985 (McNicoll et al. 2010). The deposit consists of the structurally dismembered Upper Duck lens, which holds the majority of the ore, the Lower Duck lens, and the Sleeper zone. The Cu-Zn-massive sulphides are hosted by aphyric and quartz-phyric felsic tuffs and fragmental rocks (mineralized sequence), and were formed by pervasive hydrothermal subseafloor replacement of the originally permeable volcanoclastic host rocks (Doyle and Allen 2003; McNicoll et al. 2010; Piercey et al. 2012; 2014). The mineralized sequence overlies a thick succession of hydrothermally altered footwall aphyric felsic flows (Fig. 5; Squires and Moore 2004). Together they represent the 'Mineralized Block', which has yielded U-Pb zircon ages of 509 ± 3 Ma (McNicoll et al. 2010). The 'Upper Block' is structurally juxtaposed along the Duck Pond thrust on top of the Mineralized Block and

consists of an unaltered bimodal volcanic sequence with metalliferous mudstones in the Duck Pond area at the contact between the felsic volcanic rocks of the Bindons Pond formation and mafic volcanic rocks of the Lake Ambrose formation (Squires and Moore 2004; Piercey et al. 2012). Felsic volcanic rocks in the Upper Block at Duck Pond yielded U-Pb zircon ages of 513 ± 2 Ma, with ~ 563 Ma inherited zircons similar to the ages of underlying rocks (Dunning et al. 1991; McNicoll et al. 2010). Production of the Upper Duck lens started in May 2007 (McNicoll et al. 2010) and is scheduled to end permanently in mid-2015 (Teck Resources Ltd, Q1_2015 report).

Boundary deposit

The Boundary deposit is located ~ 4.5 kilometres northeast of the Duck Pond deposit and was also discovered by Noranda, in 1979-1980. The Boundary deposit consists of three shallow lenses (outcrop to subcrop): the North, South, and Southeast zones (Figs. 1B, 6; Squires and Moore 2004; Piercey et al. 2014). The North and South zones are a structural offset along the Wagner fault and represent portions of a once single lens (Wagner 1993; Piercey et al. 2014). The mineralization at the Boundary lenses is predominantly comprised of Fe-, Cu-, and Zn-sulphides that are hosted by aphyric felsic tuff, flows, and breccias at and below the contact with quartz-phyric hanging wall felsic flows and tuff (Piercey et al. 2014). Laterally extending from the massive sulphide lens is the tuffaceous exhalative Boundary horizon that is intercalated locally with metalliferous mudstones (Fig. 7A). In the Boundary area the Mineralized Block is outcropping, whereas the Upper Block is eroded (Squires and Moore 2004; McNicoll et al. 2010; Piercey et al. 2014). The mineralized sequences in the Mineralized Block of the Boundary and Duck Pond deposits correlate with similar lithofacies, alteration style, and

host rock age (509 ± 3 Ma; Squires and Moore 2004; McNicoll et al. 2010; Piercey et al. 2014).

Boundary West showing

The Boundary West showing (Figs. 1B, 6) and was discovered by Noranda by testing EM conductors and subsequently resulted in the intersection of 8 metres of stringer mineralized felsic quartz-crystal tuff in hole 374-60 (deepened as hole TP88-01). The felsic tuffs are spatially associated with cherty to metalliferous mudstones that are overlain by locally peperitic mafic flows that are preserved in a 45° NE-plunging synclinal structure (Fig. 7B-C; Squires and Moore 2004). Detrital shales are intercalated with the felsic volcanic rocks and the metalliferous mudstones. The mineralized Boundary West crystal tuffs correlate with the mineralized sequence hanging wall quartz-phyric volcanic rocks that immediately overlie the Boundary North deposit, occurring at a slightly higher stratigraphic level (Squires and Moore 2004).

Old Camp showing

The original Old Camp showing (Figs. 1B, 8) comprises a weakly Zn-enriched metalliferous mudstone over an interval of 6.4 m intersected in drill hole TP88-58. Several metalliferous mudstones occur at, or up to 200 m below, the contact between chlorite altered, quartz-phyric felsic volcanic flows and tuffs, and mafic volcanic rocks (Fig. 8B) interpreted to be stratigraphically slightly above the Boundary deposit. The mineralized sequence of the Boundary deposit occurs stratigraphically ~ 100 m deeper, but is nevertheless correlated with the mineralized Old Camp sequence (Squires and Moore 2004). The bimodal volcanic succession of the Old Camp area is structurally

overlain by detrital shales and siltstones of the Wigwam Pond group/Noel Paul's Brook group via the Overview thrust (Fig. 8B; Squires and Moore 2004; Piercey et al. 2014).

Keats Pond showing

The Keats Pond showing (Fig. 1B) consists of 30 to 50 % chlorite altered fragmental rhyolite that underlies a sequence of reworked and sheared detrital shale to polymictic conglomerate interpreted to be VMS-related. Locally, the sedimentary rocks are intercalated with metalliferous mudstones and intruded by andesitic intrusive volcanic rocks (Fig. 9A).

North Moose Pond showing

The North Moose Pond showing (Fig. 1B) contains an area of float containing intense chlorite alteration and chalcopyrite stringers underlain by a bimodal volcanic sequence that has anomalous base metal values (Squires and Moore 2004). This bimodal succession is spatially associated with metalliferous mudstones and structurally overlain by detrital shales and volcanoclastic turbidites. The contact between the sedimentary and volcanic rocks is marked by the Trout Brook fault (Fig. 9B; Squires and Moore 2004). The detrital shales are locally intruded by andesitic dykes. Based on drill core logging, the stratigraphy in drill hole NM00-01 and NM01-05 the stratigraphy is inferred to be overturned (Fig. 9C). Carbonaceous material that possibly represents a graptolite fragment in a volcanoclastic turbidite/tuff sequence that overlies metalliferous mudstones, tentatively suggests a Late Cambrian/Early Ordovician age (E. Burden, *pers. comm.* 2015)

South Moose Pond alteration zone

The South Moose Pond alteration zone (Fig. 1B) contains an area (the “NW flank”) of about 2x1 km with stringer and disseminated pyrite, sphalerite, chalcopyrite, and galena in felsic and mafic flows, but overall well-stratified units are lacking (Squires and Moore 2004). Metalliferous mudstones occur as interflow mudstones in mafic volcanic rocks in drill hole SM97-08. Detrital shales in drill hole SM97-06 structurally overlie, via the Overview thrust, the mafic volcanic rocks (Fig. 9B-C).

Bell Island

Bell Island is located ~25 km west-northwest of St John’s in Conception Bay (Fig. 1C). The Island consists of an interbedded succession of sandstones, shales, siltstones, and oolitic ironstones of Upper Cambrian to Middle Ordovician age, presumably conformable lying upon Precambrian Gondwanan continental crust; these rocks have had no influence from hydrothermal activity. Shale samples were taken from two coastal outcrops from the Lower Ordovician Beach Formation/Bell Island Group (The Beach, Lance Cove), and from one outcrop along the coast from the Middle Ordovician Powersteps Formation/Wabana Group (Powersteps) (Fig. 1C).

Mudstone Stratigraphy, Lithofacies, and Mineralogy

Lemarchant deposit

The Lemarchant metalliferous mudstones, independently of their stratigraphic position, are finely laminated, brown to black, graphite-rich, and carbonaceous, and have a thickness of <1 m to 20 m (Fig. 10A). The main sulphide phases are pyrite (framboidal and euhedral) and pyrrhotite, with minor chalcopyrite, sphalerite, arsenopyrite and galena, which commonly occur parallel to laminations or as cross-cutting polymetallic veins (Fig. 10B). Barium minerals include massive and bladed barite, celsian and

hyalophane, and witherite. Precious metals occur in the form of electrum, which is predominantly associated with chalcopyrite and galena in the later-stage polymetallic veins (Fig. 10B). Detailed geological, mineralogical, and lithogeochemical studies have shown these metalliferous mudstones have a hydrothermal origin (Lode et al. 2015).

Cookstown showing

In the Cookstown drill hole CT11-01, laminated to reworked dark-grey to black cherty shales range from 0.2 to 5 metres in thickness and are locally intercalated with fine-grained crystal (feldspar) lithic tuff. The main sulphide phase is pyrrhotite with minor chalcopyrite and traces of galena. Pyrrhotite occurs as semi-continuous layers parallel to lamination, in cross-cutting veins, as patches (Fig. 10C-D), or as pseudomorphs after euhedral pyrite. Locally, pyrrhotite veins show pyrrhotite halos that extend into the generally sulphide-poor matrix (Fig. 10E). Calcite is present as gangue in sulphide-rich veins. The mudstone matrix predominantly consists of clay, chlorite, and quartz, with carbonaceous material present as laminae or finely disseminated in the matrix.

Higher Levels prospect

The sedimentary rocks at the Higher Levels prospect consist predominantly of metalliferous mudstones and lesser detrital shales that reach a drilled thickness of ~18 m in the core of a syncline. The mudstones are finely laminated, organic matter and/or graphitic carbon-rich. The main sulphide phases are pyrite, chalcopyrite, sphalerite, minor pyrrhotite, and galena. Pyrite occurs predominantly as abundant framboids in the mudstone matrix and as euhedral crystals in cross-cutting veins (Fig. 10F-G). Chalcopyrite and sphalerite are mainly present interstitially between euhedral pyrite in

these veins. Sphalerite locally displays chalcopryite disease and also forms pseudomorphs after pyrite framboids. Pyrrhotite and galena are minor phases and are present as inclusions in pyrite. Covellite locally forms supergene rims around chalcopryite (Fig. 10G). Gangue minerals in these veins consist of ferroan dolomite to Mg-Mn-bearing ankerite, quartz, and subhedral to euhedral hydrothermal graphite that is associated with sulphides and the other gangue minerals (Fig. 10H). The mudstone matrix consists of quartz, chlorite, sericite, carbonates, and carbonaceous material. Accessory minerals include apatite, monazite, rutile, and gersdorffite.

Beaver Lake prospect

The Beaver Lake prospect contains metalliferous mudstones that locally are intercalated with detrital shale beds up to 5 m thick. The metalliferous mudstones are finely laminated, carbonaceous and sulphide-rich, with sulphides occurring predominantly finely disseminated and parallel to lamination (Fig. 10I), but also in veins that cross-cut the lamination. The matrix is rich in framboidal pyrite and fine-disseminated graphite. Subhedral to euhedral hydrothermal graphite occurs in veins associated with pyrite, sphalerite, chalcopryite, and gersdorffite, and carbonates. Sphalerite locally displays chalcopryite-disease. Cross-cutting veins consist predominantly of euhedral pyrite, sphalerite, chalcopryite, and the gangue minerals quartz, ankerite, dolomite, and chlorite (Fig. 10J). Mass-wasting textures, whereby felsic volcanic detritus are intermingled with metalliferous mudstones, are present in the drill holes BL11-01 and BL11-02. Shearing, strong foliation, and tectonic cataclastic brecciation of the volcanic and sedimentary rocks is common (Fig. 3C). Small-scale

parasitic buckle folds are observed in the drill holes BL11-01 and BL11-03, with cleavage developed parallel to the axial plane of the fold.

Duck West showing

The altered felsic rocks of the Duck West showing are interbedded with about 6 m of detrital shale (Fig. 11A) that overlies mineralized tuff. The sedimentary rocks are silty shales, locally with finely disseminated and euhedral pyrite and strong carbonate alteration. The mineralized tuff is sulphide-rich, consisting predominantly of colloform to euhedral pyrite and minor sphalerite with a matrix of recrystallized quartz.

Duck Pond deposit area

Laminated sulphide-rich (pyrite, pyrrhotite) mudstones occur in 10 to 30 cm thick beds in the unmineralized Duck Pond Upper Block ($\sim 514 \pm 2$ Ma, U-Pb zircon age), as interflow mudstones in mafic pillow lavas of the Lake Ambrose formation, or at the contact between the Lake Ambrose formation mafic volcanic rocks and the felsic rhyolite flows and volcaniclastic rocks of the Bindons Pond formation (Piercey et al. 2012). The Upper Block is structurally juxtaposed upon the 5 Ma younger Duck Pond Mineralized Block, and metalliferous mudstones occurring in this Upper Block are genetically not related to massive sulphide mineralization present in the Mineralized Block. The main sulphide phases in the Upper Block mudstones are pyrrhotite, framboidal pyrite, chalcopyrite, and sphalerite, with apatite and carbonates as common gangue minerals (Piercey et al. 2012). Shales from the Cambrian Serendipity zone horizon are structurally incorporated into the Duck Pond thrust and are locally tectonically intermingled with mineralized tuff fragments of the Duck Pond mineralized sequence (Fig. 5; Squires and Moore 2004).

Boundary deposit

Metalliferous mudstones occur at the fringes of the Boundary South Zone and reach up to 4 m in thickness. They are commonly interbedded with mineralized tuff of varying thickness and grain size (mm to dm scale). They are brown to black, finely laminated with sulphides occurring predominantly parallel to lamination. In proximity to the massive sulphides, the mudstones are intercalated with beds of mineralized lapilli tuff (replacement-style mineralization) (e.g., drill hole BD00-169; Figs. 7A, 11B). The grain size and thickness of the tuff beds intercalated with the mudstones decreases with increasing distance from mineralization (e.g., drill hole BD10-009; Figs. 7A, 11B-C). The finely laminated metalliferous mudstones are framboid-rich with euhedral pyrite overgrowing the framboids, and chalcopyrite and sphalerite occurring interstitially between the framboids (Fig. 11D).

Boundary West showing

The Boundary West showing has metalliferous mudstones that occur at the upper contact of the Boundary deposit hanging wall quartz-phyric to aphyric felsic volcanic flows to volcanoclastic rocks and overlying mafic volcanic flows (Fig. 7B-C). The metalliferous mudstones are up to ~4 m thick, are locally reworked, intercalated with lapilli tuff layers, and exhibit peperitic textures with the pillowed mafic volcanic rocks; the peperite forms up to a ~12 m thick sequence. Felsic volcanoclastic rocks that are intermingled with metalliferous mudstone (up to 4 m thick) are interpreted to represent mass wasting deposits. The main sulphide phases are framboidal pyrite, which forms a finely disseminated sulphide matrix, euhedral pyrite that is overgrowing the framboids,

and interstitial chalcopyrite and sphalerite (Fig. 11E-F). The latter commonly displays chalcopyrite disease.

Old Camp showing

The metalliferous mudstones associated with the Old Camp showing are up to ~5 m thick and occur at three stratigraphic levels in the Boundary deposit quartz-phyric hanging wall that extends laterally to the Old Camp area. They are finely laminated, dark-brown, graphitic carbon- and sulphide-rich mudstones (Fig. 11G) that are locally reworked and/or intercalated with cherty layers. Framboidal pyrite is abundant in the matrix and occasionally overgrown by euhedral pyrite. Sphalerite, chalcopyrite, and euhedral pyrite are associated with ankerite-dolomite-chlorite-quartz-gangue in veins (Fig. 11H). Structurally juxtaposed mid-Ordovician sedimentary rocks of up to 130 m drill-intersected thickness occur primarily in the upper section of the stratigraphy and consist of tectonized dark grey to black graphitic carbon-rich silty shales, volcanoclastic turbidites, and polymictic pebble- to cobble-sized conglomerates with a shaly matrix (Figs. 8B, 11I). These sedimentary rocks are strongly sheared and reworked, contain mylonitized mafic volcanic “rafts”, and are locally intruded by mafic dykes. Fragments of metalliferous mudstones are locally incorporated into shales and volcanoclastic rocks associated with faulting (Fig. 11J).

Keats Pond showing

The Keats Pond showing consists of a sequence of detrital, volcanoclastic-rich shales to polymictic conglomerates with a shaly matrix that overlie altered felsic volcanic rocks. These shales and conglomerates locally contain clasts of mineralized tuff and a thin horizon of metalliferous mudstones. The metalliferous mudstones are finely

laminated, dark brown to grey with finely disseminated sulphides parallel to lamination. The sulphides consist of finely disseminated framboidal and euhedral pyrite, which also occurs in cross-cutting veins (Fig. 12A). The contact between the metalliferous mudstone horizon and the detrital shale is sheared, but is interpreted to be conformable.

North Moose Pond showing

Metalliferous mudstones at the North Moose Pond showing stratigraphically overlie stringer mineralized felsic volcanic rocks and reach a thickness of up to 3 m. They grade into and are progressively diluted by shard-rich volcanoclastic turbiditic rocks. The metalliferous mudstones are finely laminated with sulphides occurring predominantly parallel to lamination and in minor cross-cutting veins (Fig. 12B). The main sulphide phases are framboidal pyrite in the matrix, and euhedral pyrite that is associated with interstitial sphalerite and chalcopyrite. Sphalerite displays chalcopyrite disease (Fig. 12C). In drill hole NM01-05 mafic volcanic rocks contain interflow mudstones, which locally are peperitic. Sheared detrital shales tectonically overlie the mafic volcanic rocks, are (tectonically) intercalated with felsic volcanic rocks, and intruded by mafic volcanic dykes. A metalliferous mudstone horizon occurs within the detrital shale in spatial proximity to the mafic volcanic rocks. Based on sedimentary textures (dewatering structures) the stratigraphy is likely overturned (Fig. 12D); accordingly, stratigraphic up is down-hole (Fig. 9C). The North Moose Pond volcanoclastic rocks (fine-grained to coarse-grained tuff) and detrital shales that occur stratigraphically above the volcanic rocks and metalliferous mudstones have planar and continuous bedding, are locally graded, which indicates a deposition from turbidity currents and suspension during a quiescent episode throughout the bimodal volcanism (McPhie et al. 1993).

