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Applications of trace element chemistry of pyrite and chalcopyrite in glacial sediments to mineral exploration targeting: Example from the Churchill Province, northern Quebec, Canada



Charley J. Duran^{a,*}, Hugo Dubé-Loubert^{b,d}, Philippe Pagé^{a,c}, Sarah-Jane Barnes^a, Martin Roy^d, Dany Savard^a, Ben J. Cave^a, Jean-Philippe Arguin^{a,c}, Eduardo T. Mansur^a

^a Université du Québec à Chicoutimi, Sciences de la Terre, Chicoutimi, QC, Canada

^b Ministère de l'Énergie et des Ressources Naturelles, Bureau de la Connaissance Géoscientifique du Québec, Val-d'Or, QC, Canada

^c IOS Services Géoscientifiques Inc., Chicoutimi, QC, Canada

^d Université du Québec à Montréal, Département des sciences de la Terre et de l'atmosphère, Montréal, QC, Canada

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ABSTRACT

Bedrock in arctic and subarctic regions is covered by glacial deposits making the discovery of new mineral deposits difficult. Indicator mineral methods using glacial sediment have thus been developed for mineral exploration in such drift-covered areas. However, sulfide indicator minerals have been under utilized because it was thought that they would not survive glacial transport and post-depositional oxidation during soil formation. In this contribution we show that the 0.25-1 mm non-ferromagnetic heavy mineral concentrates of Quaternary till and esker samples from the Churchill province in northern Quebec, Canada, contain thousands of pyrite and chalcopyrite grains and a few sulfarsenide grains. Accordingly, sulfide minerals do survive glacial and glaciofluvial transport, even in the relatively oxidizing environment of the eskers, and their presence indicates the potential presence of mineralized bedrock up ice. The study area is therefore ideal to test the use of sulfide mineral chemistry for mineral assessment and vectoring. The composition of the pyrite and chalcopyrite grains recovered from the glacial deposits have been determined by LA-ICP-MS and compared with known values for sulfides in magmatic and hydrothermal deposits. Although some elements (e.g. Ag, Cu, Zn, Pb, W, Ba, La, and Yb) are enriched in narrow rims on some sulfide grains, indicating their limited mobility during oxidation, most elements have not been mobilized and reflect initial sulfide compositions in bedrock sources. The binary diagram Co/Sb versus Se/As shows that most of the pyrite grains in surficial sediments are of magmatic origin although some are from hydrothermal sources. The hydrothermal pyrites are enriched in hydrothermal pathfinders (Au, Hg, Ag, Tl, Pb, Zn, Cu, and Mo). The ternary diagram Se-Cd-Ni shows that chalcopyrites from both magmatic and hydrothermal deposits are present in glacial sediments. The high Cd/Zn ratios of the hydrothermal chalcopyrites are indicative of a high crystallization temperature, typical of metamorphosed VMS or SEDEX deposits. Integrated maps combining bedrock geology, glacial transport directions, sample locations, and sulfide grain compositions and populations can be used to delineate target sectors for mineral exploration. Here sulfides have been transported over ~100 km roughly towards north, from sources in the Rachel-Laporte Zone and the Labrador Trough, where metasedimentary/metavolcanic rocks and mafic/ultramafic intrusive rocks are favorable hosts for hydrothermal and magmatic mineralization, respectively.

1. Introduction

With discoveries of outcropping and subcropping (shallow) mineral deposits on the wane, developing new exploration methods for targeting mineral deposits buried by glacial sediments has become essential. Regions that have been widely affected by glaciations (e.g. Canada, Greenland, Fennoscandia, Great Britain, and western Siberia) represent vast territories where thick glacial deposits commonly mask the bedrock and thus limit the usefulness of conventional mineral-targeting methods (e.g. detailed bedrock mapping, geophysics). To overcome this problem, exploration methods based on till matrix geochemical analyses and indicator minerals have been developed to

* Corresponding author.

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E-mail address: charley.duran@hotmail.fr (C.J. Duran).

explore in glaciated terrains (McClenaghan, 2005; McClenaghan et al., 2014; McClenaghan and Paulen, 2018). These methods have proven to be effective in the exploration for a wide range of mineral deposit types (Averill, 2001, 2011; McClenaghan and Paulen, 2018; Manéglia et al., 2018). More recently, the chemistry of some very common and abundant indicator minerals, such as magnetite (Makvandi et al., 2016; Pisiak et al., 2017) and apatite (Belousova et al., 2002; Rukhlov et al., 2016), has been used to increase the chances of detecting mineralized bedrock signatures that might otherwise be diluted in the glacial cover. Although indicator mineral methods have not included systematic mineral chemistry of specific sulfide minerals such as pyrite and chalcopyrite.

Sulfides are important indicator minerals for two reasons: 1) they are abundant in most metallic mineral deposits and rare in most barren rocks; and 2) they form under wide variety of conditions (e.g. Naldrett et al., 1967; Berner, 1970) leading to distinctive signatures in their trace element chemistry (e.g. Barnes et al., 2008; Large et al., 2009; Duran et al., 2015, 2016a; Cook et al., 2016; George et al., 2017). Therefore, they would seem to be ideal indicator minerals. However, when exposed to the atmosphere or in contact with surface or groundwater, sulfide minerals begin to oxidize (e.g. Rosso and Vaughan, 2006). Thus, preservation of sulfide minerals in surface and near-surface rocks and in unconsolidated sediments is uncommon, particularly in tropical supergene environments where rare relict sulfides can only be found several meters below the surface (e.g. Oberthür and Melcher, 2005). This lack of preservation has led to the misconception that in all climates sulfide minerals are not preserved in surface sediments and the potential of sulfides as indicator minerals has been neglected. However, burial rates are fast in glaciated terrains and till matrix can be relatively impermeable, which results in very limited chemical weathering. Accordingly, several studies have documented abundant and/or pristine sulfide minerals in till samples (e.g. Peuraniemi, 1982, 1984; Nikkarinen et al., 1984; Sarala and Peuraniemi, 2007; McClenaghan et al., 2011, 2018; Peuraniemi and Eskola, 2013). Therefore, the application of the trace element chemistry of sulfide indicator minerals could be a powerful complement to till geochemistry and other indicator mineral methods.

This contribution demonstrates the potential use of sulfide trace element chemistry for mineral exploration targeting, through the study thousands of pyrite and chalcopyrite grains and few sulfarsenide (arsenopyrite and löllingite) grains recovered from till and esker samples collected in northern Quebec, Canada, during a large surficial mapping program conducted by the Ministère de l'Énergie et des Ressources Naturelles (MERN) of Quebec. By compiling geochemical data for pyrite and chalcopyrite from known mineral deposits around the world, we have developed discriminant diagrams for hydrothermal and magmatic derived sulfides. The sulfides recovered from the glacial sediments have been classified using these diagrams and the results integrated with bedrock geology and glacial history to indicate which areas have high potential to host magmatic or hydrothermal mineralization. The main implication rising from this study is that the trace element chemistry of sulfide minerals recovered from glacial sediments can be used to define the metallogenic potential of the source rocks.

2. Geological background

2.1. Bedrock geology

In Quebec, the Churchill Province is bounded by the Archean Superior and Nain provinces to the west and east, respectively, and by the Proterozoic Grenville Province to the south (Fig. 1). The bedrock of the Churchill Province mainly consists of Archean to Mesoproterozoic rocks, which are divided in three main zones: the Labrador Trough, the Core Zone, and the Torngat Orogen (Fig. 1b).

The Labrador Trough is a basin, characterized by a thrust-fold belt with a NNW-SSE orientation, extending over 850 km from the Ungava Bay in the north to the Grenville Province in the south. The Labrador Trough is mainly composed of volcanic and metasedimentary rocks of Archean to Paleoproterozoic ages (Hoffman, 1988; Wardle et al., 2002; Clark and Wares, 2004, 2005). These rocks, which consist of alternating igneous lithologies associated with rift and platform sediments (e.g. dolomite, chert, sandstone, tholeiitic basalt, rhyolite, gabbro, peridotite, iron formation), have been highly deformed during the New Quebec Orogen (i.e. collision of the Superior Province with the Core Zone) from 2.4 to 1.79 Ga (Clark and Wares, 2004, 2005). The New Quebec Orogen is commonly subdivided from west to east into four lithotectonic domains: (1) the Kaniapiskau Supergroup (autochtonous low-grade metavolcanics and metasediments); (2) a central metavolcanics-metasedimentary belt with voluminous gabbro sills and pillow basalts; (3) the Rachel-Laporte Zone (allochtonous medium to high-grade supracrustal rocks and gneissic-migmatitic complexes); (4) the Kuujjuaq Domain (amphibolite facies schists and gneisses) (Clark and Wares, 2004, 2005). Based on stratigraphy and zircon provenance and geochronology (Henrique-Pinto et al., 2017 and references therein), the Kaniapiskau Supergroup is interpreted to have deposited over several sedimentation cycles in an intracratonic rift transitioning to passive margin platform. The Rachel-Laporte rocks are interpreted to represent the accretionary wedge formed during overthrusting of the Superior Province by the Core Zone. The high metamorphic grades are consistent with crustal thickening associated with the transition from arc-continent collision to pro-foreland basin.