South Moose Pond alteration zone

The South Moose Pond showing is comprised of strongly sheared detrital shales to polymictic pebble to cobble conglomerate that locally contain mineralized clasts of felsic tuff and the sequence overlies mafic volcanic rocks. The detrital shales are intercalated with reworked laminated dark brown metalliferous mudstones (Fig. 12E). Metalliferous mudstones also occur as interflow mudstones within variably sheared mafic volcanic rocks. The matrix of the metalliferous mudstones contains framboidal and euhedral pyrite and minor chalcopyrite and galena. Quartz-carbonate (ankerite-dolomite)-chlorite veins are commonly associated with euhedral pyrite and chalcopyrite. Tight parasitic folds in tuff layers and overall strong shearing indicate a complex stratigraphy in the South Moose Pond area.

Bell Island

The Bell Island black shales were deposited in tidal-influenced to subtidal offshore environments and contain rhythmic layering of thin- to medium-bedded shales and silt- to sandstone (Fig. 12G). The black shales are laminated micaceous silty shales with abundant carbonaceous material in form of diffuse organic matter and algal fragments (Fig. 12H).

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

Metalliferous mudstones and graphitic shales were sampled from drill core from 12 deposits, prospects, and showings within the Tally Pond belt (excluding the Upper Block Duck Pond mudstones) and from three locations on coastal outcrops on Bell Island. Detailed sampling procedures are given in Appendix A. Samples for whole-rock lithogeochemical studies were analysed for major and minor elements by lithium

metaborate/tetraborate fusion followed by HNO_3 dissolution and analysis by inductively coupled plasma (atomic) – emission spectroscopy (ICP-ES). Carbon (C) and sulphur (S) were obtained by infrared spectroscopy and mercury (Hg) was obtained by the cold vapour 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 (HFSE), trace metals, and many low field strength elements (LFSE) were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) in the Department of Earth Sciences at Memorial University, using screw-top Teflon® bomb (Savillex®) multi-acid dissolution. The multi-acid (HNO_3 , HF, HCl, H_3BO_3 , and H_2O_2) whole-rock dissolution process was a modified version of that of Jenner et al. (1990) and Longerich et al. (1990) to account for the high amounts of carbonaceous material in the samples. These procedures and detailed QA/QC protocol are provided in Appendix A.

Results

Lithogeochemistry

Immobile elements and sediment provenance: Homogenization of detritus in sedimentary basins results in basin muds that contain immobile trace element patterns similar to their source regions (Bhatia and Crook 1986; Nesbitt and Markovics 1997). Processes such as chemical weathering, diagenesis, hydrothermal alteration, or low-grade metamorphism, do not significantly alter the ratios of immobile elements like the HFSE (e.g., Zr), the REE (e.g., La), and the compatible elements (e.g., Sc). Hence, ratios of these elements are useful for provenance studies and to reconstruct the evolution of the tectonic environments in which the sediments were deposited (Taylor and McLennan

1985; Kolata et al. 1996; McLennan et al. 2003). In Th/Sc-Zr/Sc space and ternary diagrams like La-Th-Sc and Th-Sc-Zr/10 (Fig. 13D-F), the Tally Pond belt metalliferous mudstones and detrital shales overlap the fields of the Lemarchant mudstones. This indicates that they share similar source rocks, such as upper crustal rocks with predominantly continental island arc and to a lesser extent continental island arc characteristics (Fig. 13D-F). Samples trending towards the La-apex, suggest potential La-scavenging from seawater during sedimentation (e.g., Bau 1991; 1993). The data shown in the ternary Th-Sc-Zr/10 diagram and the Th/Sc versus Zr/Sc plot indicate that the Tally Pond belt source rocks are zirconium depleted, as previously reported by Squires and Moore (2004) and McNicoll et al. (2010).

Hydrothermal versus detrital element signatures: Samples from Lemarchant metalliferous mudstones and Bell Island have been plotted on Boström-type diagrams (Fig. 14 A-B; Boström et al. 1972; Boström 1973) and are clearly distinct: the Lemarchant metalliferous mudstones predominantly fall within the hydrothermal sediment field with 40 to 80% hydrothermal component, whereas the Bell Island black shales plot in the detrital sediment field. All Tally Pond belt samples that do plot within the hydrothermal sediment field are metalliferous mudstones, whereas those plotting in the detrital sediment field are detrital shales and/or tuff samples. The two Cookstown samples have intermediate features (Fig. 14 A-B). Metalliferous mudstones from the Upper Block at the Duck Pond deposit also fall within the hydrothermal fields in the Boström-type diagrams (Piercey et al. 2012). Characteristic for metalliferous mudstones that are stratigraphically immediately associated with massive sulphides of the Lemarchant deposit (within five metres), are elevated Ba- and Hg levels (up to 130,200

ppm Ba and up to 17,700 ppb Hg, ranging from 646 to 130,200 ppm Ba and 2.5 to 17,700 ppb Hg). The Ba in the Lemarchant metalliferous mudstones is predominantly hosted in barite and celsian and minor in hyalophane and witherite. The anomalous Hg-Ba in the Lemarchant mudstones is in part due to the boiling present in Lemarchant hydrothermal system; however, Ba-Hg-enrichment is a feature common in alteration in VMS throughout the Tally Pond belt (e.g., Collins 1989). Metalliferous mudstones and detrital shales from the Tally Pond belt outside Lemarchant have Ba values that are up to 3792 ppm and Hg contents up to 8790 ppb (Fig. 14C). The Bell Island black shales and two Beaver Lake samples (one shale, one mudstone) have very low Hg values close to and/or below the detection limit of 5 ppm (Fig. 14C). To distinguish the high Ba and Hg contents that are associated with massive sulphide mineralization in hydrothermal systems from sedimentary-diagenetically-derived Ba, a plot with Ba/Al versus (Zn+Hg)/Al was utilized (Fig. 14D). Ba, Zn, and Hg are interpreted to represent hydrothermally derived components of the mineralization, and Al the detrital constituents. In this plot (Fig. 14D), proximal Lemarchant metalliferous mudstones show trends towards high Ba/Al and (Zn+Hg)/Al ratios, whereas detrital shales of the Tally Pond belt, as well as the Bell Island black shales have low ratios. The data of the metalliferous mudstones of the Tally Pond belt plot between those two fields defined by Lemarchant mudstones and detrital shales (Fig. 14D). Results shown in Figure 14E delineates that metalliferous mudstones have higher Fe- and S-contents than detrital shale and tuff samples. The Lemarchant mudstones have $\text{Fe}_2\text{O}_{3\text{T}}$ that ranges from 13 to 55 wt% and 2 to 42 wt% S, with mudstones that are closely associated with the massive sulphides having higher Fe and S values than those that are located in more distal environments

(Lode et al. 2015). The other Tally Pond belt metalliferous mudstones generally range from 8 to 50 wt% $\text{Fe}_2\text{O}_{3\text{T}}$ and 6 to 38 wt% S, whereas the detrital shales and tuffs have lower Fe- and S-values (6 and 29 wt% $\text{Fe}_2\text{O}_{3\text{T}}$ and 0.03 to 24.7 wt% S). Similarly, metalliferous mudstones of the Tally Pond belt have higher Zn and Pb values (76 to 33264 ppm Zn and 21 to 4508 ppm Pb) than the detrital shales (30 to 3254 ppm Zn and 2 to 912 ppm Pb) and partially overlap with the field of the Lemarchant proximal mudstones (40 to 162,512 ppm Zn and 8 to 25,600 ppm Pb) (Fig. 14F).

Rare earth element and Y (REY) signatures: The rare earth element and Y (REY) characteristics of the metalliferous mudstones and detrital shales of the Tally Pond belt, as well as from the Bell Island black shales are shown in Figure 15A-F. Data for the Duck Pond mudstones are from Piercey et al. (2012). All measurements are normalized to the post-Archean Australian shale using the data of McLennan (1989). The Lemarchant mudstones are LREE-depleted and have relatively flat HREE patterns, negative Ce anomalies ($\text{Ce}/\text{Ce}^* < 1$), and predominantly positive Eu anomalies (Eu/Eu^* up to 3.5) (Fig. 15A). Ce/Ce^* and Eu/Eu^* were calculated using the equations after McLennan (1989) where $\text{Ce}/\text{Ce}^* = (\text{Ce}_{\text{sample}}/79.6) / \sqrt{((\text{La}_{\text{sample}}/38.2) * (\text{Pr}_{\text{sample}}/8.83))}$ and $\text{Eu}/\text{Eu}^* = (\text{Eu}_{\text{sample}}/1.08) / \sqrt{((\text{Sm}_{\text{sample}}/5.55) * (\text{Gd}_{\text{sample}}/4.66))}$, respectively. The Duck Pond mudstones also display a negative Ce anomaly, but have a positive Y anomaly, HREE enrichments, and a smaller positive Eu anomaly (Fig. 15A). Black shales from Bell Island have flat REY signatures with no significant anomalies. The Cookstown samples have similar REY signatures as the Bell Island shales; however, they do show small Ce anomalies ($\text{Ce}/\text{Ce}^* \sim 0.7$) (Fig. 15B). All other Tally Pond belt mudstones have intermediate REY patterns with varying Eu anomalies from slightly negative to strongly

positive ($\text{Eu}/\text{Eu}^* = 0.9\text{--}3.1$), negative Ce anomalies ($\text{Ce}/\text{Ce}^* = 0.5\text{--}0.9$), and none to small positive Y anomalies. The Tally Pond belt shales have $\text{Eu}/\text{Eu}^* = 0.8\text{--}2.0$ and negative Ce anomalies ($\text{Ce}/\text{Ce}^* = 0.7\text{--}0.99$), with one mineralized tuff from Duck West having a strong positive Eu anomaly of $\text{Eu}/\text{Eu}^* = 6.8$, and one sample from South Moose Pond having a positive Ce anomaly of $\text{Ce}/\text{Ce}^* = 1.5$. To assess whether the Ce-anomalies are true anomalies or caused by a positive La-anomaly the samples are plotted in the Ce/Ce^* versus Pr/Pr^* diagram (Fig. 15G). Accordingly, the Ce-anomalies of the Lemarchant samples are interpreted to be true Ce-anomalies.

Discussion

Evaluating hydrothermal versus detrital origins and the paleo-redox environment

Sedimentary rocks occurring in the Tally Pond volcanic belt were deposited in a graben/caldera basin related to arc-rifting with active volcanism and hydrothermal activity (Evans and Kean 2002; Piercey et al. 2014). Hydrothermal metalliferous mudstones have complex geochemical patterns reflecting variable inputs from: 1) hydrothermal-exhalative matter; 2) volcanoclastic to epiclastic material; 3) detrital sedimentation; and 4) hydrogenous elements scavenged from seawater onto hydrothermal particles (Boström and Peterson 1966; German and Von Damm 2003; Peter and Goodfellow 2003). Exhalative metalliferous mudstones form as seafloor hydrothermal plume fallout when hot, reduced, metal- and sulphide-rich (Fe, Mn, Cu, Ni, Pb, Zn, Hg, As, Ba, S) vent fluids are discharged and mix with the cold, oxidized, sulphate-rich ambient seawater (Boström and Peterson 1966; Haymon and Kastner 1981; Gurvich 2006). Furthermore, detrital input, represented by Al and Ti, is a negligible component in exhalative sediments (Boström et al. 1969; Gurvich 2006). As such, hydrothermal

metalliferous mudstones, as those from Lemarchant, have elevated Fe and base metals, and plot within the hydrothermal fields on Boström-type plots (Fig. 14 A-B; Boström 1973; Boström et al. 1972; Lode et al. 2015). Accordingly, samples from Higher Levels, Beaver Lake, Boundary, Boundary West, North and South Moose Pond, Keats Pond, Old Camp that overlap the field of the Lemarchant mudstones and Boström's hydrothermal sediment field (~30-80% hydrothermal component) can be identified as metalliferous mudstones with a hydrothermal exhalative origin (Fig. 14 A-B). A mineralized tuff sample from Duck West also falls within the hydrothermal sediment field (Fig. 14 A-B), and is likely a mixture of both tuff and hydrothermal material. The Beaver Lake and Duck West prospects, as well as the Boundary West, Old Camp, and South Moose showings have detrital shales that are either intercalated with the metalliferous mudstones and bimodal volcanic rocks (e.g., Beaver Lake, Boundary West, Figs. 3C, 7B-C), and/or overlie the volcanic sequences (e.g., Old Camp, North and South Moose Pond, Figs. 8B, 9C). These Tally Pond belt detrital shales cluster around Boström's detrital sediment field and thus, are not of hydrothermal origin. Nevertheless, the Boundary West shales, the South Moose Pond shale, and some shale samples from Higher Levels have minimal hydrothermal components (up to 20%), which may have been a result of slight contributions from hydrothermal fluids (Fig. 14 A-B). The Cookstown metalliferous mudstones/shales have intermediate geochemical characteristics and plot between the hydrothermal and detrital fields (Fig. 14 A-F). Based on the geochemistry and the petrographic observations, they are interpreted to be non-exhalative detrital shales that were overprinted by hydrothermal fluids metalliferous that penetrated the semi-consolidated sediment (e.g., Doyle and Allen 2003). This is reflected by the sulphide-

poor matrix and sulphide-rich (pyrrhotite, chalcopyrite, minor galena) cross-cutting veins and patches (Fig. 10C-E). Comparable to the Lemarchant mudstones, the other Tally Pond belt metalliferous mudstones also have noticeably elevated base and transition metal (Fe, Zn, Pb), and S contents (Fig. 14E-F), reflecting the presence of polymetallic sulphides that were derived from hydrothermal fluids (Boström 1973; Gurvich 2006; Jones et al. 2006). The sulphide mineralogy of the metalliferous mudstones is also consistent with whole rock geochemical results (Figs. 10G, 11D, 11F, 11H, 12C).

Alteration – major element systematics: Immediately after precipitation, metalliferous mudstones are subject to hydrothermal and diagenetic alteration processes due to ongoing hydrothermal activity (Gurvich 2006; Hannington 2014). Under these conditions major elements are variably mobile, and alkali elements have considerable mobility (Nesbitt and Young 1982; Nesbitt 2003). In plots such as the A-CN-K and A-CN-K-FM molar diagrams (Fig. 13A-B), the immobile Al_2O_3 is compared to the mobile alkali elements (Nesbitt and Young 1982). In A-CN-K space, the Lemarchant metalliferous mudstones (orange field) lie within the sericite (illite/muscovite) and also in the carbonate-dolomite dominated fields of the diagram. Only one North Moose Pond and one Higher Levels mudstone sample show strong carbonate alteration. The rest of the Tally Pond belt metalliferous mudstones and shales follow the sericite trend similar to the Lemarchant mudstones (Lode et al. 2015). However, two distinct alteration trends are recognizable in the metalliferous mudstones and the detrital shales of the Old Camp showing. The shales plot around the average shale field, comparable to the Bell Island shales, whereas the metalliferous mudstones are closer to the sericite and carbonate alteration fields indicating hydrothermal alteration (Fig. 13A). In A-CN-K-FM space, a

clear distinction between graphitic shales and metalliferous mudstone of the Tally Pond belt is noticeable: the mudstones overlap with the field of the Lemarchant mudstones, whereas detrital shales lie outside of this field (Fig. 13B). The Tally Pond belt metalliferous mudstones plot near the FM-part of the diagram towards the sulphide-oxide apex and the chlorite-smectite trend, and for the Lemarchant mudstones also towards the calcite-dolomite apex; the shales trend towards muscovite/illite and feldspars. Also trending towards muscovite/illite, with only minor carbonate contribution, are the Bell Island black shales (Fig. 13B). Accordingly, the major element alteration signatures represent a valuable proxy for exploration by distinguishing hydrothermal alteration in detrital and hydrothermal shales. A positive correlation between Al_2O_3 and TiO_2 that goes through the origin ($r^2 = 0.802$ without the Duck West outlier; Fig. 13C) in the Tally Pond belt shales and mudstones, indicates that both were likely immobile during post-depositional processes, such as diagenesis and alteration (Barrett and MacLean 1994).

Evaluating indicators for vent proximity; i.e., proximity to massive sulphides

Metalliferous sedimentary rocks generally have a greater lateral extent than the associated VMS deposits, which are small targets for exploration (Franklin et al. 1981; Doyle and Allen 2003; Peter 2003; Gibson et al. 2007). Hydrothermal plume processes result in distinct variations in mineralogy and chemistry as a function of vent proximity and proximity to massive sulphide mineralization (Franklin et al. 1981; Kalogeropoulos and Scott 1989; Peter 2003; Gibson et al. 2007; Slack et al. 2009). Accordingly, it is important to identify these geochemical fingerprints and the potential as ore bearing horizons, and to delineate proximal metalliferous mudstones from distal ones and from less prospective detrital shales (e.g., Spry et al. 2000; Peter 2003). In particular, a

combination of Ba-enrichment, REY-systematics with positive Eu anomalies, high base metal contents, chondritic Y/Ho ratios (~27), as well as high Fe/Ti and low Al/(Al+Fe+Mn) indicate to a hydrothermal derivation of the sediment and precipitation from high temperature ($T > 250^{\circ}\text{C}$) fluids (Boström et al. 1972; Boström 1973; Slack et al. 2009; Lode et al. 2015).