The Core Zone, which is mainly composed of granitoid, gneiss, paragneiss, migmatite, and amphibolite of Archean to Proterozoic ages, is considered as a ruban-like microcontinent (Wardle et al., 2002; Corrigan et al., 2009; Lafrance et al., 2014). The rocks of the Core Zone form a 280 km wide corridor with a NNW-SSE orientation and have undergone amphibolite to granulite metamorphism. A voluminous Proterozoic intrusion: the De Pas Batholith, extends over several hundreds of km within the Core Zone and consist of granitic to charnockitic rocks. This batholith likely resulted from arc magmatism related to the subduction of the Superior Province beneath the Core Zone (Van der Leeden et al., 1990). In the east, the Core Zone collided with the Nain Province to form the Torngat Orogen. The Torngat Orogen consists of lithotectonic domains of intrusive rocks forming high-grade metamorphic complexes, separated by ductile deformation corridors of Paleoproterozoic ages (Houle and Perreault, 2007).

2.2. Metallogeny

From an economic perspective, the Churchill Province is well known for the iron ore of the Labrador Trough (e.g. Neal, 2000). However, the mineral potential of the Churchill Province in northern Quebec for base and precious metals is poorly known due to the thick cover of Quaternary sediments. However, numerous showings have been identified (Fig. 1b) and suggest a complex metallogenic setting. The transitional geodynamic regime from a rift to a pro-foreland basin could be favorable to several types of ore deposits (Groves and Bierlein, 2007). Rifting in the Labrador Trough could be associated with Ni-Cu-PGE mineralization at craton margins (e.g. Barnes and Lightfoot, 2005; Begg et al., 2010). This environment is ideal for fast magma ascent through prominent crustal sutures and interaction with S-rich sediments. Two major Canadian Ni-Cu-PGE mining camps associated with komatiitic rocks are located in this environment around the Circum-Superior belt: the Thompson Nickel and Cape Smith belts. Given the large amount of mafic/ultramafic rocks in the Labrador Trough, the potential for Ni-Cu-PGE deposits is high (Houlé et al., 2015). Several prospects are being explored across the Labrador Trough (i.e. www. northern-shield.com) and several showings have been reported in the study area (Lafrance et al., 2014; Charette et al., 2016). The Labrador Trough may also have strong potential to host volcanogenic massive sulfides (VMS) and sedimentary exhalative (SEDEX) deposits that developed in the passive margin or arc-continent collision settings

(Franklin et al., 2005; Hannington et al., 2005; Leach et al., 2005). For instance, sulfide-rich boulders and lake-bottom organic sediments enriched in Pb, Zn, Hg, Bi, Sn, and Sb, suggestive of SEDEX mineralization, have been identified in the northwestern part of the Labrador Trough (www.northern-shield.com). In addition, Cu-Zn-Mo-Pb-Ag-Au showings of VMS and/or SEDEX have been identified during bedrock

mapping surveys (Lafrance et al., 2014; Charette et al., 2016) in the southwestern part of our study area (Rachel-Laporte Zone). Given the predominance of granitoid rocks in the Core Zone, granite-related deposits could also be found. The Strange Lake peralkaline granite-hosted rare-earth element (REE) deposit is approximately 100 km to the east of our study area (Salvi and Williams-Jones, 1995; McClenaghan et al.,



Fig. 1. Location of the study area: a) digital elevation model with location of all the collected till and esker samples (n > 600) and glacial features (eskers, glacial lineations, and drumlins); in map sheet 24B glacial features are mainly trending towards the northwest and in map sheet 24G glacial features are mainly trending towards the north; and b) bedrock geological map with mineral showings and till and esker samples containing sulfide and/or sulfarsenide minerals (n = 301). Note that sulfide counts per sample are not normalized to sample weight.

2017b). Finally, a considerable number of gold grains in till has been found in the Core Zone to the southeast of our study area, between the contact with the Labrador Trough and the De Pas Batholith (McClenaghan et al., 2017a), suggesting possible potential for orogenic gold mineralization in the local mafic volcanic rocks.

2.3. Surficial geology

The Labrador Sector of the Laurentide ice sheet was highly dynamic during the last glacial cycle, with significant migrations of its ice divide system and marked changes in its thermal regime associated, among others, with fast flowing ice corridors (ice streams) (Veillette et al., 1999; Clark et al., 2000; Roy et al., 2009; Margold et al., 2015) and extensive glaciofluvial landforms (Storrar et al., 2013). The main landscape of the study area consists of glacially-fluted terrain that was formed by a massive ice stream converging northward towards Ungava Bay (Figs. 1a and 2a) (Clark et al., 2000; Jansson et al., 2003; Margold et al., 2015). This landscape is dominated by a swarm of mega-scale

glacial lineations alternating with crag and tails landforms (Fig. 2b), which are broken in places by areas of partially-fluted ribbed (Rogen) moraines (Fig. 2c) (Dubé-Loubert et al., 2014a).

The head of this 150 km long ice stream system originated from the contact between the Labrador Trough and the Rachel-Laporte Zone (Fig. 1b). The Ungava ice streams were marine terminating and were active late into deglaciation, until the ice lost its contact with the postglacial Iberville Sea (Veillette et al., 1999; Margold et al., 2018). Erosion and sediment transport associated with this ice flow is the last glacial event that affected the study area. It completely obliterated earlier erosional events and no erosional marks (striations and/or grooves) or glacial landforms associated with previous ice movements have been preserved (Dubé-Loubert et al., 2014a). We thus assume a unidirectional dispersal train in the area affected by this paleo-ice stream system.

One of the most difficult parameters to quantify in drift prospecting is the distance the detrital material has been glacially transported. Ice streams represent an important and efficient mechanism by which the



Fig. 2. a) Satellite (Rapideye) image showing the distribution of landform systems in the Ungava Bay lowlands; b) example of crag and tails and mega-scale lineations forming the main glacial landsystem and converging towards the Ungava Bay in the north part of the study area; c) field of fluted ribbed moraines mapped in the study area. Ice flow roughly from right to left; d) example of esker aligned roughly N-S sampled during this study.

glacial processes can displace significant amounts of sediments over relatively long distances (Stokes and Clark, 2001; Livingstone et al., 2012; Paulen et al., 2017). Primmer et al. (2015) have shown that within around 10 km down-ice from a Rb source, initial Rb concentration in till decreased by > 50%. After 75 km, the initial Rb concentration has been reduced by approximately 75% (Primmer et al., 2015). Paulen et al. (2017) have also demonstrated that the Strange Lake REE dispersal train in northern Quebec and Labrador has a remarkably long dispersal train of > 40 km down-ice of a REE source formed by an ice stream trending northeastward.

Eskers in the study area are aligned roughly N-S (Fig. 2a) and reflect the overall pattern of retreat of the ice margin towards the south (Dubé-Loubert et al., 2014a). They are composed of rounded pluri-decimetric boulders supported by a gravely and sandy matrix. Their spatial distribution extends from the south-west to the northern part of the study area where the landscape was affected by the incursion of the postglacial Iberville Sea. Most of the northern eskers terminate into the Iberville Sea and were likely formed late during the deglaciation. They are usually small in size, with a height and width average of 5 to 6 m and 20 to 25 m, respectively (Fig. 2d). Eskers are mostly discontinuous, alternating between small ridges of ice-contact sediments and sandy outwash sequences (Dubé-Loubert et al., 2014a). The effective distance of transport by glacial meltwater is, as in the case of glacial sediment, difficult to quantify. Dispersal trains in eskers may originate from the erosion of pre-existing terrains in glacial sediments or from the erosion of the underlying bedrock (Brushett and Amor, 2013). Consequently, esker samples show either an indirect or close relationship with the underlying bedrock depending on the type of material eroded (till or rock), as well as on the areal extent of the subglacial meltwater catchment (Brushett and Amor, 2013). Relative to till, esker sampling is considered to give a reconnaissance overview of the mineral potential of a region as compared to a more local bedrock signature provided by till (McClenaghan and Kjarsgaard, 2007). In the study area, the eskers, from their size and the lithology of the clasts, suggest erosion/transport of local material. As a result, the results obtained from esker samples are interpreted as reflecting a slightly displaced signature of the underlying bedrock.

3. Methods

3.1. Sampling

The Churchill Province in northern Quebec consists of Archean to Proterozoic basement rocks, which have undergone a complex



Fig. 3. Microphotographs in reflected light of typical sulfide and sulfarsenide grains recovered from glacial sediments in this study: a) euhedral pyrite grain with cubic shape; b) subhedral pyrite grain with chalcopyrite inclusions; c) anhedral pyrite grain with angular faces surrounded by a thin oxidation rim; d) anhedral pyrite grain displaying porosity; e) anhedral pyrite grain with angular faces and fragmental aspect; f) anhedral, rounded pyrite grain with a thin oxidation rim; g) subhedral chalcopyrite grain; h) anhedral chalcopyrite grain with cubanite or pentlandite exsolution; i) anhedral chalcopyrite grain with rounded shape and fragmental aspect; j) anhedral chalcopyrite grain with a thin oxidation rim; k) anhedral chalcopyrite grain with fragmental aspect; l) anhedral compared by a thin oxidation rim; k) anhedral chalcopyrite grain with fragmental aspect; here are a specific to the fragmental aspect; here are a spe



Fig. 4. Typical examples of time-signal diagrams showing trace element distribution in chalcopyrite: a) and b) profiles show flat patterns indicating homogeneous trace element composition; c), d), e), and f) profiles show peaks marked with black arrows that indicate inclusions of pentlandite (Pn), sphalerite (Sph), galena (Gn), and scheelite (Sch), respectively.



Fig. 5. Typical examples of time-signal diagrams showing trace element distribution in pyrite: a) profile shows flat patterns indicating homogeneous trace element composition; b) and c) profiles show undulant patterns indicating trace element compositional zoning; d), e), and f) profiles show peaks marked with black arrows that indicate inclusions of molybdenite (Mo), oxide, and sphalerite (Sph) inclusions, respectively.

geodynamic and metamorphic history (Henrique-Pinto et al., 2017). The study area covers ca. 31,250 km² south to the Ungava Bay in northern Quebec (Fig. 1), in which a variety of mineral deposits has been documented (Lafrance et al., 2013; Charette et al., 2016). The vast majority of these rocks are covered by thick Quaternary sediments consisting of glacial diamicton (till) and narrow corridors of glacio-fluvial sediments (eskers) (Dubé-Loubert et al., 2014a and 2014b; Dubé-Loubert et al., 2016). Heavy mineral concentrates prepared from till and esker samples collected across this area revealed the presence of numerous pyrite and chalcopyrite grains and a few sulfarsenide grains (löllingite and arsenopyrite), indicative of the occurrence of prospective sulfide-rich rocks in the region. Consequently, this area is ideal to test sulfide indicator mineral chemistry for mineral assessment and vectoring.

More than 600 till and esker samples were collected across two 1:250,000 scale NTS map sheets (24G and 24B of the National Topographic System of Canada) by the MERN during a surficial mapping program carried out between 2012 and 2015. For each sample site, 10 kg was collected for till and 15 kg was collected for esker, following the procedures described in McClenaghan et al. (2013). The samples were processed by IOS Services Géoscientifiques Inc. to produce 250-1000 µm non-ferromagnetic heavy mineral concentrates, following the procedures described in Plouffe et al. (2013). Sulfide and sulfarsenide indicator minerals were picked from the diamagnetic fraction (apparent magnetic susceptibility > 0.4 Amp) of the $250-1000 \,\mu m$ heavy mineral concentrates, after removal of the magnetic fraction. Sulfide and sulfarsenide grains were found in a total of 301 till and esker samples. Between 1 and 61 grains of sulfide/sulfarsenide per sample were picked. On average, the samples contained around 10 grains, in which cases all the grains were selected. However, some samples contained hundreds of grains, which required random subsampling from an analytical perspective (time versus cost). Only the grains selected for analysis are reported in this study and the sulfide abundance is used as a relative assessment. A total of 1831 sulfide and sulfarsenide grains were removed from the sediment samples and mounted in epoxy sections and polished (Appendix A). The entire sections were scanned using a Zeiss EVO-MA15 HD 2013 scanning electron microscope at IOS Services Géoscientifique Inc. to determine sulfide and sulfarsenide species (based on their major element compositions) before characterizing their trace element compositions by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

3.2. LA-ICP-MS analysis

Analyses by LA-ICP-MS of individual sulfide/sulfarsenide grain were performed at LabMaTer (UQAC) using an Excimer 193 nm RESOlution M-50 laser ablation system (Australian Scientific Instrument) equipped with a double volume cell S-155 (Laurin Technic) and coupled with an Agilent 7900 mass spectrometer. A beam size of 55 μ m, a stage movement speed of 10 μ m/s, a laser frequency of 15 Hz and a fluence of 3 J/ cm² were used to analyze the sulfide and sulfarsenide grains. For large grains, line scans were made, and for small grains, spot analyses were favored. The gas blank was measured for 30 s before switching on the laser for at least 30 s. The ablated material was carried into the ICP-MS by an argon–helium gas mix at a rate of 0.8–1 L/min for Ar and 350 mL/ min for He, and 2 mL/min of nitrogen was also added to the mixture. Data reduction was carried out using the Iolite package for Igor Pro software (Paton et al., 2011) and data plotting was completed in the ggplot2 package for R (Wickham, 2009).

Maps of the element distribution were made on one or several grains using the same frequency and fluence, but various beam sizes and stage movement speeds, to optimize spatial resolution and analysis time of the areas being mapped. The maps were generated using the Iolite package based on the time-resolved composition of each element. The maps indicate the relative concentration of the elements and are semiquantitative. The following isotopes were quantified: ²⁹Si, ⁴⁹Ti, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁹Co, ⁶¹Ni, ⁶⁵Cu, ⁶⁶Zn, ⁷⁵As, ⁸²Se, ⁸⁸Sr, ⁹⁵Mo, ¹⁰¹Ru, ¹⁰³Rh, ¹⁰⁸Pd, ¹⁰⁹Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹³⁰Te, ¹³⁷Ba, ¹³⁹La, ¹⁷²Yb, ¹⁸²W, ¹⁸⁵Re, ¹⁸⁹Os, ¹⁹³Ir, ¹⁹⁵Pt, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb, and ²⁰⁹Bi. Because the analyzed sulfide and sulfarsenide minerals contain very little Ni, the correction of polyatomic interference of ⁶¹Ni⁴⁰Ar on ¹⁰¹Ru was not necessary. Similarly, the polyatomic interference of ⁶³Cu⁴⁰Ar on ¹⁰³Rh was not corrected as pyrite and sulfarsenide minerals contain very little Cu, and this interference in chalcopyrite is too important to be corrected. Direct interference of ¹⁰⁸Cd on ¹⁰⁸Pd and ¹¹⁵Sn on ¹¹⁵In were corrected manually by monitoring ¹¹¹Cd and ¹¹⁸Sn, respectively.