The metalloid Ba is typically enriched in many VMS deposits (Lydon 1984; Large 1992; Huston et al. 2010) and is a useful proxy for geochemical fingerprinting (Collins 1989; Lode et al. 2015). The enrichment of Ba related to VMS systems is a result of thermochemical breakdown of feldspars in the hydrothermal reaction zone that releases Ba^{2+} into the reduced hydrothermal fluids (German and Von Damm 2003; Hannington et al. 2005; Griffith and Paytan 2012). In contact with seawater sulphate barite precipitates at or near the seafloor in proximity to the hydrothermal vent site, because it is highly insoluble in oxidized seawater (Ohmoto and Goldhaber 1997; Huston and Logan 2004; Griffith and Paytan 2012). In other deposits, the Ba is incorporated into micas, carbonates, and other clays during fluid-rock reaction of the VMS-hosting sequence (e.g., Collins 1989; Peter 2003; Piercey et al. 2014). The presence of barite and generally high Ba-levels (up to 130.00 ppm) found in Lemarchant mudstone samples proximal to mineralization strongly favours a hydrothermal origin and a vent proximal location of deposition (Lode et al. 2015). However, a lack of barite does not necessarily indicate a vent distal environment. VMS mineralization formed by replacement style in a reduced subseafloor environment may have Ba present in the hydrothermal fluids, but no seawater SO_4^{2-} available for barite formation, which results in footwall and hanging wall

rocks with Ba-enrichments without exhalative barite occurrences (e.g., Duck Pond and Boundary deposits; Collins 1989; Piercey et al. 2014).

In contrast to the vent-proximal Lemarchant mudstones, the other Tally Pond belt metalliferous mudstones have no observed barite. Based on their overall low Ba levels, it is proposed that they precipitated in a more vent-distal depositional environment where less Ba from hydrothermal fluids was available (Fig. 14C). Interestingly, detrital shale samples of prospects and showings in the Tally Pond belt (not including Lemarchant) have no barite, but higher Ba-levels than some of the Tally Pond belt metalliferous mudstones (Fig. 14C). This effect may relate to the commonly observed enrichment of Ba in marine sediments that contain abundant carbonates, organic matter, Fe-Mn oxyhydroxides, and detrital matter, or may be due to Ba incorporation into clays due to fluid-rock reaction of the shales (Peter 2003; Gonneea and Paytan 2006; Griffith and Paytan 2012). To differentiate between Ba that is associated with base metal massive sulphide mineralization and Ba related to alteration or non-hydrothermal marine sedimentary processes, a Ba/Al versus (Zn+Hg)/Al diagram was utilized (Fig. 14D), where Zn+Hg and Ba represent the hydrothermally derived elements and Al the detrital component. As a consequence, it is possible to distinguish more clearly detrital shales that are characterized by lower Ba/Al and (Zn+Hg)/Al from vent proximal mudstones. Only a few of the Tally Pond belt metalliferous mudstones overlap with the proximal Lemarchant mudstone field due to lower Ba-levels. Nevertheless, because of the similarly high (Zn+Hg)/Al, it is suggested that the other Tally Pond belt metalliferous mudstones also precipitated from hydrothermal fluids, but in a more vent-distal depositional environments (Fig. 14F).

In VMS-forming environments host rocks, temperature, pH, fO_2 , and chlorinity are key factors controlling the concentration of base metals dissolved in the hydrothermal fluids (Lydon 1988; Von Damm 1990; Hannington 2014). The presence (or lack) of a positive Eu anomaly can give insights about the temperature of the hydrothermal fluids from which the metalliferous sediment precipitated (Sverjensky 1984; Bau 1991). Thereby, hydrothermal fluids and precipitates that are derived from high temperature fluids ($>250^\circ\text{C}$) have positive Eu^{2+} anomalies, because the $\text{Eu}^{2+}/\text{Eu}^{3+}$ redox equilibrium is strongly temperature-dependent (Sverjensky 1984; Bau 1991; German and Von Damm 2003; Peter 2003). Under high-T ($>250^\circ\text{C}$), 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 1991; Peter 2003). Consequently, metalliferous mudstones that display pronounced positive Eu anomalies are precipitated from high-T ($>250^\circ\text{C}$) hydrothermal fluids and sediments have none to small positive Eu anomalies when precipitated from fluids with lower temperatures (Sverjensky 1984; Bau 1991; German and Von Damm 2003; Peter 2003). Metalliferous mudstones and detrital shales sampled from the Tally Pond deposits, prospects, and showings, and black shales from Bell Island, have variable REE-signatures ranging from hydrothermal (Lemarchant mudstone-like signatures) to non-hydrothermal black shales (flat REE-patterns; i.e., Bell Island shales), and to those that have mixed signatures (Fig. 15 B-F). It is suggested that the hydrothermal fluids contributing to the metalliferous mudstones associated with the Lemarchant and Boundary deposits, and the Boundary West showing had temperatures exceeding 250°C (Fig. 15A, E-F). The detrital shales and mineralized tuff of the Duck West showing also had contributions from high-T ($T>250^\circ\text{C}$) fluids (Fig. 15C).

Accordingly, the presence of positive Eu anomalies is a useful indicator to reduced, high-T hydrothermal fluids that mixed with oxygenated water. However, a lack of positive Eu anomalies can either imply that the temperatures were below 250°C, or there were reduced ambient seawater conditions (Bau 1991; Peter 2003). Reducing conditions increases the stability of Eu^{3+} in complexes and accordingly, no Eu anomalies occur (Bau 1991). Furthermore, most detrital sediments, particularly those of felsic/crustal provenance, also have no positive Eu anomalies (Peter and Goodfellow 2003); a pattern reflected in the overall flat REE patterns of the Bell Island black shales (Fig. 15 B). 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).

Paleoredox of the hydrothermal fluids can also be determined from the Ce-systematics of the mudstones and shales. The presence of negative Ce anomalies in hydrothermal sediments is inherited from mixing of the vent fluids with Ce-depleted oxygenated seawater (German and Elderfield 1990; Hannington 2009). In reduced vent fluids flat REE patterns are expected, and negative Ce anomalies do not occur, as Ce^{3+} will not oxidize to Ce^{4+} 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). Larger contributions of detrital material to the hydrothermal matter can mask and flatten hydrothermal signatures, such as positive Eu, Y, and negative Ce anomalies (Peter and Goodfellow 2003). Accordingly, those deposits that have metalliferous mudstones samples with predominantly $\text{Ce}/\text{Ce}^* < 1$ and $\text{Eu}/\text{Eu}^* > 1$ were deposited in an a

predominantly oxic environment with contributions of high temperature ($T > 250^{\circ}\text{C}$) hydrothermal fluids, i.e., Higher Levels, Beaver Lake, North and South Moose Pond, Duck Pond Upper Block, Boundary, Boundary West (Fig. 15C-F). The flat REY pattern of the metalliferous mudstone sample from Keats Pond (Fig. 15F) and detrital shale samples from Old Camp (Fig. 15D) and North Moose Pond (Fig. 15F) suggest reduced conditions and/or a strong dilution by detrital material. The presence of bioturbation in samples from Higher Levels, Beaver Lake, and possibly in shales from North and South Moose Pond supports the oxygenated ambient water conditions at the time of formation of the sediment (e.g., Savrda and Bottjer 1989) suggesting that the flat REY pattern was inherited from sedimentary detritus and not due to reducing conditions.

The REE-patterns of the metalliferous mudstones occurring in the Upper Block of Duck Pond indicate that they precipitated from hydrothermal fluids with low to intermediate temperatures, not exceeding 250°C , and that the constituents of the Duck Pond mudstones had longer residence times in the plume and more mixing of hydrothermal fluids with seawater. As a result, more scavenging of elements from seawater onto hydrothermally derived particles, such as Fe oxyhydroxides occurred (Rudnicki 1995; Mills and Elderfield 1995; Peter 2003), resulting in samples with negative Ce anomalies, elevated HREE, and a strongly pronounced positive Y anomaly in the Duck Pond mudstones. Accordingly, the Duck Pond mudstones are suggested to represent distal stratigraphic equivalents to the proximal Lemarchant mudstones (Piercey et al. 2012; Lode et al. 2015).

Sediment provenance – basin setting and tectonic environment

Provenance-related immobile element systematics of the Tally Pond belt metalliferous mudstones and detrital shales have continental to oceanic island arc signatures (Fig. 13D-F). This is consistent with provenance from local host rocks, which are bimodal island arc sequences with transitional to calc-alkalic character (Squires and Moore 2004; Rogers et al. 2006). Furthermore, 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). A rifted arc environment is also consistent with much of the mineralogy, compositions and paragenesis of the phases in the hydrothermal metalliferous mudstones and the detrital shales and volcanoclastic-epiclastic sediments of the Tally Pond belt.

It is notable, however, that two distinct age populations are found in the Tally Pond volcanic rocks: 513 ± 2 Ma in the Lemarchant area and the Duck Pond Upper Block and 509 ± 3 Ma in the Duck Pond Mineralized Block and equivalents (e.g., Dunning et al. 1991; McNicoll et al. 2010). Even though these ages overlap with a 95 % confidence interval and 2σ error ellipses (no overlap for 1σ errors), the reproducibility of these two ages suggests that they represent two separate age clusters (Fig. 16D; G. Dunning, *pers. comm.* 2015). Additionally, the stratigraphy of the Lemarchant area and the Upper Block at Duck Pond share strong similarities and both contain abundant metalliferous mudstones.

A duration of up to 4 Ma for a hydrothermal system also appears unlikely, because hydrothermal activity occurs as episodic pulses and generally exists not longer than <10,000 years (Cathles et al. 1997). Only in exceptional cases can long-lived

hydrothermal systems last for ~1 Ma (Cathles et al. 1997). Therefore, it is proposed that VMS-forming hydrothermal activity related to the bimodal volcanism in the Tally Pond belt occurred during two rifting phases: at ~513 Ma (Lemarchant) and ~509 Ma (Duck Pond, Boundary) (Fig. 16A-B, D). Geochronological studies by McNicoll et al. (2010) suggested that these age clusters represent two subpopulations of crystallization ages of extrusive, pyroclastic, and intrusive volcanic rocks of the Tally Pond belt. The Lemarchant deposit is interpreted to have formed in shallow water (<1200 m) at temperatures between 250 to ~325°C, and to have undergone fluid phase separation with a magmatic fluid contribution to the hydrothermal system (Fig. 16C; Gill and Piercey 2014; Gill 2015; Lode et al. 2015). This is supported by the sulphide mineralogy, which is enriched in sulphosalts, Zn-Pb phases, including low Fe sphalerite, and precious metal bearing phases; metal assemblages, including enrichments in epithermal suite elements; and bladed barite and carbonates, features common to epithermal-type deposits (Gill and Piercey 2014; Lode et al. 2015). The nearby Lemarchant microgranite is suggested to represent the synvolcanic intrusion providing the heat to drive the hydrothermal circulation (McNicoll et al. 2010; Squires and Moore 2004) and potentially contributed magmatic fluids and volatiles to the hydrothermal system. In contrast, the Duck Pond Cu-Zn-Pb massive sulphides have very simple mineralogy and are interpreted to have formed at greater depths (>1200 m below seawater level) and higher temperatures (~350°C), where the fluids could not boil and phase separation did not occur (Fig. 16C).

The Duck Pond metalliferous mudstones occur within the ~513 Ma Upper Block at the contact of felsic and mafic volcanic rocks of the Bindons Pond and Lake Ambrose formations, respectively (Piercey et al. 2012). This Upper Block correlates in age and

813 stratigraphy with the bimodal volcanic sequence and metalliferous mudstones in the
814 Lemarchant deposit. The Lemarchant massive sulphides and metalliferous mudstones are
815 interpreted to have been deposited in a smaller scale basin during the first rifting phase at
816 ~513 Ma, and were then subsequently covered by mafic volcanic rocks during and/or
817 immediately after deposition of the massive sulphides and metalliferous mudstones.
818 Hydrothermal activity continued during the emplacement of the basalts as indicated by
819 the presence of abundant interflow mudstones at the Lemarchant deposit (Fig. 2; Lode et
820 al. 2015). These interflow mudstones occur as within basaltic flows and pillow basalts
821 and are identified to have a hydrothermal origin by detailed geochemical studies on
822 different mudstone types in Lode et al. (2015). Second stage rifting and hydrothermal
823 activity is interpreted to have been associated with the formation of the Duck Pond and
824 Boundary deposits, and other prospects at ~509 Ma (e.g., Boundary West, Old Camp,
825 North and South Moose Pond; Fig. 16B). Locally, some of the detrital shales that occur in
826 the northeastern parts of the Tally Pond belt have stratigraphic relationships that correlate
827 with Duck Pond and Boundary and suggest deposition in the basin related to the second
828 phase of rifting. These suggested Mid-Cambrian graphitic shales are more abundant in
829 the northeastern part of this basin than in the southwestern area, which argues that the
830 area of the second phase rifting may have had more space available to accommodate
831 these sediments. The detrital shales and volcanoclastic to epiclastic sediments of the Mid-
832 Ordovician (Katian to Sandbian) Wigwam Pond group/Noel Paul's Brook group that
833 were deposited in the Victoria Arc basin with horst and graben topography, were strongly
834 deformed during the final closure of the Iapetus in the Late Ordovician resulting in the
835 black shale mélange (Zagorevski et al. 2010). This black shale mélange forms a thick

cover sequence on top of the Cambrian Tally Pond volcanic rocks (Squires and Moore 2004, Zagorevski et al. 2010).

In essence, it is proposed that both rifting phases (~513 Ma and ~509 Ma) in the Tally Pond belt are associated with the formation of massive sulphides and exhalative metalliferous mudstones, i.e., two exhalative mudstone horizons occur. Additionally, during the 509 Ma event deposition of non-hydrothermal graphitic shales gradually increased, which occur predominantly in the northeastern part of the Tally Pond belt. In detail, the first horizon is represented by metalliferous mudstones of the Beaver Lake, Higher Levels, Duck Pond (Upper Block) and is related to the ~513 Ma Lemarchant hydrothermal event, which also caused the hydrothermal overprint of the Cookstown shales. The metalliferous mudstones from Boundary, Boundary West, Old Camp, Keats Pond, and North and South Moose Pond represent the second horizon and is genetically associated with the younger, ~509 Ma Duck Pond/Boundary hydrothermal event. Based on intercalated detrital shales and metalliferous mudstones in the Tally Pond belt (predominantly the northeastern part), it is suggested that deposition of detrital shales occurred already in the Mid-Cambrian, coincident with and following VMS formation (e.g., Serendipity and North Moose Pond). The gradual grading of Mid-Cambrian metalliferous mudstones into volcanoclastic-epiclastic sediments and detrital shales, suggests that the hydrothermal activity eventually decreased (~ <509 Ma) and deposition of detrital shales prevailed, i.e., at North Moose Pond. This is also supported by the REY patterns of the Tally Pond metalliferous mudstones, which have mixed hydrothermal and non-hydrothermal (detrital and volcanoclastic-epiclastic) signatures (Fig. 15B-F). Therefore, the base of the detrital shales represents a transitional period in the evolution

of the basin, when the hydrothermal systems of the second rifting phase were still active, but the contributions of detrital matter continuously increased. It is proposed that a possibly Silurian compressional environment, which may be related to inversion of the Penobscot backarc basin, caused juxtaposition of the older 513 Ma bimodal sequences of the first rifting phase (e.g., Lemarchant, Duck Pond Upper Block) on top of the younger 509 Ma sequence of the second rifting phase (e.g., Duck Pond, Boundary) (Fig. 16D; Squires and Moore 2004; Zagorevski et al. 2010). Also very much appreciated are the reviews and suggestions of the reviewers and the editor, Ali Polat, of the *Canadian Journal of Earth Sciences*, which greatly improved the manuscript.

Conclusions

The Tally Pond volcanic belt metalliferous mudstones provide an understanding the relationship of exhalative metalliferous mudstones that are genetically associated with VMS mineralization in bimodal volcanic environments. Hydrothermally derived mudstones are characterized by: 1) elevated Fe and base metals, and plot within the hydrothermal fields on Boström-type plots; 2) an enrichment in base metal sulphides and in Ba/Al and (Zn+Hg)/Al ratios; and 3) REY systematics that are indicative of deposition from high temperature fluids (i.e., $\text{Eu}/\text{Eu}^* > 1$), with or without evidence for mixing with oxygenated seawater ($\text{Ce}/\text{Ce}^* < 1$). Detrital shales in the Tally Pond belt are locally spatially associated with mineralization, when either intercalated with hydrothermal metalliferous mudstones and/or when intermingled with mineralized tuff or mudstone fragments. The Tally Pond volcanic belt is proposed to have two rifting phases that are associated with VMS-forming hydrothermal systems, at ~513 Ma (Lemarchant) and at ~509 Ma (Duck Pond/Boundary).

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References

- Aur Resources, L. 2007. Duck Pond Mine, Official Ceremony, May 9, 2007. Company brochure. For updated information see Teck Resources website - www.teck.com.
- Barrett, T.J., and MacLean, W.H. 1994. Chemostratigraphy and hydrothermal alteration in exploration for VHMS deposits in greenstones and younger rocks. In *Alteration and Alteration Processes Associated with Ore-Forming Systems*. Edited by D.R. Lentz. Geological Association of Canada. pp. 433-467.

- 907 Bau, M. 1991. Rare-Earth Element Mobility during Hydrothermal and Metamorphic
 908 Fluid Rock Interaction and the Significance of the Oxidation-State of Europium.
 909 Chemical Geology **93**(3-4): 219-230. doi: Doi 10.1016/0009-2541(91)90115-8.
- 910 Bau, M. 1993. Effects of Syn-Depositional and Postdepositional Processes on the Rare-
 911 Earth Element Distribution in Precambrian Iron-Formations. European Journal of
 912 Mineralogy **5**(2): 257-267.
- 913 Bau, M., and Dulski, P. 1996. Distribution of yttrium and rare-earth elements in the
 914 Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa.
 915 Precambrian Research **79**(1-2): 37-55.
- 916 Beyssac, O., and Rumble, D. 2014. Graphitic carbon: a ubiquitous, diverse, and useful
 917 geomaterial. Elements **10**: 415-420.
- 918 Bhatia, M.R., and Crook, K.A.W. 1986. Trace element characteristics of graywackes and
 919 tectonic setting discrimination of sedimentary basins. Contributions to
 920 Mineralogy and Petrology **92**(2): 181-193.
- 921 Boström, K. 1973. The Origin and Fate of Ferromanganoan Active Ridge Sediments.
 922 Stockholm Contributions In Geology **27**(2).
- 923 Boström, K., Joensuu, O., Valdés, S., and Riera, M. 1972. Geochemical history of South
 924 Atlantic Ocean sediments since Late Cretaceous. Marine Geology **12**(2): 85-121.
 925 doi: [http://dx.doi.org/10.1016/0025-3227\(72\)90023-0](http://dx.doi.org/10.1016/0025-3227(72)90023-0).
- 926 Boström, K., and Peterson, M.N. 1966. Precipitates from hydrothermal exhalations on the
 927 East Pacific Rise. Economic Geology **61**(7): 1258-1265.
- 928 Boström, K., Peterson, M.N., Joensuu, O., and Fisher, D.E. 1969. Aluminum-poor
 929 ferromanganoan sediments on active oceanic ridges. Journal of Geophysical
 930 Research **74**(12): 3261-3270. doi: Doi 10.1029/Jb074i012p03261.
- 931 Buschette, M. 2015. Hydrothermal alteration and lithogeochemistry of the Boundary
 932 volcanogenic massive sulfide (VMS) deposit, central Newfoundland, Canada. *In*
 933 Department of Earth Sciences. Memorial University of Newfoundland, St. John's.
- 934 Carey, S., and Sigurdson, H. 1984. A model of volcanogenic sedimentation in marginal
 935 basins. *In* Marginal Basin Geology: Volcanic and Associated Sedimentary and
 936 Tectonic Processes in Modern and Ancient Marginal Basins. *Edited by* B.P.
 937 Kokelaar and M.F. Howells, Geological Society Special Publication. pp. 37-58.
- 938 Cathles, L.M., Erendi, A.H.J., and Barrie, T. 1997. How long can a hydrothermal system
 939 be sustained by a single intrusive event? Economic Geology **92**(7-8): 766-771.
- 940 Collins, C.J. 1989. Report on lithogeochemical study of the Tally Pond Volcanics and
 941 associated alteration and mineralization. Unpublished Report for Noranda
 942 Exploration Company Limited (Assessment File 012A/1033 Newfoundland
 943 Department of Mines and Energy, Mineral Lands Division).
- 944 Copeland, D.A. 2009a. Assessment Report 012/1486 on Prospecting, Lithogeochemical
 945 Sampling and Data Interpretation on the Harpoon Property (Licenses 7695M,
 946 10461M, 10464M, 10465M, 10607M, 12357M, 12885M, 13583M, 13448M,
 947 13449M and 13667M) and the South Tally Pond Property (Licences 8183M,
 948 9569M and 14158M) Lake Ambrose Area, Newfoundland and Labrador. NTS
 949 12A/10 and 12A/07. Paragon Minerals Corporation.
- 950 Copeland, D.A. 2009b. Assessment Report on Soil Sampling on the Harpoon Property
 951 (Licences 7695M, 10464M and 10465), Lake Ambrose Area, Newfoundland and
 952 Labrador. NTS 12A/10 and 12A/07.

- Copeland, D.A., McClenaghan, S.H., and Piercey, S.J. 2008. 9th year Assessment Report on Diamond Drilling, Litho geochemistry, Pulse EM Surveying and Linecutting on Licence 8183M, South Tally Pond Property, Rogerson Lake Area, Newfoundland and Labrador, NTS 12A/10 and 12A/07. Newfoundland and Labrador Geological Survey Assessment File 012A/1459.
- Copeland, D.A., Toole, R.M., and Piercey, S.J. 2009. 10th Year Supplementary Assessment Report on Soil Sampling, Linecutting, Titan 24 Geophysical Surveying, Diamond Drilling and Petrography, Licence 8183M, South Tally Pond Property, Rogerson Lake Area, Newfoundland and Labrador, NTS 12A/10 and 12A/07. Newfoundland and Labrador Geological Survey Assessment File.
- de Ronde, C.E.J., Butterfield, D.A., and Leybourne, M.I. 2012. Metallogenesis and Mineralization of Intraoceanic Arcs I: Kermadec Arc—Introduction. *Economic Geology* **107**(8): 1521-1525. doi: 10.2113/econgeo.107.8.1521.
- Doyle, M.G., and Allen, R.L. 2003. Subsea-floor replacement in volcanic-hosted massive sulfide deposits. *Ore Geology Reviews* **23**(3-4): 183-222.
- Dunning, G.R., Kean, B.F., Thurlow, J.G., and Swinden, H.S. 1987. Geochronology of the Buchans, Roberts Arm, and Victoria Lake groups and Mansfield Cove Complex, Newfoundland. *Canadian Journal of Earth Sciences = Journal Canadien des Sciences de la Terre* **24**(6): 1175-1184.
- Dunning, G.R., Swinden, H.S., Kean, B.F., Evans, D.T.W., and Jenner, G.A. 1991. A Cambrian island arc in Iapetus; geochronology and geochemistry of the Lake Ambrose volcanic belt, Newfoundland Appalachians. *Geological Magazine* **128**(1): 1-17.
- Evans, D.T.W., and Kean, B.F. 2002. The Victoria Lake Supergroup, central Newfoundland - its definition, setting and volcanogenic massive sulphide mineralization. Newfoundland and Labrador Department of Mines and Energy, Geological Survey, Open File NFLD/2790. Open File NFLD/2790.
- Evans, D.T.W., Kean, B.F., and Dunning, G.R. 1990. Geological Studies, Victoria Lake Group, Central Newfoundland Current Research Report, Geological Survey Branch, Report: 90-1: 131-144.
- Franklin, J.M., Lydon, J.W., and Sangster, D.F. 1981. Volcanic-associated massive sulfide deposits. In *Economic Geology 75th Anniversary Volume. Edited by B.J. Skinner*. pp. 485-627.
- Fraser, D., Giroux, G.A., Copeland, D.A., and Devine, C.A. 2012. NI-43-101 Technical Report and Mineral Resource Estimate on the Lemarchant Deposit, South Tally Pond VMS Project, central Newfoundland, Canada for Paragon Minerals Corporation. National Instrument 43-101 Technical Report.
- German, C.R., and Elderfield, H. 1990. Application of the Ce Anomaly as a Paleoredox Indicator: The Ground Rules. *Paleoceanography* **5**(5): 823-833. doi: 10.1029/Pa005i005p00823.
- German, C.R., and Von Damm, K.L. 2003. Hydrothermal Processes. In *Treatise on Geochemistry*. Pergamon, Oxford. pp. 181-222.
- Gibson, H.L., Allen, R.L., Riverin, G., and Lane, T.E. 2007. The VMS model: Advances and application to exploration targeting. In *Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration. Edited by B. Milkereit*, Toronto, ON. pp. 717-730.

- 999 Gill, S.B., and Piercey, S.J. 2014. Preliminary mineralogy of barite-associated sulphide
1000 mineralization in the Ordovician Zn-Pb-Cu-Ag-Au Lemarchant volcanogenic
1001 massive sulphide deposit, Newfoundland and Labrador. *Current Research -*
1002 *Geological Survey of Canada* **2013-17**: 15. doi: 10.4095/292708.
- 1003 Gonneea, M.E., and Paytan, A. 2006. Phase associations of barium in marine sediments.
1004 *Marine Chemistry* **100**: 124-135.
- 1005 Griffith, E.M., and Paytan, A. 2012. Barite in the ocean - occurrence, geochemistry, and
1006 palaeoceanographic applications. *Sedimentology* **59**(6): 1-19. doi:
1007 10.1111/j.1365-3091.2012.01327.x.
- 1008 Gurvich, E.G. 2006. Metalliferous sediments of the World Ocean - Fundamental theory
1009 of deep sea hydrothermal sedimentation. Springer, Berlin Heidelberg. pp. 1-416.
- 1010 Hannington, M.D. 2009. Modern submarine hydrothermal systems - a global perspective
1011 on distribution, size, and tectonic settings. *In Submarine Volcanism and*
1012 *Mineralization: Modern through Ancient. Edited by B.L. Cousens and S.J.*
1013 *Piercey. Geological Association of Canada. pp. 91-148.*
- 1014 Hannington, M.D. 2014. Volcanogenic massive sulfide deposits. *In Treatise on*
1015 *Geochemistry 2nd Edition. Edited by H.D. Holland, and Turekian, K.K. Elsevier*
1016 *Ltd. pp. 319-350.*
- 1017 Hannington, M.D., de Ronde, C.E.J., and Petersen, S. 2005. Sea floor tectonics and
1018 submarine hydrothermal systems. *In Economic Geology: One Hundredth*
1019 *Anniversary Volume, 1905-2005. Edited by J.W. Hedenquist and J.F.H.*
1020 *Thompson and R.J. Goldfarb and J.P. Richards. Society of Economic Geologists,*
1021 *Littleton, CO, USA. pp. 111-142.*
- 1022 Hannington, M.D., and Scott, S.D. 1989. Gold mineralization in volcanogenic massive
1023 sulfides; implications of data from active hydrothermal vents on the modern sea
1024 floor. *Economic Geology Monographs* **6**: 491-507.
- 1025 Harazim, D., Callow, R.H.T., and McIlroy, D. 2013. Microbial mats implicated in the
1026 generation of intrastratal shrinkage ('synaeresis') cracks. *Sedimentology* **6**(7):
1027 1621-1638.
- 1028 Haymon, R.M., and Kastner, M. 1981. Hot spring deposits on the Eas Pacific Rise 21°N:
1029 preliminary description of mineralogy and genesis. *Earth and Planetary Science*
1030 *Letters* **53**: 363-381.
- 1031 Hinchey, J.G. 2011. The Tunks Volcanic Belt, Victoria Lake Supergroup, Central
1032 Newfoundland - Geology, Tectonic Setting, and Volcanogenic Massive Sulfide
1033 Mineralization. Newfoundland and Labrador Department of Natural Resources,
1034 Geological Survey.
- 1035 Hinchey, J.G., and McNicoll, V. 2009. Tectonostratigraphic architecture and VMS
1036 mineralization of the southern Tunks Volcanic Belt: New insights from U-Pb
1037 geochronology and lithogeochemistry. *In Current Research. Edited by C.P.G.*
1038 *Pereira and D.G. Walsh. Geological Survey Branch, St. John's, NL, Canada. pp.*
1039 *13-42.*
- 1040 Humphris, S.E., and Bach, W. 2005. On the Sr isotope and REE compositions of
1041 anhydrites from the TAG seafloor hydrothermal system. *Geochimica et*
1042 *Cosmochimica Acta* **69**(6): 1511-1525.

- 1043 Huston, D.L., and Logan, G.A. 2004. Barite, BIFs and bugs; evidence for the evolution of
1044 the Earth's early hydrosphere. *Earth and Planetary Science Letters* **220**(1-2): 41-
1045 55.
- 1046 Huston, D.L., Pehrsson, S., Eglington, B.M., and Zaw, K. 2010. The Geology and
1047 Metallogeny of Volcanic-Hosted Massive Sulfide Deposits: Variations through
1048 Geologic Time and with Tectonic Setting. *Economic Geology* **105**(3): 571-591.
1049 doi: 10.2113/gsecongeo.105.3.571.
- 1050 Jenner, G.A. 1996. Trace element geochemistry of igneous rocks: Geochemical
1051 nomenclature and analytical geochemistry. *In* Trace Element Geochemistry of
1052 Volcanic Rocks: Applications for Massive Sulfide Exploration. . *Edited by* D.A.
1053 Wyman. Geological Association of Canada, Short Course Notes. pp. 51-77.
- 1054 Jenner, G.A., Longerich, H.P., Jackson, S.E., and Fryer, B.J. 1990. ICP-MS - A powerful
1055 tool for high-precision trace element analysis in Earth sciences: Evidence from
1056 analysis of selected U.S.G.S. reference samples. *Chemical Geology* **83**: 133-148.
- 1057 Jones, S., Gemmell, J.B., and Davidson, G.J. 2006. Petrographic, Geochemical, and Fluid
1058 Inclusion Evidence for the Origin of Siliceous Cap Rocks Above Volcanic-Hosted
1059 Massive Sulfide Deposits at Myra Falls, Vancouver Island, British Columbia,
1060 Canada. *Economic Geology* **101**(3): 555-584. doi: 10.2113/gsecongeo.101.3.555.
- 1061 Kalogeropoulos, S.I., and Scott, S.D. 1989. Mineralogy and geochemistry of an Archean
1062 tuffaceous exhalite; the Main Contact Tuff, Millenbach Mine area, Noranda,
1063 Quebec. *Canadian Journal of Earth Sciences = Journal Canadien des Sciences de*
1064 *la Terre* **26**(1): 88-105.
- 1065 Kolata, D.R., Huff, W.D., and Bergström, S.M. 1996. Ordovician K-bentonites of eastern
1066 North America. *Geological Society of America Special Papers* **313**: 1-89.
- 1067 Large, R.R. 1992. Australian volcanic-hosted massive sulfide deposits; features, styles,
1068 and genetic models. *Economic Geology* **87**: 471-510.
- 1069 Lode, S., Piercey, J.S., and Devine, C.A. 2015. Geology, Mineralogy, and
1070 Lithogeochemistry of Metalliferous Mudstones Associated with the Lemarchant
1071 Volcanogenic Massive Sulfide Deposit, Tally Pond Belt, Central Newfoundland.
1072 *Economic Geology* **110**: 1835-1859.
- 1073 Longerich, H.P., Jenner, G.A., Fryer, B.J., and Jackson, S.E. 1990. Inductively coupled
1074 plasma-mass spectrometric analysis of geological samples: A critical evaluation
1075 based on case studies. *Chemical Geology* **83**: 105-118.
- 1076 Lydon, J.W. 1984. Ore deposit models; 8, Volcanogenic sulphide deposits; Part I, A
1077 descriptive model. *Geoscience Canada* **11**(4): 195-202.
- 1078 Lydon, J.W. 1988. Ore deposit models #14; Volcanogenic massive sulphide deposits;
1079 Part 2, Genetic models. *Geoscience Canada* **15**(1): 43-65.
- 1080 McLennan, S.M. 1989. Rare earth elements in sedimentary rocks; influence of
1081 provenance and sedimentary processes. *Reviews in Mineralogy* **21**: 169-200.
- 1082 McLennan, S.M., Bock, B., Hemming, S.R., Hurowitz, J.A., Lev, S.M., and McDaniel,
1083 D.K. 2003. The roles of provenance and sedimentary processes in the
1084 geochemistry of sedimentary rocks. *In* Geochemistry of Sediments and
1085 Sedimentary Rocks: Evolutionary Considerations to Mineral Deposit-Forming
1086 Environments. *Edited by* D.R. Lentz. Geological Association of Canada, St.
1087 John's, NL, Canada. pp. 7-38.