Internal standardization was based on ⁵⁷Fe using stoichiometric iron values (w/w%) of each mineral specie, i.e. 46.55% Fe for pyrite, 30.43% Fe for chalcopyrite, 34.30% Fe for arsenopyrite and 27.15% Fe for löllingite (e.g. Vaughan and Craig, 1978). Three reference materials (RM) were used for external calibration: i) Laflamme Po727, a synthetic FeS doped with ~40 ppm platinum-group elements (PGE) and Au and supplied by Memorial University of Newfoundland, was used to calibrate for PGE and Au; ii) MASS-1 (Wilson et al., 2002), a ZnCuFeS pressed powder pellet doped with 50-70 ppm of most chalcophile elements and supplied by the United States Geological Survey (USGS), was used to calibrate for Cu, Zn, Se, Te, Hg, and Tl; iii) GSE-1g, a natural basaltic glass fused and doped with most elements at 300-500 ppm, was supplied by the USGS and was used to calibrate for Si, Ti, V, Cr, Mn, Co, Ni, As, Sr, Mo, Ag, Cd, In, Sn, Sb, Ba, La, Yb, W, Re, Pb, and Bi using preferred values from the GeoReM database (Jochum et al., 2005). Two more RM were used for quality control: i) JB-MSS5, which is a synthetic FeS sulfide containing 50-70 ppm of most chalcophile elements supplied by James Brenan (Dalhousie University, Canada); and ii) UQAC-FeS-1, which is a synthetic sulfide recently developed at UQAC. MASS-1 and GSE-1g were also used for some elements as quality control reference materials (OCRM) for validation. The results for the OCRM were generally in good agreement with the working values (Appendix A). Differences between the concentrations measured in this study and the published QCRM working values can be of multiple source, noticeably the low level of confidence (provisional/informational) of reported working values for several elements in the QCRM, heterogeneity and non-matrix-matched materials (physical and chemical) i.e. silicate glass (GSE-1G), pressed pellets (MASS-1 and UQAC-FeS-1), hydrous content (MASS-1), tiny fused sulfide (JB-MSS5). However, the diagram



Fig. 6. Typical example of a time-signal diagram showing profile with flat pattern reflecting homogeneous trace element distribution in löllingite.

presented in Appendix A shows an acceptable trend of positive correlation between our values and the working values.

During data reduction, the entirety of the signal was integrated, despite the presence of inclusions, for two reasons. First, the presence of some inclusions (e.g. pentlandite and sphalerite) may be indicative of specific context. Moreover, these inclusions may have formed by exsolution at low temperature, reflecting the presence of some elements (e.g. Ni and Zn) in solid solution within a high-temperature precursor. Thus, integrating all the signal allows to maximize the information. Second, integration of the entire signal does not require detailed assessment of each signal, which allows faster data reduction. Fast data reduction is essential for developing an effective method that could be used on large number of grains or databases in an exploration program. Other types of inclusions might have been encountered, such as silicate and oxides minerals, but as these minerals do not contain significant amounts of chalcophile elements their presence (and thus their integration) remains trivial for the purpose of this study.



Fig. 7. Typical example of a LA-ICP-MS multielement map of a single pyrite grain (from esker sample 93720115 located in map sheet 24G). Note the concentric zoning displayed by Co, Ni, As, and Se, and the sector zoning displayed by Bi. More importantly, the presence of Re and Pt in the pyrite suggests a magmatic origin.



Fig. 8. Typical example of a LA-ICP-MS multielement map of a single pyrite grain (from till sample 93724168 located in map sheet 24B). Note the presence of a Bi-Te-Pb-rich inclusion.

4. Mineral grain shapes

Typical examples of sulfide (pyrite and chalcopyrite) and sulfarsenide (löllingite and arsenopyrite) grains recovered from till and esker samples are shown in Fig. 3. Pyrite grains display variable morphologies, ranging from euhedral grains exhibiting cubic shapes to anhedral grains exhibiting rounded or angular shapes with a fragmental aspect. Thin rims are common on the outsides of some grains. These rims are assumed to be oxidation coronas that developed on the pyrite surface due to high reactivity with air or water (Rosso and Vaughan, 2006) before, during, or after glacial transport. Some grains appear to be porous, regardless of their morphology. Some grains also have inclusions readily visible on their cut and polished surface. Chalcopyrite grains display less variable morphologies, ranging from subhedral grains to anhedral grains exhibiting angular shapes with a fragmental aspect. As in the case of pyrite, some chalcopyrite grains also have inclusions and oxidation coronas, but they appear to be less developed than in the case of pyrite. In a few cases, exsolutions (probably cubanite or pentlandite) have been observed in chalcopyrite. Sulfarsenide grains display subhedral to anhedral morphologies and do not seem to have oxidation coronas. The shapes of sulfide and sulfarsenide grains do not appear to be related to variations in trace element distribution and composition presented in the next section.



Fig. 9. Typical example of a LA-ICP-MS multielement multi-grain map of chalcopyrite. The chalcopyrite grains show obvious compositional inter-grain variations in Co, Ni, Zn, Se, Ag, Cd, In, Sn, Te, Pb, and Bi. The chalcopyrite grains come from the same esker sample (sample 93724123 located in map sheet 24B).

5. Trace element chemistry

5.1. Distribution

Time-signal diagrams (Figs. 4–6) and multielement maps (Figs. 7–10) were used to examine the spatial distribution of elements within minerals and to detect the presence of inclusions. For example, the peaks in Co and Ni in a chalcopyrite grain (Fig. 4c) indicate the presence of pentlandite inclusions, whereas the peaks in Pb in another chalcopyrite grain (Fig. 4d) indicate galena inclusions. Multielement maps show zonation pattern that indicate complex crystallization

histories, such as in the case of pyrite (Fig. 7). Multi-grain multielement maps (Figs. 9 and 10) show which elements display strong variations and hence which elements have the greatest potential to provide discrimination information. The combination of certain types of inclusions, element associations, and zonations may be indicative of ore processes. From an indicator mineral perspective, this is the first step to identify possible bedrock sources.

Within most chalcopyrite grains, trace elements are homogeneously distributed (Fig. 9). However, the multi-grain multielement maps show that chalcopyrite grains have wide range of compositions for Co, Ni, Zn, Se, Ag, Cd, In, Sn, Te, Pb, and Bi (Fig. 9) and therefore these elements



Fig. 10. Typical example of a LA-ICP-MS multielement multi-grain map of löllingite. The löllingite grains show obvious compositional inter-grain variations in Co, Ni, Sb, Te, Au, and Bi. The löllingite grains come from the same esker sample (sample 93720062 located in map sheet 24G).



Fig. 11. Box and whisker diagrams of the concentrations of each element in each mineral specie. For some elements, the lower whisker, lower quartile, and median value are the same because most analyses are below or equal to the limit of detection.

could be useful in discriminating chalcopyrite from different metallogenic environments. Although not presented on the maps, the timesignal diagrams show that some grains host inclusions and/or exsolutions of pentlandite, sphalerite, galena, and scheelite (Fig. 4). The chalcopyrite-pentlandite association is typical of magmatic ore deposits (e.g. Duran et al., 2016b; Duran et al., 2017) whereas the association of chalcopyrite with sphalerite, galena, or scheelite is more common in hydrothermal ore deposits (e.g. Sillitoe and Thompson, 1998).

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Pyrite grains show both homogeneous trace element distribution and zonation. Trace elements showing the more obvious zonation are Co, Ni, Se, and As (Fig. 7). Time-signal diagrams show the presence or absence of some elements (Fig. 5). Some grains are enriched in Pt, Pd, Te, and Re (a few ppm), which is common of pyrite from magmatic environments (e.g. Djon and Barnes, 2012; Piña et al., 2016), whereas other grains are enriched in Au, Bi, Sb, Tl, and Hg, which is typical of pyrite from hydrothermal environments (e.g. Large et al., 2009; Genna and Gaboury, 2015; Patten et al., 2016). Several grains host inclusions of chalcopyrite, sphalerite, molybdenite, and/or oxides. Although chalcopyrite and oxide inclusions are not diagnostic of a given metallogenic context, the sphalerite- or molybdenite-pyrite association is more common in hydrothermal ore deposits (e.g. Genna and Gaboury, 2015; Lawley et al., 2013).

Within most sulfarsenide grains, trace elements are homogeneously distributed as indicated by the time-signal diagrams (Fig. 6) and the multi-grain multielement maps (Fig. 10). The maps also show that the grains contain variable concentrations of Co, Ni, Sb, Te, Au, and Bi. No

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inclusion was identified in the time-signal diagrams, but the maps reveal the presence of one Bi-rich inclusion in one löllingite grain. It is unclear whether the lack of inclusions in sulfarsenide grains is typical or only true for the limited number of grains (n = 80) examined in this study.

Multielement maps of pyrite, chalcopyrite, and löllingite also show enrichment in Ti, V, Mn, Cu, Zn, Ag, Sn, Ba, La, Yb, Hg, Tl, and Pb in a thin oxidation rim around sulfide and sulfarsenide grains. Enrichment in these elements illustrates their mobility, either before or during the alteration of glacial sediments. Given that minerals undergo abrasion during glacial transport that would expose fresh crystal faces, the oxidation rim would most likely develop after deposition. Öhlander et al. (1996) have shown that the mobility of REE in till samples was the result of silicate, apatite, or other REE-bearing mineral leaching in the till A horizon prior to adsorption onto secondary oxi-hydroxides, clay minerals, and organic matter in the B horizon. The same interpretation



Fig. 12. Discrimination diagrams based on the sulfide trace element chemistry: a) Co/Sb versus Se/As for pyrite (from Duran et al., 2015); and b) Se-Ni-Cd for chalcopyrite (developed in this study based on data compilation from Barnes et al., 2006; Barnes et al., 2008; Godel et al., 2007; Godel and Barnes, 2008; Dare et al., 2010, 2011, 2014; Djon and Barnes, 2012; Piña et al., 2012; Chen et al., 2014; Duran et al., 2016a; George et al., 2017). Both diagrams allow the discrimination between magmatic and hydrothermal sources.

could be extended to all the elements enriched in the oxidation rim. Given the very thin rim around the outside of sulfide and sulfarsenide grains, alteration was interpreted as being very limited and having no effect on the original compositions within the grains, even for the sulfide grains coming from oxidizing environments like eskers.

5.2. Composition

A total of 639 chalcopyrite grains, 1112 pyrite grains, 9 arsenopyrite grains, and 71 löllingite grains were analyzed. The complete dataset is available in Appendix A. Fig. 11 displays box and whisker plots for the concentrations of each element (in isotopic mass order) in each mineral species. Overall, chalcopyrite, pyrite, arsenopyrite, and löllingite exhibit wide ranges of composition, spanning several orders of magnitude.



Fig. 13. Binary discrimination diagram Co/Sb versus Se/As for pyrite grains (n = 1112) from till and esker samples, with density contours. Note that most pyrite grains (n = 968) plot in the magmatic field. However, a small population of pyrite (n = 37) is plotting in the hydrothermal field. The difference in compositions suggests different origins. The pyrite grains that plot near the boundary separating the magmatic and hydrothermal fields have an undetermined origin (n = 107).

In chalcopyrite, Co, Ni, Zn, As, Se, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, W, Au, Hg, Tl, Pb, and Bi values are mainly above the limits of detection and display important variations. The variations in ppm are as follows: 0.003 < Co < 1059; 0.199 < Ni < 74,250; 0.052 < Zn < 4138; 0.020 < As < 357;0.488 < Se < 6929;0.021 < Ru < 0.551;0.002 < Pd < 107;0.005 < Ag < 663;0.007 < Cd < 72.7;0.011 < Sn < 213;0.007 < Sb < 9.04;0.001 < In < 66.9;0.002 < W < 8277;0.076 < Te < 146;0.005 < Au < 20.6;0.060 < Hg < 82.5; 0.001 < Tl < 13.7; 0.010 < Pb < 35,600;and 0.001 < Bi < 200. High Co, As, Se, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, Au, Hg, Tl, and Bi values are not related to inclusions and reflect chalcopyrite compositions. Although many chalcopyrite grains have high Ni, Zn, W, or Pb concentrations, the extreme values in these elements (i.e. thousands of ppm) are related to pentlandite, sphalerite, scheelite, or galena inclusions, respectively. Vanadium, Cr, Mn, Sr, Mo, Ba, La, Yb, Re, Os, Ir, and Pt values are in general equal or below the limits of detection. Extreme V, Cr, Mn (up to 21.6, 36.5, and 426 ppm, respectively), Sr, Ba, La, Yb (up to 103, 6086, 43.5, and 9.43 ppm, respectively), Re and Mo (up to 66.9 and 3.01 ppm respectively) concentrations in chalcopyrite are likely due to oxide, silicate, and molybdenite inclusions. The highest Os, Ir, and Pt values do not exceed 0.4 ppm and likely represent elevated concentrations in chalcopyrite because chalcopyrite usually does not contain these elements. Although Ti values are above the limit of detection, most values are close to the median value (3 ppm) and the few extreme values (up to 5903 ppm) are likely due to oxide inclusions.

In pyrite, Co, Ni, Cu, Zn, As, Se, Sr, Pd, Ag, W, Re, Au, Hg, Pb, and Bi values are mainly above the limits of detection and display important variations. The variations in ppm are as follows: 0.051 < Co < 102,876; 0.115 < Ni < 11,824; 0.017 < Cu < 16,432; 0.037 < Zn < 3398;0.019 < As < 6936;0.349 < Se < 912;0.001 < Sr < 95.9;0.001 < W < 7681;0.001 < Pd < 220;0.001 < Ag < 21.4;0.001 < Au < 1.9; 0.022 < Hg < 6.52; 0.001 < Pb < 694; and 0.001 < Bi < 91.2. Two analyses (45-XIV-15 and 45-XI-3) have mixed values related to Zn and Cu sulfides showing false-extreme concentrations of 44% Zn (associated with thousands ppm of Cd and tens ppm of In and Hg) and 72% Cu (associated with hundreds ppm of Ag and Sn and thousands ppm of Bi), respectively. The exposed surface of these grains was composed of pyrite whereas few microns below the surface, another



Fig. 14. Binary diagrams Pb versus Zn, Mo versus Cu, Tl versus Ag, and Au versus Hg for pyrite grains (n = 1112) from till and esker samples, showing that the population of hydrothermal pyrite (red dots, n = 37) is usually enriched in these trace elements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mineral was present (i.e. sphalerite and a Cu sulfide, respectively). These mixed analytical results are presented in the figures and tables along with the other pyrites results to demonstrate that a few outlier results do not affect the interpretation while data processing remains fast. High Co, Ni, As, Se, Sr, Pd, Au, and Hg values are not related to inclusions and reflect pyrite compositions. Although some pyrite grains have high Cu, Ag, Pb, Bi, Zn, or W concentrations, the extreme values in these elements are likely related to chalcopyrite (or other Cu sulfides), galena, sphalerite, or scheelite inclusions. Chromium, Mn, Mo, Ru, Rh, Cd, In, Sn, Sb, Te, Ba, La, Yb, Os, Ir, Pt, and Tl values are, in general, equal or below the limits of detection. Extreme Cr, Mn (up to 289 and 10,194 ppm respectively), Ba, La, Yb (up to 1909, 2840, and 12.3 ppm, respectively), and Mo (up to 4190 ppm) concentrations are likely related to oxide, silicate, and molybdenite inclusions. The highest Ru, Rh, Cd, Sn, In, Sb, Te, Os, Ir, and Tl values do not exceed a few ppm and thus represent elevated concentrations in pyrite because these elements are not commonly enriched in pyrite. Although Ti and V values are above the limits of detection, most of them are close to the median value (14 and 0.04 ppm, respectively) and the few extreme values (up to 36,774 and 121 ppm, respectively) are likely related to oxide inclusions.

In arsenopyrite and löllingite, Ti, Co, Ni, Cu, Zn, Se, Mo, Ru, Rh, Pd, Cd, Sb, Te, Re, Pt, Au, Hg, Pb, and Bi values are mainly above the limits of detection and display important variations. The variations in ppm are as follows: 0.133 < Ti < 153; 25.5 < Co < 94,400; 6.4 <

Ni < 153,500; 0.055 < Cu < 8700; 0.079 < Zn < 50; 1.44 < Se < 37.8; 0.008 < Mo < 0.41; 0.007 < Ru < 0.93; 0.001 < Rh < 0.45; 0.003 < Pd < 13.8; 0.013 < Cd < 1; 0.043 < Sb < 670; 0.85 < Te < 78.2; 0.004 < Re < 5.46; 0.004 < Pt < 4.07; 0.003 < Au < 72.2; 0.88 < Hg < 207; 0.004 < Pb < 1670; 0.02 < Bi < 18.1. Some arsenopyrite and löllingite grains are particularly enriched in Co, Ni, Sb, Te, Au, Hg, Pb, and Bi, relative to chalcopyrite and pyrite, and these high concentrations are not related to inclusions. Vanadium, Cr, Mn, Sr, Ag, In, Sn, Ba, La, Yb, W, Os, Ir, and Tl values are in general equal or below the limits of detection and the highest values do not exceed a few ppm, reflecting thus low concentrations in these elements and the absence of any inclusion.

6. Application to mineralization discrimination

Pyrite and chalcopyrite are the most widespread sulfide minerals in the Earth's crust (Vaughan, 2006). These sulfide minerals are commonly found in magmatic and hydrothermal deposits. In magmatic systems, pyrite and chalcopyrite exsolve from high-temperature phases that crystallized from sulfide liquids segregated from mafic/ultramafic magmas after S saturation was reached (e.g. Fleet, 2006). In this context, pyrite may also replace primary pyrrhotite and pentlandite, thus inheriting a magmatic signature (Piña et al., 2013, 2016; Duran et al., 2015). In hydrothermal systems, pyrite and chalcopyrite precipitate from fluids, in which S and metals are transported as ionic complexes, when pressure, temperature, and/or oxido-reduction conditions change (e.g. Reed and Palandri, 2006).