- 1088 McNicoll, V., Squires, G., Kerr, A., and Moore, P. 2010. The Duck Pond and Boundary
1089 Cu-Zn deposits, Newfoundland: new insights into the ages of host rocks and the
1090 timing of VHMS mineralization. *Canadian Journal of Earth Sciences* **47**(12):
1091 1481-1506.
- 1092 McPhie, J., Doyle, M.G., and Allen, C.R. 1993. Volcanic Textures - A guide to the
1093 interpretation of textures in volcanic rocks. Centre for Ore Deposit and
1094 Exploration Studies, University of Tasmania. pp. 1-196.
- 1095 Mills, R.A., Wells, D.M., and Roberts, S. 2001. Genesis of ferromanganese crusts from
1096 the TAG hydrothermal field. *Chemical Geology* **176**: 283-293.
- 1097 Mills, R.A., and Elderfield, H. 1995. Hydrothermal activity and the geochemistry of
1098 metalliferous sediment. *Geophysical Monograph* **91**: 392-407.
- 1099 Nesbitt, H.W. 2003. Petrogenesis of siliciclastic sediments and sedimentary rocks. *In*
1100 *Geochemistry of Sediments and Sedimentary Rocks: Evolutionary Considerations*
1101 *to Mineral Deposit-Forming Environments. Edited by D.R. Lentz. Geological*
1102 *Association of Canada, St. John's, NL, Canada. pp. 39-52.*
- 1103 Nesbitt, H.W., and Markovics, G. 1997. Weathering of granodioritic crust, long-term
1104 storage of elements in weathering profiles, and petrogenesis of siliciclastic
1105 sediments. *Geochimica et Cosmochimica Acta* **61**(8): 1653-1670.
- 1106 Nesbitt, H.W., and Young, G.M. 1982. Early Proterozoic climates and plate motions
1107 inferred from major element chemistry of luitites. *Nature* **299**: 715-717.
- 1108 Ohmoto, H., and Goldhaber, M.B. 1997. Sulfur and Carbon Isotopes. *In Geochemistry of*
1109 *Hydrothermal Ore Deposits, Third Edition. Edited by H.L. Barnes. John Wiley*
1110 *and Sons. pp. 517-611.*
- 1111 Peter, J.M. 2003. Ancient iron formations: their genesis and use in the exploration for
1112 stratiform base metal sulphide deposits, with examples from the Bathurst Mining
1113 Camp. *In Geochemistry of Sediments and Sedimentary Rocks: Secular*
1114 *Evolutionary Considerations to Mineral Deposit-Forming Environments. Edited*
1115 *by D.R. Lentz. Geological Association of Canada. pp. 145-176.*
- 1116 Peter, J.M., and Goodfellow, W.D. 2003. Hydrothermal sedimentary rocks of the Heath
1117 Steele Belt, Bathurst mining camp, New Brunswick; Part 3, Application of
1118 mineralogy and mineral and bulk compositions to massive sulfide exploration.
1119 *Economic Geology Monographs* **11**: 417-433.
- 1120 Piercey, S.J. 2007. Volcanogenic Massive Sulphide (VMS) Deposits of the
1121 Newfoundland Appalachians, Canada: An Overview of their Setting,
1122 Classification, Grade-Tonnage Data, and Unresolved Questions. *Digging Deeper,*
1123 *Vols 1 and 2: 931-934.*
- 1124 Piercey, S.J. 2014. Modern Analytical Facilities 2. A Review of Quality Assurance and
1125 Quality Control (QA/QC) Procedures for Lithogeochemical Data. 2014 **41**. doi:
1126 <http://dx.doi.org/10.12789/geocanj.2014.41.035>.
- 1127 Piercey, S.J., Squires, G.C., Brace, T., and Lode, S. 2012. Initial Report: Hydrothermal
1128 mudstones from the Duck Pond volcanogenic massive sulfide (VMS) deposit,
1129 Central Mobile Belt Newfoundland and Labrador, Canada: Part 1 – Geology and
1130 Lithogeochemistry. *In CAMIRO Project 08E04 2012 Annual Report, The*
1131 *Geochemistry of Shales as Vectors to Ore Deposits. p. 41.*
- 1132 Piercey, S.J., Squires, G.C., and Brace, T.D. 2014. Lithostratigraphic, Hydrothermal, and
1133 Tectonic Setting of the Boundary Volcanogenic Massive Sulfide Deposit,

- 1134 Newfoundland Appalachians, Canada: Formation by Subseafloor Replacement in
 1135 a Cambrian Rifted Arc. *Economic Geology* **109**(3): 661-687. doi:
 1136 10.2113/econgeo.109.3.661.
- 1137 Pollock, J. 2004. Geology and Paleotectonic History of the Tally Pond Group, Dunnage
 1138 Zone, Newfoundland Appalachians: An Integrated Geochemical,
 1139 Geochronological, Metallogenic and Isotopic Study of a Cambrian Island Arc
 1140 Along the Peri-Gondwanan Margin of Iapetus. *In* Department of Earth Sciences.
 1141 Memorial University, St. John's, NL, Canada. p. 420.
- 1142 Pollock, J.C., Wilton, D.H.C., and van Staal, C.R. 2002. Geological studies and definition
 1143 of the Tally Pond Group, Victoria Lake Supergroup, Exploits Subzone,
 1144 Newfoundland Appalachians. *Current Research - Newfoundland. Geological*
 1145 *Survey Branch, Report: 02-1*, pp.155-167, Mar 2002.
- 1146 Ranger, M.J., Pickerill, R.K., and Fillion, D. 1984. Lithostratigraphy of the Cambrian? -
 1147 Lower Ordovician Bell Island and Wabana groups of Bell, Little Bell, and Kellys
 1148 islands, Conception Bay, eastern Newfoundland. *Canadian Journal of Earth*
 1149 *Sciences = Journal Canadien des Sciences de la Terre* **21**(11): 1245-1261.
- 1150 Rogers, N., van Staal, C., Zagorevski, A., Skulski, T., Piercey, S.J., and McNicoll, V.
 1151 2007. Timing and tectonic setting of volcanogenic massive sulphide bearing
 1152 terranes within the Central Mobile Belt of the Canadian Appalachians. *In*
 1153 *Proceedings of Exploration 07: Fifth Decennial International Conference on*
 1154 *Mineral Exploration. Edited by B. Milkereit*, Toronto, ON. pp. 1199-1205.
- 1155 Rogers, N., van Staal, C.R., McNicoll, V., Pollock, J., Zagorevski, A., and Whalen, J.
 1156 2006. Neoproterozoic and Cambrian arc magmatism along the eastern margin of
 1157 the Victoria Lake Supergroup: A remnant of Ganderian basement in central
 1158 Newfoundland? *Precambrian Research* **147**(3-4): 320-341.
- 1159 Rudnicki, M.D. 1995. Particle formation, fallout and cycling within the buoyant and non-
 1160 buoyant plume above the TAG vent field. *Geological Society, London, Special*
 1161 *Publications* **87**(1): 387-396. doi: 10.1144/gsl.sp.1995.087.01.30.
- 1162 Rumble, D. 2014. Hydrothermal graphitic carbon. *Elements* **10**: 427-433.
- 1163 Sáez, R., Moreno, C., González, F., and Almodóvar, G. 2011. Black shales and massive
 1164 sulfide deposits: causal or casual relationships? Insights from Rammelsberg,
 1165 Tharsis, and Draa Sfar. *Mineralium Deposita* **46**(5): 585-614. doi:
 1166 10.1007/s00126-010-0311-x.
- 1167 Savrda, C.E., and Bottjer, D.J. 1989. Anatomy and implications of bioturbated beds in
 1168 "black shale" sequences: Examples from the Jurassic Posidonienschiefer
 1169 (Southern Germany). *PALAIOS* **4**(4): 330-342.
- 1170 Slack, J.F., Grenne, T., and Bekker, A. 2009. Seafloor-hydrothermal Si-Fe-Mn exhalites
 1171 in the Pecos greenstone belt, New Mexico, and the redox state of ca. 1720 Ma
 1172 deep seawater. *Geosphere* **5**(3): 302-314. doi: 10.1130/ges00220.1.
- 1173 Sparkes, B.A. 2005. Assessment Report of Prospecting, Compilation, Trenching, Basal
 1174 Till Sampling and Geochemical Investigations on Licences 7695M (Fifth Year)
 1175 and 10607M (First Year), Harpoon Brook Property, (Rubicon Minerals
 1176 Corporation Project NF442), Lake Ambrose (NTS 12A/10), Newfoundland.
 1177 Rubicon Minerals Corporation. 24 pages plus appendices.
- 1178 Spry, P.G., Peter, J.M., and Slack, J.F. 2000. Meta-exhalites as exploration guides to ore.
 1179 *In* *Metamorphosed and metamorphogenic ore deposits. Edited by P.G. Spry and*

- 1180 B. Marshall and F.M. Vokes. Society of Economic Geologists, Littleton, CO. pp.
1181 163-201.
- 1182 Squires, G.C., MacKenzie, A.C., and MacInnis, D. 1991. Geology and genesis of the
1183 Duck Pond volcanogenic massive sulfide deposit. *In* Metallogenic Framework of
1184 Base and Precious Metal Deposits, Central and Western Newfoundland. *Edited by*
1185 H.S. Swinden and D.T.W. Evans and B.F. Kean. Geological Survey of Canada,
1186 Ottawa, ON, Canada. pp. 56-64.
- 1187 Squires, G.C., and Moore, P.J. 2004. Volcanogenic massive sulphide environments of the
1188 Tally Pond Volcanics and adjacent area; geological, lithogeochemical and
1189 geochronological results. *In* Current Research. *Edited by* C.P.G. Pereira and D.G.
1190 Walsh and B.F. Kean. Geological Survey Branch, St. John's, NL. pp. 63-91.
- 1191 Squires, G.C., and Hinchey, J.G. 2006. Geology of the Tally Pond Volcanic Belt and
1192 Adjacent Areas (parts of NTS 12A/09 & 12A/10). Map 2006-01. Government of
1193 Newfoundland and Labrador, Department of Natural Resources, Geological
1194 Survey, Map 2006-01, Open File 012A/1202.
- 1195 Sverjensky, D.A. 1984. Europium Redox Equilibria in Aqueous-Solution. *Earth and*
1196 *Planetary Science Letters* **67**(1): 70-78. doi: Doi 10.1016/0012-821x(84)90039-6.
- 1197 Swinden, H.S. 1988. Introduction to volcanogenic sulphide deposits in Newfoundland. *In*
1198 *The volcanogenic sulphide districts of central Newfoundland. Edited by* H.S.
1199 Swinden and B.F. Kean. Geological Association of Canada. pp. 1-26.
- 1200 Swinden, H.S. 1991. Paleotectonic settings of volcanogenic massive sulphide deposits in
1201 the Dunnage Zone, Newfoundland Appalachians. *Canadian Institute of Mining*
1202 *and Metallurgy Bulletin* **84**(946): 59-89.
- 1203 Swinden, H.S., and Kean, B.F. 1988. Volcanogenic Sulphide Districts of Central
1204 Newfoundland. Mineral Deposits Division, Geological Association of Canada.
- 1205 Swinden, H.S., Jenner, G.A., Kean, B.F., and Evans, D.T.W. 1989. Volcanic rock
1206 geochemistry as a guide for massive sulphide exploration in central
1207 Newfoundland. *In* Current Research. Newfoundland Department of Mines. pp.
1208 201-219.
- 1209 Taylor, S.R., and McLennan, S.M. 1985. The continental crust: its composition and
1210 evolution. Blackwell Scientific Publications, Oxford.
- 1211 Teck Resources Ltd. 2015. April 21, 2015. Teck reports unaudited first quarter results for
1212 2015. www.teck.com.
- 1213 van Staal, C.R., and Barr, S.M. 2011. Lithospheric architecture and tectonic evolution of
1214 the Canadian Appalachians and associated Atlantic margin. *In* Chapter 2 Tectonic
1215 Styles in Canada: the LITHOPROBE Perspective. *Edited by* J.A. Percival and
1216 F.A. Cook and R.M. Clowes. Geological Association of Canada. pp. 3-55.
- 1217 Von Damm, K.L. 1990. Seafloor hydrothermal activity; black smoker chemistry and
1218 chimneys. *Annual Review of Earth and Planetary Sciences* **18**: 173-204.
- 1219 Wagner, D.W. 1993. Volcanic stratigraphy and hydrothermal alteration associated with
1220 the Duck Pond and Boundary volcanogenic massive sulphide deposits, Central
1221 Newfoundland. *Earth Sciences*. Carleton University, Ottawa, ON, Canada. pp.
1222 430.
- 1223 Webb, G.E., and Kamber, B.S. 2000. Rare earth elements in Holocene reefal
1224 microbialites; a new shallow seawater proxy. *Geochimica et Cosmochimica Acta*
1225 **64**(9): 1557-1565.

- 1226 Williams, H. 1979. Appalachian Orogen in Canada. *Canadian Journal of Earth Sciences*
1227 **16**(3): 792-807.
- 1228 Williams, H., Colman-Sadd, S.P., and Swinden, H.S. 1988. Tectonostratigraphic
1229 subdivisions of central Newfoundland. *In* Current Research, Part B. Geological
1230 Survey of Canada, Ottawa, ON, Canada. pp. 91-98.
- 1231 Zagorevski, A., van Staal, C.R., and McNicoll, V.J. 2007. Distinct Taconic, Salinic, and
1232 Acadian deformation along the Iapetus suture zone, Newfoundland Appalachians.
1233 *Canadian Journal of Earth Sciences = Revue Canadienne des Sciences de la Terre*
1234 **44**(11): 1567-1585.
- 1235 Zagorevski, A., van Staal, C.R., Rogers, N., McNicoll, V.J., and Pollock, J. 2010. Middle
1236 Cambrian to Ordovician arc-backarc development on the leading edge of
1237 Ganderia, Newfoundland Appalachians. *Geological Society of America Memoirs*
1238 **206**: 367-396. doi: 10.1130/2010.1206(16).
1239
1240
- 1241
- 1242

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List of Figures

Figure 1A-C

A) Overview map showing the 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; Piercey 2007). 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 belt deposits: 39 – Lemarchant; 40 – Duck Pond; 41 – Boundary; 42 – 45 – Point Leamington belt deposits, B) Geological map of the Tally Pond volcanic belt and adjacent areas (parts of NTS 12A/09 & 12A/10. The Tally Pond belt hosts the Lemarchant deposit, the Duck Pond and Boundary mines, and other prospects and showings. Deposits, prospects, and showings and given locations contain metalliferous mudstones and/or graphitic shales were sampled. Map modified after Map 2006-1 from G.C. Squires and J.G. Hinchey, and Copeland, 2009-012A-1486, C) Overview map of Bell Island. Outcrops from Lance Cove, The Beach, and Powersteps were sampled. Map modified after Ranger et al. (1984) and Harazim et al. (2013).

Figure 2

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Southwest-northeast cross-section of the Mineralized Block (Block below the Duck Pond) with the main Duck Pond ore body (Upper Duck lens) with locations of the geochronological samples. The unmineralized Upper Block is tectonically juxtaposed on top of the Mineralized Block. Modified after Squires and Moore (2004) and McNicoll et al. (2010) and references therein.

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Map area of the Boundary deposits and the synclinal structure of the Boundary West showing. Massive sulfides of the Boundary North and South zones are projected to surface. Not shown: Boundary Southeast Zone, which is located 200 m southeast of the South Zone. Modified after unpublished drafts of G. Squires and Darren Hennessey, Teck Resources Ltd., and M. Buschette (2015).

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1314 **Figure 10A-J**

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A) Core photograph of a dark brown finely laminated metalliferous mudstone with a sulphide-rich cross-cutting vein. Keats Pond, 374-64, 47.9 m, B) Core photograph of a brown finely laminated metalliferous mudstone. North Moose Pond, NM00-01, 172.2 m, C) Reflected light image of a finely laminated framboid-rich metalliferous mudstone with thick carbonate-quartz-sulphide veins cross-cutting the lamination. Sulphides in veins are predominantly euhedral pyrite (Py), interstitial chalcopyrite (Ccp) and sphalerite (Sp), and pyrrhotite. Sphalerite displays chalcopyrite disease. North Moose Pond, NM00-01, 171.5 m, D) Syneresis cracks/dewatering structures in a volcanoclastic silt- to sandstone. North Moose Pond, NM00-01, 173.3 m, E) Graphitic shale with mineralized tuff fragments. South Moose Pond, SM97-06, 145.8 m, F) Reflected light image of a locally reworked graphite-rich metalliferous mudstone. Lamination cross-cut by quartz (Qz)-carbonate veins. Carbonates consist of ferroan dolomite to Mg-Mn-bearing ankerite (Dol-Ank). Sulphides in veins are euhedral pyrite (Py), chalcopyrite (Ccp), and minor galena. Contact of vein to framboidal mudstone lined by hematite (Hem). Carbonate alteration extends into mudstone matrix. South Moose Pond, SM97-06, 145.5 m, G) Rhythmic layering of black shales and siltstones. Bell Island, The Beach, Beach Formation, and H)

Transmitted light image (II polars) of a thin-section of a laminated siltic black shale with finely disseminated organic matter (OM) and possible algal remnants (Alg). Sediment matrix predominantly consists of quartz, K-feldspar, albite, chlorite, clay, and muscovite (Ms), with accessory apatite, rutile, and zircon. Bell Island, The Beach, Beach Formation.

Figure 13A-F

A) Ternary A-CN-K diagram $A = Al_2O_3$, $CN = CaO + Na_2O$, and $K = K_2O$, B) Ternary A-CN-K-FM diagram. $A = Al_2O_3$, $CNK = CaO + Na_2O + K_2O$, and $FM = (FeO + Fe_2O_3) + MgO$. Cal = Calcite, Dol = Dolomite, Fsp = feldspar, Musc = Muscovite, Ill = Illite, Kaol = Kaolinite, Gib = Gibbsite, Chl = Chlorite, Hbl = Hornblende, Plg = Plagioclase, Sm = Smectite, C) Al_2O_3 versus TiO_2 , D) The Th/Sc versus Zr/Sc diagram, E) and F) La-Th-Sc and Th-Sc-Zr/10 plots. Orange fields represent areas of data of Lemarchant metalliferous mudstones (Lode et al. in press). Diagrams A) and B) are after Nesbitt (2003), C) after Barrett and MacLean (1994), and D) to F) Immobile element plots after Bhatia and Crook (1986).

Figure 14A-F

Fe-Ti/Al-Fe-Mn (A) and Fe-Al-Mn (B) discrimination diagrams after Boström et al. (1972, 1973). Selected base metal, transition element, and hydrothermal element plots: C) Ba versus Hg (after Piercey et al., 2012), D) Ba/Al versus $(Zn + Hg)/Al$, where Ba, Zn, and Hg represent the hydrothermally derived components of the mineralization, and Al is a detrital constituent, E) Total S versus Fe_2O_3 (T), and F) Zn versus Pb.

Figure 15A-G

REE plus Y geospider plots of the Tally Pond belt metalliferous mudstones and graphitic shales: A) Lemarchant (red) and Duck Pond (green) metalliferous mudstones, B) Bell

1403 Island and Cookstown mudstones and shales, C) Beaver Lake and Duck West mudstones,
1404 shales, and mineralized tuff, D) Higher Levels and Old Camp mudstones and shales E)
1405 Boundary West and South Moose Pond mudstones and shales, and F) Boundary, Keats
1406 Pond, and North Moose Pond mudstones and shales. All samples are normalized to the
1407 post-Archean Australian shale of McLennan (1989). G) Ce/Ce* versus Pr/Pr* diagram to
1408 determine whether Ce anomalies are true anomalies or caused by positive La-anomalies.
1409 Accordingly, the positive Ce anomalies in the Lemarchant samples are true Ce anomalies.
1410 Ce/Ce* and Pr/Pr* values are calculated based on McLennan (1989) and the equation
1411 $Pr/Pr^* = (Pr_{\text{sample}}/8.83)/SQRT((Ce_{\text{sample}}/79.6)*(Nd_{\text{sample}}/3.39))$. Diagrams are after Webb
1412 and Kamber (2000), modified after Bau and Dulski (1996).

1413 **Figure 16A-E**

1414 A-B) Simplified two phase rifting model for the Middle Cambrian, early Penobscot arc
1415 magmatism of the Tally Pond group (513 - 509 Ma). C) Diagram of the two-phase curve
1416 for seawater and areas of maximum vent temperatures for modern hydrothermal systems
1417 with conditions for the Lemarchant and Duck Pond/Boundary hydrothermal systems.
1418 Light green dashed outlined area: depth-temperature ranges of maximum vent
1419 temperatures for selected ridge-related hydrothermal systems (Indian Ocean, East Pacific
1420 Rise, Mid-Atlantic Ridge, and NE Pacific ridges, and sediment covered ridges). Dark
1421 green dashed outlined area: depth-temperature ranges of maximum vent temperatures for
1422 selected arc-related hydrothermal systems (backarc, arc volcano). Orange stripe: possible
1423 temperature/water depth range for the Lemarchant hydrothermal system in a rifted arc
1424 setting. Red stripe: possible temperature/water depth range for the Duck Pond/Boundary
1425 hydrothermal system in a rifted arc setting. Modified after Hannington et al. (2005). D)

1426 Overview of U-Pb zircon ages of felsic volcanic or volcanoclastic rocks within the Tally
1427 Pond volcanic belt. Modified after McNicoll et al. (2010) and references therein.
1428 E) Simplified diagram of the, possibly Silurian, compressional phase juxtaposing the
1429 older 513 Ma sequence (Lemarchant, Upper Duck Pond Block), over the younger 509 Ma
1430 sequence (Duck Pond/Boundary).
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Table 1 Summary table of deposits, prospects, and showings and mudstone/shale associations in the Tally Pond volcanic belt

	Location	Type if Unit	Associated rocks	Dominant signature	Paleoredox	Other features
1	Lemarchant deposit Zn-Pb-Cu-Ba-(Au-Ag) VMS	- Exhalative metalliferous mudstones	- At contact between felsic and overlying mafic volcanic rocks, with or without close association with massive sulphides - As interflow mudstones within the hanging wall mafic volcanic rocks	Hydrothermal, vent proximal: - Elevated Fe/Al and base-metal values - Positive Eu anomalies and chondritic Y/Ho	Oxygenated - Presence of barite associated with mudstones and massive sulphides - Presence of Ce anomalies	- Shallow (for VMS) depositional environment (<1200 m, T: >250°C: pos. Eu anomalies) - Ba-Hg-enrichment due to epithermal input to VMS
2	Cookstown Showing	- Graphitic shales	Intercalated with felsic and mafic volcanic rocks	Non-hydrothermal: - Overall flat REE patterns, but: - Sulphide-poor shales cross-cut by sulphide-rich veins (hydrothermal input) => Non-hydrothermal shales overprinted by hydrothermal fluids	(Partially) oxygenated - Presence of bioturbation - Presence of small neg. Ce anomalies	T <250°C - No pos. Eu anomalies
3	Higher Levels prospect	- Exhalative metalliferous mudstones - Minor graphitic shales	- Metalliferous mudstones host mineralization - Mudstones occur within mafic volcanic rocks that overlie felsic volcanic rocks	Hydrothermal, vent distal: - Elevated Fe/Al and base-metal values - Predominantly no positive Eu anomalies, one exception - Small Ce anomalies - Low Ba-levels	(Partially) oxygenated - Presence of bioturbation - Presence of small to large Ce anomalies To reduced - Presence of abundant graphite	If oxygenated: - T predominantly <250°C - No pos. Eu anomalies, except one sample with a strong pos. Eu anomaly If reduced: - T >250°C possible
4	Beaver Lake prospect	- Exhalative metalliferous mudstones - Graphitic shales	Metalliferous mudstones and graphitic shales intercalated with felsic and mafic volcanic rocks	Metalliferous mudstones with hydrothermal signatures - Elevated Fe/Al and base-metal values - Positive Eu anomalies Graphitic shales - Overall flat REE patterns (non-hydrothermal)	(Partially) oxygenated - Presence of bioturbation - Presence of Ce and Eu anomalies To reduced - Presence of abundant graphite - Flat REE patterns	If oxygenated: - T predominantly <250°C - No pos. Eu anomalies, except one sample with a pos. Eu anomaly If reduced: - T >250°C possible
5	Duck West showing	- Graphitic shales - Mineralized tuff	Jig-saw fit altered felsic volcanic rocks intercalated with graphitic shales and mineralized tuff	- Graphitic shale non-hydrothermal, but hydrothermally overprinted - Tuff with replacement-style mineralization	(Partially) oxygenated - Presence of Eu, but no Ce anomalies	T: >250°C - Pos. Eu anomalies
6	Duck Pond deposit From Piercy et al. (2012)	- Exhalative metalliferous mudstones	- At contact between felsic and mafic volcanic rocks and as interflow mudstones	Hydrothermal, vent proximal: - Elevated Fe/Al and base-metal values - Small positive Eu anomalies and chondritic to seawater-like Y/Ho	Oxygenated - Presence of Ce anomalies	T >250°C
7	Boundary deposit	- Exhalative metalliferous mudstones - Mineralized tuff	Mineralized tuff that is intercalated with metalliferous mudstones in lateral extension from massive sulphides	Metalliferous mudstones with hydrothermal signatures - Elevated Fe/Al and base-metal values - Positive Eu anomalies	(Partially) oxygenated - Presence of Eu, but no Ce anomalies	T: at least partially >250°C - Small pos. Eu anomalies
8	Boundary West showing	- Exhalative metalliferous mudstones - Graphitic shales	- Metalliferous mudstones associated with felsic tuffs and overlain by mafic flows - Graphitic shales intercalated with felsic volcanic rocks and metalliferous mudstones	Metalliferous mudstones with hydrothermal signatures - Elevated Fe/Al and base-metal values - Positive Eu anomalies Graphitic shales - Overall flat REE patterns (non-hydrothermal)	(Partially) oxygenated - Presence of Eu, but no Ce anomalies	T: >250°C - Pos. Eu anomalies
9	Old Camp showing	- Exhalative metalliferous mudstones - Graphitic shales	- Metalliferous mudstones associated with felsic and mafic volcanic rocks - Graphitic shales overlying felsic volcanic rocks	Metalliferous mudstones with hydrothermal signatures - Elevated Fe/Al and base-metal values - But predominantly no or small positive Eu anomalies Graphitic shales - Overall flat REE patterns (non-hydrothermal)	Reduced - Flat REE patterns - Graphite-rich - Organic matter-rich to (partially) oxygenated - Small pos. Eu and neg. Ce anomalies	- No pos. Eu anomalies), except one sample If reduced: - T >250°C possible If oxygenated: - T predominantly <250°C (only small Eu anomalies)
10	Keats Pond showing	- Predominantly graphitic shales - Minor exhalative metalliferous mudstones	- Metalliferous mudstones associated with andesitic volcanic rocks and intercalated with graphitic shales	Metalliferous mudstones with hydrothermal signatures - Elevated Fe/Al and base-metal values - But predominantly no positive Eu anomalies	Reduced - Flat REE patterns - Graphite-rich - Organic matter-rich	- No pos. Eu anomalies) If reduced: - T >250°C possible
11	North Moose Pond showing	- Predominantly metalliferous mudstones - Graphitic shales	- Metalliferous mudstones associated with felsic and mafic volcanic rocks - Graphitic shales overlying felsic volcanic rocks	Metalliferous mudstones with hydrothermal signatures - Elevated Fe/Al and base-metal values - Small pos. Eu anomalies Graphitic shales - Overall flat REE patterns (non-hydrothermal)	(Partially) oxygenated - Presence of Ce and Eu anomalies - Potentially presence of bioturbation To reduced - Presence of abundant graphite - Flat REE patterns	(If oxygenated: - T predominantly < or ~250°C - Small pos. Eu anomalies If reduced: - T >250°C possible
12	South Moose Pond showing	- Predominantly metalliferous mudstones - Graphitic shales	- Metalliferous mudstones associated with mafic volcanic rocks - Graphitic shales overlying mafic volcanic rocks	Metalliferous mudstones with hydrothermal signatures - Elevated Fe/Al and base-metal values - Small pos. Eu anomalies Graphitic shales - Overall flat REE patterns (non-hydrothermal)	(Partially) oxygenated - Presence of small Eu anomalies - Potentially presence of bioturbation To reduced - Presence of abundant graphite	((If oxygenated: - T predominantly < or ~250°C - Small pos. Eu anomalies If reduced: - T >250°C possible

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Sample #	CNF36588	CNF36589	CNF36591	CNF36592	CNF36594	CNF36595	CNF36599	CNF36600	CNF36601	CNF36581	CNF25036	CNF25034	CNF25040	
Drill Hole	BL11-01	BL11-01	BL11-01	BL11-01	BL11-02	BL11-02	BL11-03	BL11-03	BL11-03	BD10-09	TP88-01	TP88-01	BW10-09	
Section N	Beaver Lake	Beaver Lake	Beaver Lake	Beaver Lake	Beaver Lake	Beaver Lake	Beaver Lake	Beaver Lake	Beaver Lake	Boundary	Boundary W	Boundary W	Boundary W	
Northing (UTM)	5380677	5380677	5380677	5380677	5380970	5380970	5380996	5380996	5380996	5389274.98	5389441	5389441	5389436.895	
Easting (UTM)	522791	522791	522791	522791	523064	523064	523195	523195	523195	540915.52	540068	540068	540070.376	
Sample Drill Hole Depth (m)	33.1	133.18	177.27	208.45	245.75	248.91	156.32	165.2	213.8	11.64	70.3	131.18	25.24	
Description	IFS	MM	GS	MM	MM	GS	MM	GS	GS	MM	MM	T	GS	
C(total) %	IR	0.28	9.04	2.77	4.69	1.50	1.49	2.74	3.30	14.00	1.31	1.12	0.55	4.81
S(total) %	IR	0.03	30.70	5.53	13.50	18.00	7.66	10.20	4.05	5.90	29.10	8.06	5.61	6.59
Hg ppb	FIMS	2.50	2.50	66.00	291.00	299.00	75.00	191.00	162.00	339.00	6440.00	8790.00	683.00	480.00
SiO2 %	ICP-ES	55.16	25.78	61.96	55.88	45.32	40.78	61.30	63.93	52.76	26.83	75.39	70.94	57.72
Al2O3 %	ICP-ES	21.39	4.66	13.09	7.06	9.51	24.56	9.28	8.75	10.31	6.17	2.79	9.12	10.45
Fe(total) ¹ %	ICP-ES	10.23	35.21	7.99	17.09	23.07	10.92	12.71	7.11	8.19	34.92	7.56	6.73	9.85
MnO %	ICP-ES	0.03	0.02	0.02	0.02	0.03	0.05	0.02	0.12	0.02	0.13	0.01	0.17	0.07
MgO %	ICP-ES	0.32	0.46	1.09	0.57	0.88	1.70	0.50	1.42	0.75	1.79	0.14	1.56	1.45
CaO %	ICP-ES	1.14	1.04	1.04	0.85	1.54	1.86	0.40	3.61	1.22	0.03	0.08	0.37	2.62
Na2O %	ICP-ES	3.42	0.29	0.73	0.25	0.17	1.30	0.50	0.88	0.16	0.07	0.04	0.05	1.07
K2O %	ICP-ES	1.33	0.97	3.01	1.61	2.78	7.08	2.23	1.73	3.30	1.27	0.86	3.35	2.94
TiO2 %	ICP-ES	1.58	0.22	0.32	0.29	0.48	1.06	0.27	0.31	0.45	0.11	0.10	0.13	0.37
P2O5 %	ICP-ES	0.25	0.13	0.06	0.30	0.78	0.07	0.11	0.08	0.63	0.02	0.01	0.02	0.04
LOI %	ICP-ES	4.02	29.80	10.51	14.66	14.70	10.65	10.64	10.44	20.33	20.08	6.76	6.50	12.84
Total %	ICP-ES	98.88	98.55	99.82	98.58	99.26	100.00	97.95	98.37	98.10	91.43	93.73	98.94	99.42
Ba ppm	ICP-ES	420.00	1269.00	1098.00	3204.00	2060.00	3792.00	590.00	2421.00	463.00	782.00	395.00	651.00	1882.00
Sc ppm	ICP-ES	41.00	5.00	10.00	7.00	12.00	38.00	9.00	9.00	10.00	9.00	4.00	9.00	20.00
Be ppm	ICP-ES	2.00	0.50	2.00	2.00	2.00	3.00	1.00	2.00	2.00	0.50	0.50	1.00	1.00
V ppm	ICP-ES	759.00	772.00	792.00	1025.00	548.00	464.00	991.00	1052.00	6011.00	88.00	132.00	37.00	1021.00
Li ppm	ICP-MS	20.87	2.17	5.25	2.42	2.87	6.91	3.47	2.88	0.98	8.87	1.60	8.39	5.10
Sr ppm	ICP-MS	124.46	36.33	41.93	27.75	49.39	66.69	34.81	70.83	31.81	7.31	7.16	12.18	74.92
Y ppm	ICP-MS	4.89	8.18	15.92	11.01	19.99	11.07	11.50	9.46	20.68	12.37	2.46	11.63	9.40
Zr ppm	ICP-MS	15.56	48.48	101.59	67.70	84.80	187.51	86.66	69.42	84.68	78.56	21.04	97.81	53.91
Nb ppm	ICP-MS	1.73	3.08	6.33	3.85	4.58	7.43	3.02	2.79	6.47	0.78	1.52	2.46	1.59
Cs ppm	ICP-MS	1.65	0.94	1.90	1.09	1.54	2.74	1.18	0.96	2.51	0.81	0.42	1.58	1.97
Ba_2 ppm	ICP-MS	419.16	903.88	1046.57	1657.78	1638.41	2626.80	571.23	2263.67	420.08	676.10	405.86	582.72	2167.38
La ppm	ICP-MS	8.58	10.92	41.52	13.92	26.14	3.58	15.08	12.89	27.60	10.19	3.98	16.56	5.43
Ce ppm	ICP-MS	18.29	17.10	78.67	23.28	42.28	7.47	27.14	24.76	45.88	20.74	7.14	33.61	9.93
Pr ppm	ICP-MS	2.45	2.86	10.05	3.61	6.85	1.13	3.99	3.26	6.96	2.81	1.01	4.52	1.57
Nd ppm	ICP-MS	11.20	11.06	36.93	13.90	28.32	4.69	15.35	12.41	27.52	11.61	3.62	17.64	6.04
Sm ppm	ICP-MS	3.26	2.02	7.53	2.56	7.05	1.35	3.22	2.45	6.27	2.74	0.82	3.95	1.45
Eu ppm	ICP-MS	0.98	0.39	1.07	0.64	2.86	0.35	0.58	0.60	1.34	0.91	0.39	0.90	0.51
Gd ppm	ICP-MS	2.55	1.48	5.22	2.27	6.32	1.37	2.53	1.94	6.01	2.56	0.59	2.85	1.36
Tb ppm	ICP-MS	0.33	0.23	0.65	0.32	0.80	0.22	0.35	0.29	0.78	0.37	0.08	0.32	0.23
Dy ppm	ICP-MS	1.51	1.39	3.20	1.92	3.92	1.63	2.05	1.73	4.13	2.42	0.47	1.85	1.50
Ho ppm	ICP-MS	0.26	0.31	0.63	0.39	0.75	0.43	0.43	0.38	0.80	0.49	0.10	0.46	0.35
Er ppm	ICP-MS	0.58	1.03	1.85	1.21	2.03	1.66	1.42	1.26	2.07	1.51	0.31	1.56	1.14
Tm ppm	ICP-MS	0.09	0.19	0.34	0.27	0.34	0.39	0.29	0.25	0.30	0.31	0.05	0.30	0.24
Yb ppm	ICP-MS	0.52	1.34	2.50	1.64	2.14	2.65	1.84	1.71	2.10	1.76	0.39	2.27	1.37
Lu ppm	ICP-MS	0.08	0.20	0.43	0.27	0.36	0.48	0.34	0.29	0.35	0.32	0.08	0.47	0.24
Hf ppm	ICP-MS	5.68	1.71	6.97	2.87	4.63	9.26	3.76	3.15	5.55	3.50	2.98	4.70	2.68
Ta ppm	ICP-MS	0.17	0.16	0.56	0.30	0.28	0.42	0.39	0.23	0.63	0.05	0.13	0.20	0.15
Tl ppm	ICP-MS	0.15	3.81	2.02	4.89	2.98	2.69	2.96	1.84	3.60	17.53	2.18	3.07	3.20
Pb ppm	ICP-MS	16.27	310.90	37.19	301.23	465.84	73.99	184.82	69.22	112.08	4569.15	2124.15	775.50	71.21
Bi ppm	ICP-MS	0.13	0.82	0.31	0.68	0.86	2.16	0.54	0.35	0.93	63.59	6.49	0.78	0.42
Th ppm	ICP-MS	2.96	5.00	8.84	5.44	6.52	7.67	5.17	4.76	9.68	3.38	1.65	4.69	3.98
U ppm	ICP-MS	0.88	24.30	15.52	12.53	15.02	11.04	16.95	8.21	30.17	10.66	2.95	1.77	6.64
Cr ppm	ICP-MS	6.58	36.52	32.40	77.99	70.34	42.79	45.32	44.01	126.59	9.90	10.57	5.60	70.62
Fe ppm	ICP-MS	52398.26	183645.68	41580.40	93708.54	104642.71	57838.51	76059.17	43477.05	47939.66	208325.75	50988.42	50046.40	60578.27
Mn ppm	ICP-MS	194.88	102.48	121.69	163.40	190.64	343.24	93.52	823.08	128.30	928.98	65.81	1174.01	482.94
Co ppm	ICP-MS	2.53	14.88	8.49	11.22	16.92	37.05	8.38	8.78	16.98	118.65	3.49	4.63	18.84
Ni ppm	ICP-MS	3.08	245.68	200.45	214.81	123.52	74.64	222.99	176.62	1164.98	65.21	29.71	21.32	129.50
Cu ppm	ICP-MS	13.76	528.82	195.45	409.73	346.86	69.90	198.75	155.38	723.80	16271.66	1204.36	180.13	321.82
Zn ppm	ICP-MS	29.52	1525.44	673.05	1325.68	629.72	44.15	969.84	1376.41	880.59	33264.13	32204.31	1367.74	1699.49
As ppm	ICP-MS	6.11	1118.42	112.84	402.72	618.16	98.61	418.55	234.87	1789.71	1038.30	286.71	219.47	239.19
Se ppm	ICP-MS	4.37	22.79	12.40	22.53	5.61	8.26	15.13	22.86	88.58	46.83	3.57	0.52	10.40
Br ppm	ICP-MS	108.91	113.83	119.97	114.25	114.98	115.96	120.92	126.67	121.58	108.06	100.20	118.16	100.82
Mo ppm	ICP-MS	1.00	222.46	97.16	82.07	47.19	51.73	110.06	34.81	252.64	131.88	49.08	12.50	17.48
Ag ppm	ICP-MS	0.12	7.01	1.35	4.97	7.11	1.83	3.91	4.02	6.99	38.55	24.29	4.27	2.76
Cd ppm	ICP-MS	0.07	11.69	8.29	10.58	2.16	0.46	10.28	17.81	3.59	99.52	121.83	4.99	17.38
Sn ppm	ICP-MS	3.27	2.95	4.95	3.46	3.44	4.29	3.40	3.60	4.40	16.25	3.93	4.92	3.52
Sb ppm	ICP-MS	6.14	374.49	12.04	68.58	123.84	45.83	72.81	36.28	136.18	147.89	59.20	33.41	88.61
Te ppm	ICP-MS	0.04	0.23	0.37	1.01	0.64	0.87	0.28	0.33	1.07	33.47	1.06	0.16	0.45
I ppm	ICP-MS	1.62	1.62	1.62	1.62	1.62	1.62	1.62	1.62	1.62	1.62	4.94	4.94	4.94
W ppm	ICP-MS	1.00	3.59	3.59	4.49	7.97	15.28	2.93	1.82	6.07	2.05	4.42	2.35	2.78
Ce/Ce*		0.02	0.02	0.03	0.02	0.02								