Depending on the system in which pyrite and chalcopyrite form, their trace element compositions vary and have been documented (e.g. Barnes et al., 2008; Large et al., 2009; Duran et al., 2015, 2016a; Cook et al., 2016, George et al., 2017). Duran et al. (2015) have developed a binary diagram Co/Sb versus Se/As for pyrites (Fig. 12a), which allows for the discrimination of those of magmatic affinity from those of hydrothermal affinity. Pyrites that form in magmatic systems are usually rich in Co and Se, but poor in Sb and As (Dare et al., 2011; Dion and Barnes, 2012; Piña et al., 2013, 2016; Duran et al., 2015), whereas those that form in hydrothermal systems are usually poor in Co and Se. but richer in Sb and As (e.g. Large et al., 2009; Maslennikov et al., 2009; Thomas et al., 2011; Reich et al., 2013; Revan et al., 2014; Patten et al., 2016). In this study, we have developed a new ternary diagram Se-Ni-Cd for chalcopyrite (Fig. 12b), which allows for the discrimination of those of magmatic affinity from those of hydrothermal affinity. Chalcopyrites that form in magmatic system tend to be rich in Ni and poor in Cd (Barnes et al., 2006; Barnes et al., 2008; Godel et al., 2007; Godel and Barnes, 2008; Dare et al., 2010, 2011, 2014; Djon and Barnes, 2012; Piña et al., 2012; Chen et al., 2014; Duran et al., 2016a), whereas those that form in hydrothermal systems tend to be poor in Ni and rich in Cd (George et al., 2017). Thus, when compositional data are plotted, a magmatic trend towards the Ni apex and a hydrothermal trend towards the Cd apex are evident.

The binary diagram Co/Sb versus Se/As for pyrite (Fig. 13) shows that the vast majority of the pyrite grains in glacial sediments in this study have relatively high ratios, suggesting a magmatic source for most grains. However, a small population with low ratios, i.e. Co- and Se-poor and Sb- and As-rich, was also identified; the composition of these grains suggests a hydrothermal origin (Fig. 13). Based on this discrimination, the pyrite grains were classified as magmatic, hydrothermal, or undetermined (when the composition plotted near the boundary separating magmatic and hydrothermal fields). Some pyrite grains from the magmatic population have significant concentrations in Pt, Pd, and Re (up to 8, 220, and 1.2 ppm, respectively) accommodated in the pyrite structure (e.g. see Pt in Fig. 7). This observation is consistent with a magmatic origin, in particular a PGE-dominated deposit. However, most of the grains classified as magmatic have very low PGE and Re concentrations, suggesting that the magmatic source had initially low contents of these elements. This low content of PGE and Re could reflect the fact that these grains are from Ni-Cu sulfide mineralization rather than PGE-dominated sulfide mineralization (Duran et al., 2016a). The pyrite grains classified as hydrothermal on the basis of the Co/Sb vs Se/As are richer in Zn, Pb, Cu, Mo, Ag (> 1 ppm), Tl, Hg (> 0.1 ppm), and Au (> 0.01 ppm) (Fig. 14). This pattern is consistent with the observation that these are all mobile elements, and thus they might be expected to be enriched in hydrothermal systems.

The ternary diagram Se-Ni-Cd for chalcopyrite (Fig. 15) shows that most chalcopyrite grains plot near the Se apex, and thus their source cannot be identified. However, two trends in the data can be observed in the figure: one towards the Ni apex and the other towards the Cd apex, suggesting magmatic and hydrothermal sources, respectively. Based on this discrimination diagram, the chalcopyrite grains were classified as magmatic, hydrothermal, or undetermined (towards the Se apex). In contrast to pyrite grains, chalcopyrite grains do not show systematic compositional variations in relation to their bedrock source because chalcopyrite composition is partly controlled by the co-crystallizing phases (George et al., 2017) and not only the system in which it formed. The enrichment of some chalcopyrite grains in In, Sn, Te, Bi, As, Au, and Pt (a few ppm to tens of ppm), would thus be a consequence of the local environment rather than the nature of the source. Nonetheless, the Cd/Zn ratio for hydrothermal chalcopyrite in general, seems to be controlled by the crystallization temperature (George et al., 2017). At relatively low temperatures (< 400 °C), such as those



Fig. 15. Ternary discrimination diagram Se-Ni-Cd for chalcopyrite grains (n = 639) from till and esker samples, with density contours. Note that most chalcopyrite plots towards the Se apex (n = 386), indicating that they have an undetermined origin. However, a population of chalcopyrite defines a magmatic trend towards the Ni apex (n = 162) and another one defines a hydro-thermal trend towards the Cd apex (n = 91).

associated with the formation of exhalative or epithermal deposits, chalcopyrite is known to be enriched in Zn relative to Cd (George et al., 2017). At higher temperatures (> 400 °C), such as in skarn or metamorphosed exhalative deposits, chalcopyrite tends to be enriched in Cd relative to Zn (George et al., 2017). Hydrothermal chalcopyrite grains identified in this study have relatively high Cd/Zn (Fig. 16), similar to those from metamorphosed exhalative deposits, suggesting high temperature of (re)-crystallization.

Currently, no discrimination diagrams have been developed for arsenopyrite or löllingite. Despite their presence in various mineral deposit types and their variable trace element compositions, arsenopyrite



Fig. 16. Binary diagram of Cd versus Zn for hydrothermal chalcopyrite (n = 91) grains from till and esker samples, with density contours and crystallization temperature trends for several types of hydrothermal deposits (from George et al., 2017). Note that most hydrothermal chalcopyrite grains plot along the recrystallized SEDEX and VMS trends, suggesting higher temperatures of crystallization.



Fig. 17. Binary diagrams Co versus Ni for sulfarsenide grains from till and esker samples, with bubble diameter expressing the concentrations of Sb, Au, Te, or Bi. Although these elements are enriched in sulfarsenides, no correlation is observed except between Co and Ni.

has been analyzed but with a focus on gold and löllingite has been too rarely analyzed, thus limiting their potential use for discrimination of magmatic versus hydrothermal sources. Although sulfarsenides are common in magmatic deposits, the occurrence of arsenopyrite and löllingite in magmatic deposits has only been documented in a few examples (e.g. Gervilla and Leblanc, 1990; Piña et al., 2015). The occurrence of these minerals appears to be more common in hydrothermal systems (Tomkins et al., 2006; Tomkins and Grundy, 2009). The arsenopyrite and löllingite grains from surficial sediment samples in this study are rich in Co and Ni (up to 9 and 15%, respectively) similar to those reported by Piña et al. (2015) and show a strong positive correlation in these elements (Fig. 17). In contrast, PGE concentrations in arsenopyrite and löllingite grains are negligible. Concentrations in Sb, Te, Au, and Bi are significant (tens to hundreds ppm) but do not show any obvious correlations (Fig. 17). Although high Co and Ni concentrations might suggest a magmatic origin, the lack of data in the literature does not allow for a definitive interpretation of either magmatic or hydrothermal origin. However, the low PGE and high Sb, Te, Au, and Bi concentrations would be consistent with the hydrothermal hypothesis.

7. Application to mineral targeting

Previous studies have shown the link between the occurrence of sulfide minerals in till samples and the proximity of underlying mineralization (e.g. Averill, 2011; McClenaghan et al., 2011, 2018). The sulfide minerals recovered from the glacial deposits of the study area is therefore suggestive of the presence of mineralization. Constraining the metallogenic context of the sulfide sources appears as an interesting result in itself, especially in areas where glacial sediments are thick, and knowledge of the underlying bedrock is limited. In our study, the trace element chemistry of sulfide minerals from glacial sediments has allowed us to identify the presence of at least two distinct mineralization types: one of magmatic affinity, and the other of hydrothermal affinity. By combining trace element chemistry with bedrock geology and glacial geology, it is possible to delineate regional vectors related to each mineralization type. To do so, we plotted the location of till and esker samples containing pyrite and chalcopyrite from both magmatic and hydrothermal origins according to our discriminant analysis (Fig. 18). In addition, we plotted the average compositions of discriminant elements for chalcopyrite, i.e. Ni and Cd (Fig. 19), and pyrite, i.e. Co, Sb, and As (Fig. 20).