Data table for Lemarchant mudstones in Lode et al. (2015)

Sample #		CNF25037	CNF25038	CNF25039	CNF25046	CNF25045	CNF25041	CNF25042	CNF25043	CNF25049	CNF25048	CNF36597	CNF36598	CNF25029	
Drill Hole		BW10-10	BW10-11	BW10-11	BW10-12	BW10-12	BW10-14	BW10-15	BW10-15	BW11-20	BW11-24	CT11-01	CT11-01	DP11-284	
Section N		Boundary W	Boundary W	Boundary W	Boundary W	Boundary W	Boundary W	Boundary W	Boundary W	Boundary W	Boundary W	Cookstown	Cookstown	Duck West	
Northing (UTM)		5389438	5389402	5389402	5389475	5389475	5389475			5389513		5377300	5377300	5386612.49	
Easting (UTM)		540071	540035	540035	540104	540104	540104			540062		521075	521075	537083.93	
Sample Drill Hole Depth (m)		56.09	3.8	12.97	95.36	101.51	39.11	142.36	142.8	23.72	44.89	22.31	22.09	636.78	
Description		MM	MM	MM	IFM	GS	MM	MM	MM	GS	MM	GS/MM	GS/MM	GS	
C(total)	%	IR	4.58	8.11	3.23	2.98	3.43	2.09	5.69	5.45	0.49	2.05	0.71	2.77	0.02
S(total)	%	IR	10.10	26.30	13.80	11.50	6.05	12.80	15.00	24.30	11.80	6.22	6.55	7.82	4.94
Hg	ppb	FIMS	545.00	235.00	1080.00	525.00	302.00	2590.00	857.00	70.00	102.00	314.00	105.00	248.00	109.00
SiO2	%	ICP-ES	52.64	22.19	65.14	62.46	48.83	51.09	55.06	42.03	38.10	78.29	50.31	46.23	53.53
Al2O3	%	ICP-ES	9.99	7.82	2.55	4.42	13.62	10.31	4.04	3.79	19.07	2.34	14.53	14.71	23.77
Fe(total) ¹	%	ICP-ES	13.09	30.23	15.94	15.53	10.05	15.42	18.67	29.95	16.52	8.80	16.81	18.88	6.24
MnO	%	ICP-ES	0.13	0.05	0.04	0.03	0.09	0.07	0.04	0.03	0.11	0.05	0.24	0.17	0.02
MgO	%	ICP-ES	1.37	0.96	0.49	1.53	2.24	1.35	0.76	0.44	4.07	0.73	3.13	3.48	1.35
CaO	%	ICP-ES	2.35	1.55	0.80	1.34	4.55	3.16	1.70	0.66	0.75	0.90	1.25	1.11	0.05
Na2O	%	ICP-ES	0.19	0.23	0.02	0.54	1.34	0.51	0.31	0.15	0.10	0.23	4.34	3.02	0.36
K2O	%	ICP-ES	2.89	2.50	0.86	0.78	3.76	3.11	1.14	1.14	6.10	0.56	1.72	2.69	6.86
TiO2	%	ICP-ES	0.28	0.33	0.10	0.15	0.63	0.43	0.16	0.19	0.80	0.10	0.50	0.65	0.36
P2O5	%	ICP-ES	0.08	0.06	0.02	0.04	0.03	0.18	0.03	0.04	0.05	0.02	0.50	0.57	0.02
LOI	%	ICP-ES	15.36	28.30	13.00	12.06	13.35	13.30	17.24	21.46	11.97	7.64	5.22	7.80	6.68
Total	%	ICP-ES	98.37	94.23	98.97	98.88	98.47	98.93	99.16	99.86	97.64	99.66	98.54	99.30	99.25
Ba	ppm	ICP-ES	1040.00	1176.00	423.00	282.00	1471.00	2335.00	391.00	377.00	3275.00	368.00	585.00	627.00	3642.00
Sc	ppm	ICP-ES	14.00	12.00	3.00	8.00	34.00	21.00	7.00	4.00	53.00	3.00	19.00	22.00	27.00
Be	ppm	ICP-ES	1.00	1.00	0.50	0.50	1.00	1.00	0.50	0.50	1.00	0.50	2.00	3.00	2.00
V	ppm	ICP-ES	598.00	825.00	353.00	225.00	684.00	385.00	289.00	594.00	402.00	161.00	522.00	1332.00	9.00
Li	ppm	ICP-MS	3.85	3.36	1.18	9.40	4.92	5.31	1.55	1.40	21.40	2.41	8.34	9.91	8.57
Sr	ppm	ICP-MS	45.18	52.38	19.80	27.59	69.80	56.51	28.01	17.22	22.31	24.60	70.59	51.51	23.11
Y	ppm	ICP-MS	12.76	12.30	3.71	3.44	6.34	15.04	4.09	5.08	4.73	12.54	32.73	52.60	12.24
Zr	ppm	ICP-MS	88.19	68.56	28.34	30.74	50.59	77.16	33.89	40.37	45.17	26.71	75.91	110.95	269.35
Nb	ppm	ICP-MS	2.33	2.59	1.46	0.51	0.50	1.57	1.32	2.37	0.22	3.21	3.62	7.17	2.11
Cs	ppm	ICP-MS	1.86	2.44	0.52	0.62	2.02	1.62	0.84	1.14	2.95	0.47	0.61	1.58	4.42
Ba_2	ppm	ICP-MS	1004.07	1077.89	404.70	274.74	1423.83	2298.56	352.77	405.92	2170.70	354.29	531.46	610.46	3630.26
La	ppm	ICP-MS	13.30	16.03	4.00	1.80	3.29	6.80	6.37	6.61	5.47	4.18	18.94	35.44	8.04
Ce	ppm	ICP-MS	25.54	26.63	7.62	3.46	6.04	14.57	12.29	12.52	12.72	8.28	31.06	51.00	20.47
Pr	ppm	ICP-MS	3.76	4.04	1.04	0.49	1.03	2.34	1.80	1.94	1.96	1.11	5.11	8.93	2.81
Nd	ppm	ICP-MS	14.90	15.47	3.97	2.19	4.17	10.48	6.71	7.17	8.50	4.18	20.93	35.48	11.66
Sm	ppm	ICP-MS	3.71	3.12	0.88	0.59	1.10	3.34	1.39	1.45	2.15	1.05	4.83	7.78	3.16
Eu	ppm	ICP-MS	0.90	0.75	0.24	0.19	0.38	2.36	0.36	0.32	0.76	0.21	1.06	1.78	1.25
Gd	ppm	ICP-MS	3.13	2.45	0.68	0.60	1.04	3.76	1.10	1.05	1.44	1.10	5.20	8.10	2.77
Tb	ppm	ICP-MS	0.40	0.32	0.11	0.10	0.17	0.53	0.14	0.16	0.18	0.25	0.81	1.32	0.50
Dy	ppm	ICP-MS	2.28	2.02	0.68	0.55	1.13	2.98	0.80	0.95	1.01	1.91	5.20	8.29	3.23
Ho	ppm	ICP-MS	0.50	0.47	0.15	0.13	0.24	0.58	0.18	0.20	0.20	0.47	1.13	1.78	0.68
Er	ppm	ICP-MS	1.58	1.57	0.48	0.44	0.80	1.81	0.55	0.70	0.67	1.57	3.12	5.08	1.96
Tm	ppm	ICP-MS	0.31	0.26	0.09	0.09	0.18	0.32	0.11	0.18	0.15	0.28	0.50	0.77	0.32
Yb	ppm	ICP-MS	1.95	1.80	0.72	0.57	1.16	2.12	0.74	0.91	0.94	1.93	2.95	4.75	2.06
Lu	ppm	ICP-MS	0.38	0.34	0.12	0.10	0.19	0.36	0.14	0.17	0.14	0.31	0.43	0.69	0.29
Hf	ppm	ICP-MS	4.36	2.90	2.18	2.67	2.55	3.34	2.52	1.55	2.64	1.14	3.71	6.86	13.97
Ta	ppm	ICP-MS	0.28	0.30	0.12	0.04	0.03	0.18	0.12	0.19	0.02	0.12	0.28	0.55	0.16
Tl	ppm	ICP-MS	4.21	6.46	7.82	3.24	2.30	36.34	5.56	5.77	5.65	1.74	0.68	1.46	8.81
Pb	ppm	ICP-MS	277.96	412.98	162.55	173.60	37.45	270.66	436.19	669.97	83.24	142.45	140.06	85.42	30.08
Bi	ppm	ICP-MS	0.47	0.93	0.33	0.55	0.31	0.25	0.57	0.46	0.11	0.22	1.22	0.38	0.14
Th	ppm	ICP-MS	6.31	7.32	2.53	2.51	2.71	3.39	3.76	4.09	1.43	2.03	4.17	8.45	9.42
U	ppm	ICP-MS	13.10	31.93	8.00	1.62	4.73	5.92	31.01	12.49	1.86	3.05	13.29	36.55	3.76
Cr	ppm	ICP-MS	46.45	45.65	16.62	22.51	55.05	32.03	21.17	24.34	66.13	19.68	42.46	83.30	1.20
Fe	ppm	ICP-MS	83912.02	174453.96	97069.37	85637.59	60684.23	85265.57	101519.44	159325.37	80825.93	49814.77	90354.82	100348.66	41629.32
Mn	ppm	ICP-MS	966.90	389.75	274.21	225.33	620.49	513.23	291.05	155.05	704.06	328.11	1770.43	1262.91	113.90
Co	ppm	ICP-MS	12.61	17.27	6.48	61.62	36.24	37.39	35.62	11.93	54.07	4.25	14.42	20.70	0.76
Ni	ppm	ICP-MS	207.10	203.95	150.69	175.04	75.59	60.31	125.54	232.65	59.36	74.47	134.18	240.34	1.66
Cu	ppm	ICP-MS	207.65	345.59	248.52	248.03	161.77	137.19	227.89	291.39	91.35	180.63	154.19	202.26	26.68
Zn	ppm	ICP-MS	1387.87	945.88	749.16	209.69	487.90	344.46	90.57	147.45	150.46	316.68	525.47	1191.89	34.31
As	ppm	ICP-MS	520.74	908.29	677.37	413.80	122.28	1087.25	617.83	947.72	47.12	222.54	15.31	1.70	319.08
Se	ppm	ICP-MS	14.17	19.39	14.02	16.58	8.56	7.19	15.37	16.02	1.67	4.06	7.68	15.11	14.61
Br	ppm	ICP-MS	96.30	104.45	102.35	118.27	103.63	101.43	96.73	91.24	98.48	104.89	115.22	127.24	152.42
Mo	ppm	ICP-MS	145.77	235.86	169.74	26.73	5.37	28.86	185.28	126.01	8.44	24.54	63.71	128.29	10.88
Ag	ppm	ICP-MS	8.02	27.11	7.87	1.69	1.12	41.36	7.68	12.62	3.43	2.97	1.29	1.66	1.63
Cd	ppm	ICP-MS	7.72	8.85	7.14	3.88	4.32	1.30	0.38	1.06	0.52	1.74	3.01	13.56	0.25
Sn	ppm	ICP-MS	3.62	3.43	2.87	2.63	3.44	3.03	2.90	2.97	2.73	2.84	2.91	3.78	4.63
Sb	ppm	ICP-MS	113.91	273.76	152.01	98.00	31.40	126.65	158.69	223.68	18.23	67.73	2.11	8.39	5.29
Te	ppm	ICP-MS	0.10	0.80	0.55	1.37	0.79	0.05	0.08	1.57	0.55	0.65	0.27	0.66	0.23
I	ppm	ICP-MS	4.94	4.94	4.94	4.94	4.94	4.94	4.94	4.94	4.94	4.94	1.62	1.62	3.39
W	ppm	ICP-MS	4.77	4.71	3.26	0.85	2.59	9.30	3.15	6.00	3.68	3.62	3.27	5.55	4.20
Ce/Ce*			0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.03	0.05	0.01
Eu/Eu*			4.76	4.32	4.22	4.31	4.10	3.16	4.22	4.49	3.97	5.29	4.83	4.61	3.90
Y/Ho			78.20	73.38	105.69	156.66	447.41	343.53	61.43	57.07	598.74	88.03	30.89	17.69	452.83
Fe(total) = (Fe ₂ O ₃ +FeO)		MM:	Metalliferous mudstone				IFS:	Interflow shale			T:	Tuff			
		IFM:	Interflow metalliferous mudstone				GS:	Graphitic shale			GS/MM:	Graphitic shale with hydrothermal overprint			

Sample #	CNF25028	CNF25060	CNF25076	CNF25059	CNF25058	CNF25057	CNF25017	CNF25087	CNF25086	CNF25088	CNF25089	CNF25092	CNF25021
Drill Hole	DP11-284	HL91-01	HL91-01	HL91-01	HL91-01	HL91-01	374-64	NM01-05	NM01-05	NM00-01	NM00-01	NM00-01	OC11-01
Section N	Duck West	Higher Levels	Higher Levels	Higher Levels	Higher Levels	Higher Levels	Keats Pond	North Moose	North Moose	North Moose	North Moose	North Moose	Old Camp
Northing (UTM)	5386612.49	5377398	5377398	5377398	5377398	5377398							5388111
Easting (UTM)	537083.93	523016	523016	523016	523016	523016							540995
Sample Drill Hole Depth (m)	639.76	11.1	16	18.41	22.7	25.05	47.95	48.42	39.24	171.48	172.17	176.85	29
Description	T	MM	MM	MM	MM	MM	MM	GS	MM	MM	MM	MM	GS
C(total)	%	IR											
S(total)	%	IR											
Hg	ppb	FIMS											
SiO ₂	%	ICP-ES											
Al ₂ O ₃	%	ICP-ES											
Fe(total) ¹	%	ICP-ES											
MnO	%	ICP-ES											
MgO	%	ICP-ES											
CaO	%	ICP-ES											
Na ₂ O	%	ICP-ES											
K ₂ O	%	ICP-ES											
TiO ₂	%	ICP-ES											
P ₂ O ₅	%	ICP-ES											
LOI	%	ICP-ES											
Total	%	ICP-ES											
Ba	ppm	ICP-ES											
Sc	ppm	ICP-ES											
Be	ppm	ICP-ES											
V	ppm	ICP-ES											
Li	ppm	ICP-MS											
Sr	ppm	ICP-MS											
Y	ppm	ICP-MS											
Zr	ppm	ICP-MS											
Nb	ppm	ICP-MS											
Cs	ppm	ICP-MS											
Ba ₂	ppm	ICP-MS											
La	ppm	ICP-MS											
Ce	ppm	ICP-MS											
Pr	ppm	ICP-MS											
Nd	ppm	ICP-MS											
Sm	ppm	ICP-MS											
Eu	ppm	ICP-MS											
Gd	ppm	ICP-MS											
Tb	ppm	ICP-MS											
Dy	ppm	ICP-MS											
Ho	ppm	ICP-MS											
Er	ppm	ICP-MS											
Tm	ppm	ICP-MS											
Yb	ppm	ICP-MS											
Lu	ppm	ICP-MS											
Hf	ppm	ICP-MS											
Ta	ppm	ICP-MS											
Tl	ppm	ICP-MS											
Pb	ppm	ICP-MS											
Bi	ppm	ICP-MS											
Th	ppm	ICP-MS											
U	ppm	ICP-MS											
Cr	ppm	ICP-MS											
Fe	ppm	ICP-MS											
Mn	ppm	ICP-MS											
Co	ppm	ICP-MS											
Ni	ppm	ICP-MS											
Cu	ppm	ICP-MS											
Zn	ppm	ICP-MS											
As	ppm	ICP-MS											
Se	ppm	ICP-MS											
Br	ppm	ICP-MS											
Mo	ppm	ICP-MS											
Ag	ppm	ICP-MS											
Cd	ppm	ICP-MS											
Sn	ppm	ICP-MS											
Sb	ppm	ICP-MS											
Te	ppm	ICP-MS											
I	ppm	ICP-MS											
W	ppm	ICP-MS											
Ce/Ce*													
Eu/Eu*													
Y/Ho													
Fe(total) = (Fe ₂ O ₃ +FeO)	MM:	Metalliferous mudstone				IFS:	Interflow shale			T:	Tuff		
	IFM:	Interflow metalliferous mudstone				GS:	Graphitic shale			GS/MM:	Graphitic shale with hydrothermal overprint		