Chalcopyrite grains of both magmatic and hydrothermal origins are present in most of the map sheet 24B and in the western part of the map sheet 24G, in which the samples define a S-N trend roughly parallel to ice flow directions (Fig. 18). The main differences are observed in the eastern part of the map sheet 24B where hydrothermal chalcopyrite is more widespread, and the northwestern part of the map sheet 24B where the samples contain only magmatic chalcopyrite (Fig. 18). Overall, the presence of chalcopyrite grains of different origins in the



Fig. 18. Distribution of till and esker samples containing a) magmatic chalcopyrite (n = 69), b) hydrothermal chalcopyrite (n = 57), c) magmatic pyrite (n = 268), and d) hydrothermal pyrite (n = 11) across the study area (see Fig. 1 for bedrock geology legend).



Fig. 19. Average concentrations of a) Cd, and b) Ni in chalcopyrite per sample. Areas of elevated average Cd or Ni values (> 10 and > 100 ppm, respectively) are outlined with dashed yellow lines (see Fig. 1 for bedrock geology legend). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

same samples across most of the study area is indicative of mixing of chalcopyrite from magmatic and hydrothermal mineralization during glacial dispersal and suggests that the different bedrock sources might be close to one another.

Pyrite grains of magmatic origin are found in all the samples containing pyrite, except for 5 samples in the map sheet 24B (Fig. 18). The abundance of these pyrite grains reflects the regional potential for magmatic mineralization. However, the widespread nature of magmatic pyrite does not allow to delineate a clear sector for the bedrock source. In contrast, pyrite grains of hydrothermal origin are found in only 8 samples, among which 7 define a S-N trend parallel to ice flow directions across the map sheets 24G and 24B (Fig. 18). These samples also contain magmatic pyrite, and as for chalcopyrite, this suggests mixing of different sources during glacial dispersal.

Despite the identification of many grains of magmatic chalcopyrite in many samples, only 2 samples have high average Ni values for chalcopyrite, i.e. > 100 ppm (Fig. 19). These samples occur in the northwestern part of the map sheet 24B, close to the contact between the Labrador Trough and the Core Zone, and where ice flow directions shift slightly from NW to N. In this area, no hydrothermal chalcopyrite has been found, which if present, would lower the average Ni values. Till and esker samples with elevated Cd values for chalcopyrite (i.e. > 10 ppm), indicating high proportions of hydrothermal chalcopyrite, are more widely distributed (Fig. 19). In the map sheet 24B, about 10 till and esker samples are located from either side of the contact between the Labrador Trough and the Core Zone, defining a trend parallel to ice flow directions. In the map sheet 24G, 3 till and esker samples define a S-N trend propagating from the Labrador Trough into the Core Zone.

The surficial sediment samples with high average Co values for pyrite (i.e. > 9500 ppm), indicating a high proportion of magmatic pyrite, are mostly located in the map sheet 24B (Fig. 20). Although no clear transport vector can be defined, the wide distribution of magmatic pyrite highlights the strong potential for magmatic mineralization. In contrast, the surficial sediment samples with high average values of As and Sb for pyrite (i.e. > 100 and 0.1 ppm, respectively), indicating a high proportion of hydrothermal pyrite, are located in the western part of the map sheets 24G and 24B and define a NW to N trend parallel to ice flow directions from the Labrador Trough northward towards the Core Zone (Fig. 20). In the western part of the map sheet 24G, the spatial distribution of As- and Sb-rich pyrite is not correlated with the high Co values in pyrite. Samples containing sulfarsenide minerals are located along this same trend (Fig. 20), which suggests that the sulfarsenide minerals may be derived from the same bedrock source(s) as the hydrothermal pyrite.

Overall, the integration of sulfide trace element data with sample distribution suggests a regional potential for magmatic mineralization along the Labrador Trough as indicated by the wide dispersal of chalcopyrite and pyrite grains of magmatic origin. In addition, we have identified a NW to N trending pattern in the western part of the study area that is defined by the alignment of samples containing chalcopyrite and pyrite of hydrothermal origin and sulfarsenide minerals. This vector strongly suggests the presence of local hydrothermal mineralization in the western part of the map sheet 24B or the southwestern part of the map sheet 24G. Moreover, this vector suggests a remarkably long glacial dispersal of about 100 km from a source in the Rachel-Laporte Zone and highlights the long-distance transport that is characteristic of an ice stream (Fig. 18b and d).



Fig. 20. Average concentrations of a) As, b) Sb, c) Co in pyrite per sample; areas of elevated average As, Sb, or Co values (> 100, > 0.1, and > 9500 ppm, respectively) are outlined with dashed yellow lines; and average concentration of d) Au in sulfarsenide per sample (see Fig. 1 for bedrock geology legend). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 21. Schematic diagram outlining areas interpreted to have potential to host sulfide mineralization based on ice flow directions and sulfide indicator mineral trace element chemistry. The green polygon represents the main dispersal area of magmatic sulfides and the green star indicates a potential target for magmatic Ni-Cu sulfide mineralization. The red polygon represents the main dispersal area of hydrothermal sulfides and the red star indicates a potential target for metamorphosed SEDEX or VMS mineralization. The black line marks the boundary between the Labrador Trough and the Core Zone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

8. Mineral potential assessment

The study of the trace element chemistry of sulfide minerals present in glacial sediments of the Churchill Province has shown the potential of this approach to constrain the metallogenic context of a region with widespread glacial cover. Our results indicate the strong likelihood of the presence of magmatic Ni-Cu and metamorphosed exhalative mineralization in the underlying rocks. Integration of the sulfide trace element chemistry with the bedrock geology and ice flow history is relatively difficult considering the long-distance glacial transport typical of an ice stream. However, results suggest sulfide sources located in the Rachel-Laporte Zone of the Labrador Trough (Fig. 21), a sector already known for its magmatic Ni-Cu and metamorphosed exhalative mineralization (Lafrance et al., 2014; Charette et al., 2016), and a dispersal over the Core Zone with a roughly northward direction. The Labrador Trough, consisting of mafic/ultramafic rocks and volcanic and metasedimentary rocks appears therefore to be an ideal source for the various types of mineralization.

The area located in the northwestern part of the map sheet 24B appears to be favorable for metamorphosed VMS and/or SEDEX (Fig. 21) since it encompasses the rocks of the Rachel-Laporte Zone, which consists of metavolcanics and metasedimentary units that have undergone upper amphibolite metamorphism (Henrique-Pinto et al., 2017). The sulfide minerals found down ice (up to 100 km) have hydrothermal signatures and the Cd/Zn of chalcopyrite indicate elevated temperatures of crystallization (George et al., 2017), consistent with the local metamorphic grade. Moreover, the rare sulfarsenide grains were found near this area and their association with hydrothermal sulfide minerals, as well as their high concentrations in Au, Sb, Bi, and Te is suggestive of a similar mineralized source. The prevalence of löllingite over arsenopyrite in surficial sediment samples also supports the conclusion about elevated temperatures of formation (Tomkins et al., 2006; Tomkins and Grundy, 2009). Other metamorphosed VMS and/or SEDEX mineralization could be found in the southeastern portion of the Labrador Trough since hydrothermal sulfide minerals with similar signatures have been found in the glacial deposits covering the Core Zone, to the north of the Rachel-Laporte Zone.

Magmatic Ni-Cu mineralization could be found associated with the mafic/ultramafic intrusions located to the south of the study area (and in the southeastern prolongation of the Labrador Trough) since magmatic sulfide minerals are abundant and widely distributed down ice (Fig. 21). Moreover, the mafic/ultramafic intrusions that could potentially host this type of mineralization are in contact with the metasedimentary units, which could have contributed to the S contamination of mafic/ultramafic magmas and triggered sulfide segregation upon emplacement (e.g. Lesher and Stone, 1996; Ripley and Li, 2003; Robertson et al., 2015; Samalens et al., 2017). Given the abundance of magmatic sulfide minerals and their wide geographic distribution, it is not possible to delineate a specific source area.

Overall, the trace element chemistry of sulfide grains recovered from glacial sediments allows to characterize the source of the sulfides and thus defines the metallogenic potential of the region. The widespread distribution of our samples at the regional scale and the limited number of grains selected for analysis do not allow to assess transport distances. Determining the proximity of various sulfide sources could be achieved in target areas using a denser sampling grid and quantifying absolute sulfide abundances in each sample.