Data table for Lemarchant mudstones in Lode et al. (2015)

Sample #	CNF25022	CNF25023	CNF25024	CNF25025	CNF25018	CNF25033	CNF25032	CNF25031	CNF25030	CNF25019	CNF25012	CNF25055	CNF25054
Drill Hole	OC11-01	OC11-01	OC11-01	OC11-01	OC11-03	OC01-03	OC01-03	OC01-03	OC01-03	OC11-03	OC11-07	OC11-08	OC11-08
Section N	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp	Old Camp
Northing (UTM)	5388111	5388111	5388111	5388111	5387989	5387989	5387989	5387989	5387989	5387989	5387678	5387690	5387690
Easting (UTM)	540995	540995	540995	540995	540581	540581	540581	540581	540581	540581	540308	540521	540521
Sample Drill Hole Depth (m)	34.38	129.9	130.93	132.1	20	28.82	37.39	91.97	103.45	122.41	196.91	73.9	202.27
Description	T	MM	MM	GS	GS	GS	GS	MM	MM	MM	GS	GS	MM
C(total)	%	IR											
S(total)	%	IR											
Hg	ppb	FIMS											
SiO2	%	ICP-ES											
Al2O3	%	ICP-ES											
Fe(total) ¹	%	ICP-ES											
MnO	%	ICP-ES											
MgO	%	ICP-ES											
CaO	%	ICP-ES											
Na2O	%	ICP-ES											
K2O	%	ICP-ES											
TiO2	%	ICP-ES											
P2O5	%	ICP-ES											
LOI	%	ICP-ES											
Total	%	ICP-ES											
Ba	ppm	ICP-ES											
Sc	ppm	ICP-ES											
Be	ppm	ICP-ES											
V	ppm	ICP-ES											
Li	ppm	ICP-MS											
Sr	ppm	ICP-MS											
Y	ppm	ICP-MS											
Zr	ppm	ICP-MS											
Nb	ppm	ICP-MS											
Cs	ppm	ICP-MS											
Ba_2	ppm	ICP-MS											
La	ppm	ICP-MS											
Ce	ppm	ICP-MS											
Pr	ppm	ICP-MS											
Nd	ppm	ICP-MS											
Sm	ppm	ICP-MS											
Eu	ppm	ICP-MS											
Gd	ppm	ICP-MS											
Tb	ppm	ICP-MS											
Dy	ppm	ICP-MS											
Ho	ppm	ICP-MS											
Er	ppm	ICP-MS											
Tm	ppm	ICP-MS											
Yb	ppm	ICP-MS											
Lu	ppm	ICP-MS											
Hf	ppm	ICP-MS											
Ta	ppm	ICP-MS											
Tl	ppm	ICP-MS											
Pb	ppm	ICP-MS											
Bi	ppm	ICP-MS											
Th	ppm	ICP-MS											
U	ppm	ICP-MS											
Cr	ppm	ICP-MS											
Fe	ppm	ICP-MS											
Mn	ppm	ICP-MS											
Co	ppm	ICP-MS											
Ni	ppm	ICP-MS											
Cu	ppm	ICP-MS											
Zn	ppm	ICP-MS											
As	ppm	ICP-MS											
Se	ppm	ICP-MS											
Br	ppm	ICP-MS											
Mo	ppm	ICP-MS											
Ag	ppm	ICP-MS											
Cd	ppm	ICP-MS											
Sn	ppm	ICP-MS											
Sb	ppm	ICP-MS											
Te	ppm	ICP-MS											
I	ppm	ICP-MS											
W	ppm	ICP-MS											
Ce/Ce*													
Eu/Eu*													
Y/Ho													
Fe(total) = (Fe ₂ O ₃ +FeO)		MM:	Metalliferous mudstone			IFS:	Interflow shale			T:	Tuff		
		IFM:	Interflow metalliferous mudstone			GS:	Graphitic shale			GS/MM:	Graphitic shale with hydrothermal overprint		

Sample #		CNF25053	CNF25052	CNF25051	CNF25015	CNF25026	CNF25027	CNF25077	CNF25078	CNF25079	CNF25083	CNF25084
Drill Hole		OC11-08	OC11-08	OC11-08	SM97-06	SM97-08	SM97-08	Bell Island	Bell Island	Bell Island	Bell Island	Bell Island
Section N		Old Camp	Old Camp	Old Camp	South Moose	South Moose	South Moose	The Beach	The Beach	Lance Cove	Powersteps	Powersteps
Northing (UTM)		5387690	5387690	5387690		5392441	5392441	Beach Fm.	Beach Fm.	Beach Fm.	Powerst. Fm.	Powerst. Fm.
Easting (UTM)		540521	540521	540521		544510	544510					
Sample Drill Hole Depth (m)		204.81	208.3	253.11	145.49	121.3	122.82					
Description		MM	MM	GS	GS	IFM	IFM	Brown shale	Gray shale	Dark gray shale	Siltic mudstone	Dark gray shale
C(total)	%	IR										
S(total)	%	IR										
Hg	ppb	FIMS										
SiO ₂	%	ICP-ES										
Al ₂ O ₃	%	ICP-ES										
Fe(total) ¹	%	ICP-ES										
MnO	%	ICP-ES										
MgO	%	ICP-ES										
CaO	%	ICP-ES										
Na ₂ O	%	ICP-ES										
K ₂ O	%	ICP-ES										
TiO ₂	%	ICP-ES										
P ₂ O ₅	%	ICP-ES										
LOI	%	ICP-ES										
Total	%	ICP-ES										
Ba	ppm	ICP-ES										
Sc	ppm	ICP-ES										
Be	ppm	ICP-ES										
V	ppm	ICP-ES										
Li	ppm	ICP-MS										
Sr	ppm	ICP-MS										
Y	ppm	ICP-MS										
Zr	ppm	ICP-MS										
Nb	ppm	ICP-MS										
Cs	ppm	ICP-MS										
Ba ₂	ppm	ICP-MS										
La	ppm	ICP-MS										
Ce	ppm	ICP-MS										
Pr	ppm	ICP-MS										
Nd	ppm	ICP-MS										
Sm	ppm	ICP-MS										
Eu	ppm	ICP-MS										
Gd	ppm	ICP-MS										
Tb	ppm	ICP-MS										
Dy	ppm	ICP-MS										
Ho	ppm	ICP-MS										
Er	ppm	ICP-MS										
Tm	ppm	ICP-MS										
Yb	ppm	ICP-MS										
Lu	ppm	ICP-MS										
Hf	ppm	ICP-MS										
Ta	ppm	ICP-MS										
Tl	ppm	ICP-MS										
Pb	ppm	ICP-MS										
Bi	ppm	ICP-MS										
Th	ppm	ICP-MS										
U	ppm	ICP-MS										
Cr	ppm	ICP-MS										
Fe	ppm	ICP-MS										
Mn	ppm	ICP-MS										
Co	ppm	ICP-MS										
Ni	ppm	ICP-MS										
Cu	ppm	ICP-MS										
Zn	ppm	ICP-MS										
As	ppm	ICP-MS										
Se	ppm	ICP-MS										
Br	ppm	ICP-MS										
Mo	ppm	ICP-MS										
Ag	ppm	ICP-MS										
Cd	ppm	ICP-MS										
Sn	ppm	ICP-MS										
Sb	ppm	ICP-MS										
Te	ppm	ICP-MS										
I	ppm	ICP-MS										
W	ppm	ICP-MS										
Ce/Ce*												
Eu/Eu*												
Y/Ho												
Fe(total) = (Fe ₂ O ₃ +FeO)		MM:	Metalliferous mudstone				IFS:	Interflow shale				
		IFM:	Interflow metalliferous mudstone				GS:	Graphitic shale				

Data table for Lemarchant mudstones in Lode et al. (2015)

Fig. 1A-C

Fig. 2

COOKSTOWN SHOWING

CT11-01_2.8-66.9m
UTM 5,377,300.00 N
UTM 521,075.00 E

arg tuff/silt lapilli tuff brx flow intrusion m sulph

0 meters 10

HIGHER LEVELS PROSPECT

NW 1800N (HL grid) 5377398N (UTM N) 1700N (HL grid) SE

HL91-02 HL91-01 HL91-03

0m -50m

Synclinal fold axis?

E.O.H. 84.7m E.O.H. 136.6m E.O.H. 59.7m

0 meters 10

BEAVER LAKE PROSPECT

BL11-01_3.7-259.4m
UTM 5,380,677.00 N
UTM 522,791.00 E

BL11-02_137.7-284.5m
UTM 5,380,970.00 N
UTM 523,064.00 E

BL11-03_15.0-246.5m
UTM 5,380,996.00 N
UTM 523,195.00 E

arg tuff/silt lapilli tuff brx flow

0 meters 20

@170m small-scale parasitic fold-hinge (in core)

= Detrital shale sample
* = Metalliferous mudstone sample (based on litho geochemistry)

Fig. 4

Fig. 5

Fig. 6

Fig. 7A-C

Fig. 9A-C

Fig. 13A-F

Fig. 14A-F

Fig. 15A-G

Fig. 16A-D

Lithogeochemistry Methods

During fieldwork 80 drill holes that contain metalliferous mudstones and graphitic shales from twelve locations in the Tally Pond volcanic belt were logged and selected mudstones and shales sampled for thin-section preparation and whole-rock analyses. Petrographic studies were undertaken on 253 thin-sections, which predominantly represent various types of mudstone, shales, and tuff. Three locations were sampled on coastal outcrops on Bell Island and from these, five shale samples prepared for thin-section and whole-rock lithogeochemical studies. From the Lemarchant deposit a detailed sampling was undertaken. The Lemarchant mudstones include those that: 1) are immediately associated with or occur within five meters of massive sulphides and represent the main stratigraphic marker between the felsic and mafic volcanic rocks (Bindons Pond formation and Lake Ambrose formation, 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 they were sampled for whole-rock geochemistry as well. Detailed analyses are presented in (Lode et al., accepted).

Metalliferous mudstones associated with the Upper Block of the Duck Pond deposit were sampled and studied in detail by Piercey et al. (2012).

High resolution backscattered electron (BSE) images were obtained using a FEI Quanta 400 scanning electron microscope (SEM) at Memorial University, which is equipped with an energy dispersive x-ray (EDX) analytical system from Bruker. Samples for whole-rock lithogeochemical studies ($n = 189$) were analyzed for major and minor elements by lithium metaborate/tetraborate fusion followed by HNO_3 dissolution and analysis by inductively coupled plasma (atomic) – emission spectroscopy (ICP-ES). Carbon (C) and sulphur (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 obtained at Activation Laboratories Ltd. (Actlabs) in Ancaster, Canada. Additional trace elements, including rare earth elements (REE), high field strength elements (HFSE), trace metals, and many low field strength elements (LFSE) were analyzed in the Department of Earth Sciences at Memorial University, using screw-top Teflon® bomb (Savillex®) multi-acid dissolution with a finish by inductively coupled plasma-mass spectrometry (ICP-MS). The whole-rock dissolution process was a modified version of that of Jenner et al. (1990) and Longerich et al. (1990) to account for the high amounts of carbonaceous material in the samples, as outlined below.

Powdered sample equivalent to 0.1000 g was put into a clean and dry screw-top Teflon® bomb (Savillex®) with 2 ml of 8N nitric acid (HNO_3) and 1 ml of hydrofluoric acid (HF) and placed on a hot plate at $\sim 70^\circ\text{C}$ for three days. If the sample was not completely dissolved after that time, the cap was carefully removed and the condensed sample liquid on the cap rinsed into the jar with 8N HNO_3 , and the bomb was left uncovered on the hot plate at about $80\text{--}100^\circ\text{C}$ to evaporate until dry. When dry, another 2 ml of 8N HNO_3 and 2 ml of hydrochloric acid (HCl) were added, the lid closed, and the

sample left for a further day on a hot plate to reflux at $\sim 70^{\circ}\text{C}$. After this additional step, or if the sample was already completely dissolved after the initial three days, the sample was evaporated until dry. When dry, 2 ml of 8N HNO_3 and 1 ml of boric acid (0.453M) were added to the sample liquid and then evaporated to dryness. To the dried sample a further 2 ml of 8N HNO_3 and 2 ml HCl were added, the cap was placed back on the jar and the sample left for 2 hours on the hot plate at $\sim 70^{\circ}\text{C}$. After 2 hours, the cap was removed and the sample liquid evaporated to dryness. When dry, 2 ml of 8N HNO_3 and 1.3 ml oxalic acid (0.22M) were added, the cap placed back on, and the sample left for 2 hours on the hot plate at $\sim 70^{\circ}\text{C}$. Subsequently, an additional 1 ml of H_2O_2 was added, the cap placed back on again, and the sample left for another 2 hours on the hot plate at $\sim 70^{\circ}\text{C}$. Since many of the samples contain abundant carbonaceous material it is noted that each additional 1 ml of HCl and 1 ml of H_2O_2 added above reduced the amount of visible residual carbonaceous material quite significantly.

Solution material from the latter step above was transferred into 120 ml snap seal container. For this, the caps are rinsed with nanopure water into the snap seal jar, 0.665 ml HF /boric solution (0.113M HF / 0.453 boric acid) is added, and the weight made up to a final weight of 60 g with nanopure water. If visible residues still remained, the sample was filtered before the final sample dissolution preparation.

Two tubes were prepared for the ICP-MS, one with the sample dissolution and one with the sample dissolution plus a trace spike solution. To each 11 ml test tubes 0.5 g of sample solution were added with one tube having 9.5 g of 0.2N HNO_3 added, whereas the second tube contained 4.5 g of 0.2N HNO_3 and 5 g of trace spike solution; both tubes were capped, shaken and mixed prior to analysis by ICP-MS.

The residues left behind in the filter paper were checked at Memorial University via scanning electron microscope - energy dispersive X-ray spectroscopy (SEM-EDX) to ascertain that no elements of interest, particularly the HFSE and REE, remained. For this, the residues were mounted on a holder with double-sided carbon tape and semi-quantitatively analyzed by EDX under low-vacuum conditions to avoid carbon-coating. The analyses of the residues yielded, with one exception, purely carbonaceous material, and hence, no important trace elements were present in the residues. One residue consisted of predominantly carbonaceous material with traces of barite. Accordingly, to avoid interferences of organic matter with Ba, Ba-values of the fusion method (ICP-ES) were used, instead of ICP-MS. To correct for a possible mass spectral interference of the isobaric phases $^{135}\text{Ba}^{16}\text{O}$ and ^{151}Eu , two standard solutions were utilized and the interference factor calculated accordingly (Jenner et al, 1990).

Quality Assurance and Quality Control

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 sulphide-rich shales (SCO-1, SDO-1 and SGR-1b) and one iron formation (FeR-1). These standards were run every twenty samples and with each analytical batch. In addition, 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 from Actlabs of the major and some minor elements, and C, S, and Hg have following % RSD precision values: major

elements range between 0.7-4.5% RSD; P_2O_5 , Ba, Sr, Y, Zr, Sc, V have % RSD values between 0.6-8.2% RSD; and 0.7-1.8% RSD for C, S, and Hg. Accuracy of the Actlabs analyzed major and minor elements ranges from 0.1-11.8% RD, from 1.8-4.8% RD for C and S, and 0.7-7.7% RD for Hg.

Analytical precision calculated for samples analyzed at Memorial University yielded the following values: low field strength elements (LFSE) range between 3.7-12.5% RSD (except Rb), and high field strength elements HFSE had 4.5-11.1% RSD. The REE (La to Lu) % RSD values range from 4.8-8.6 and base and transitional metals have a precision between 3.3-11.9% RSD.

Determination of accuracy is dependent on and limited to the quality and amount of published and certified values. For many sediment-rich samples the range of certified values is limited and/or results were obtained by methods not utilized in this study (e.g., Instrumental Neutron Activation Analysis - INAA). Therefore, accuracy values in the analyses outlined below are provided for where published data were available.

Accuracies for elements in standard FeR-1 range from 1.32-8.79% RD for most of the REE except Tm. Tm yields less a accurate value of 15.3% RD. The standard SCO-1 has an accuracy of 2.0-6.5% RD for La, Pr and Nd, 12.8% RD for Ce, and 1.9% RD for Pb. Accuracies for standard SDO-1 range from 1.9-9.1% RD for La to Gd, and Tm, 11.0-23.6% RD for Tb to Er, Yb, and Lu. Base metal and transition elements have accuracy values ranging between 3.0-13.7% RD, and Zn of 22.8% RD. SGR-1b yields accuracy values between 1.6-15.3% RD base metal and transition elements, and 0.01 to 17.6% RD for REE (La to Yb, except, Pr and Tb).