9. Benefit, limitation, and future directions

Our study demonstrates that sulfide minerals can be glacially transported over several tens of kilometers and can survive some degree of post depositional oxidation. Thus, sulfide minerals in combination with other indicator minerals can be used for mineral targeting at a regional scale. Given the rarity of sulfide minerals in most barren rocks and their abundance in many mineral deposits, the presence of sulfide minerals in glacial sediments is a strong indicator of underlying metallic mineralization. Compositional differences of sulfide minerals allow the discrimination of various sources, which may help in defining target areas for follow up exploration. Using various sulfide species in combination provides confidence in our interpretations. The ability to characterize the metallogenic setting of sulfide minerals that are recovered from glacial sediments is in itself a significant outcome that can be of major importance in exploration programs using indicator mineral methods.

The limitation of this approach is related to sampling bias, which results from sulfide grain separation and selection. Although sulfide minerals are visually distinct from other minerals, a thin oxidation rim can mask their visual appearance, and thus limit their visual identification in heavy mineral concentrates. However, this oxidation rim can be removed from heavy mineral grains using oxalic acid prior to visual examination of heavy mineral concentrates. In addition, some bias may be encountered during the selection of sulfide minerals for analysis in samples that contain hundreds of sulfide grains. Analysis by LA-ICP-MS of hundreds of sulfide grains recovered from one single sediment sample would be too time-consuming and expensive given the amount of information that would be generated (versus the analysis of hundreds of sulfide grains from several sediment samples).

Future studies are recommended to refine our approach. In our project, a follow up study of additional, denser till sampling in areas

with strong potential would help to delineate targets and transport distances with more accuracy. When possible, analysis of pyrite, chalcopyrite, and sulfarsenide minerals should be combined with analysis of other sulfide minerals such as sphalerite, galena, and/or pentlandite, and other oxide (e.g. chromite) and silicate (e.g. pyroxene) minerals. In well studied areas, blind tests could be used to assess the effectiveness of this approach before it is routinely applied to exploration programs. In general, we recommend using a unified element suite when performing LA-ICP-MS analyses of magmatic and hydrothermal sulfide minerals, so that the data can be compiled and compared to develop new discrimination diagrams. We also recommend analysing more sulfarsenide minerals as their trace element chemistry is variable and might be discriminative.

10. Concluding remarks

This study highlights the potential of the trace element chemistry of sulfide indicator minerals for defining the metallogenic context of rocks covered by glacial sediments. It is the first study to integrate the trace element chemistry of sulfide and sulfarsenide minerals in glacial sediments with knowledge of surficial geology (glacial transport trends and distance) and bedrock geology. On this basis, we established two metallogenic contexts for the mineralized sources and delineated target sectors for mineral exploration south to the Ungava Bay in the Churchill Province. The main outcomes are summarized as follows:

- (1) This study highlights sulfide mineral preservation in glacial sediments. The results showed that sulfide minerals can survive the rigours of glacial transport (over 100 km) and subsequent moderate post depositional oxidation (even in eskers).
- (2) Sulfide grains contain various inclusions (pentlandite, chalcopyrite, sphalerite, galena, scheelite, molybdenite, oxides) that can be indicators of specific ore forming settings.
- (3) The development of oxidation coronas around sulfide and sulfarsenide grains is associated with an enrichment in some elements (Ag, Cu, Zn, W, La, Yb, Ba), demonstrating their mobility before or during alteration of glacial sediments. However, these coronas are usually very thin, indicating that alteration was limited and that the initial composition of sulfide and sulfarsenide grains was not modified.
- (4) Sulfide and sulfarsenide grains have extremely variable compositions, suggesting distinct formation environments, and demonstrating the powerful applications of sulfide indicator minerals.
- (5) The application of the binary diagram Co/Sb versus Se/As developed by Duran et al. (2015) allows discrimination of two types of pyrite in the glacial sediments: a majority of magmatic pyrite and a small population of hydrothermal pyrite. The population of hydrothermal pyrite identified in this study is enriched in Pb, Zn, Mo, Cu, Tl, Ag, Au, and Hg, which are pathfinder elements for hydrothermal mineralization.
- (6) The Se-Ni-Cd ternary diagram designed in this study for chalcopyrite shows that the origin of many chalcopyrite grains cannot be distinguished. However, it allows the discrimination of two types of chalcopyrite: magmatic and hydrothermal. Hydrothermal chalcopyrite is characterized by high Cd/Zn ratios, suggesting a higher crystallization temperature typical of metamorphosed VMS or SEDEX deposits.
- (7) Despite high Co and Ni concentrations in sulfarsenide minerals (up to 9.4 and 15%, respectively), these minerals are poor in PGE but rich in Au, Sb, Te, and Bi. These compositions suggest a hydrothermal origin. The stability field of löllingite (the prevalent sulfarsenide) at higher temperature is consistent with the metamorphism of VMS and SEDEX mineralization.
- (8) The established vectors track the source of both types of mineralization towards the Labrador Trough, which in the study area consists of mafic/ultramafic intrusions and metavolcanics and

metasedimentary rocks. Near the contact with the Labrador Trough and the Rachel-Laporte Zone the metavolcanics and metasedimentary rocks have undergone upper amphibolite metamorphism and could host VMS and SEDEX mineralization. When in contact with mafic/ultramafic intrusions, these units could have provided the necessary S to trigger sulfide saturation in the mafic/ultramafic intrusions and thus form magmatic Ni-Cu deposits.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2018.10.006.

References

- Averill, S., 2001. The application of heavy indicator mineralogy in mineral exploration, with emphasis on base metal indicators in glaciated metamorphic and plutonic terrain. In: McClenaghan, M.B., Bobrowsky, P.T., Hall, G.E.M., Cook, S.J. (Eds.), Drift Exploration in Glaciated Terrain. Geol. Soc. London, Spec. Publ. 185, pp. 69–81.
- Averill, S.A., 2011. Viable indicator minerals in surficial sediments for two major base metal deposit types: Ni-Cu-PGE and porphyry Cu. Geochem.: Explor., Environ., Anal. 11, 279–291.
- Barnes, S.-J., Lightfoot, P.C., 2005. Formation of magmatic nickel sulfide ore deposits and processes affecting their copper and platinum group element contents. Econ. Geol., 100th Anniversary vol., 179–214.
- Barnes, S.-J., Cox, R.A., Zientek, M.L., 2006. Platinum-group element, gold, silver and base metal distribution in compositionally zoned sulfide droplets from the Medvezky Creek Mine, Noril'sk, Russia. Contrib. Mineral. Petr. 152, 187–200.
- Barnes, S.-J., Prichard, H.M., Cox, R.A., Fisher, P.C., Godel, B., 2008. The location of the chalcophile and siderophile elements in platinum group element ore deposits (a textural, microbeam and whole rock geochemical study): implications for the formation of the deposits. Chem. Geol. 248, 295–317.
- Begg, G.C., Hronsky, J.A.M., Arndt, N.T., Griffin, W.L., O'Reilly, S.Y., Hayward, N., 2010. Lithospheric, cratonic, and geodynamic setting of Ni-Cu-PGE sulfide deposits. Econ. Geol. 105, 1057–1070.
- Belousova, E.A., Griffin, W.L., O'Reilly, S.Y., Fisher, N.I., 2002. Apatite as an indicator mineral for mineral exploration: trace-element compositions and their relationship to host rock type. J. Geochem. Explor. 76, 45–69.
- Berner, R.A., 1970. Sedimentary pyrite formation. Am. J. Sci. 268, 1-23.
- Brushett, D., Amor, S., 2013. Kimberlite-indicator Mineral Analysis of Esker Samples, Western Labrador. Government of Newfoundland and Labrador, Department of Natural Resources, Geological Survey, Open File LAB/1620.
- Charette, B., Lafrance, I., Mathieu, G., 2016. Géologie de la région du lac Jeannin (SNRC 24B). Ministère de l'Énergie et des Ressources naturelles, Québec; RG électronique
- Chen, L.-M., Song, X.-Y., Danyushevsky, L.V., Wang, Y.-S., Tian, Y.-L., Xiao, J.-F., 2014. A laser ablation ICP-MS study of platinum-group and chalcophile elements in base metal sulfide minerals of the Jinchuan Ni–Cu sulfide deposit, NW China. Ore Geol. Rev. 65, 955–967.
- Clark, T., Wares, R., 2004. Synthèse lithotectonique et métallogénique de l'Orogène du Nouveau-Québec (Fosse du Labrador). Ministère des Ressources naturelles, de la Faune et des Parcs, Québec (MM 2004-01).
- Clark, T., Wares, R., 2005. Lithotectonic and metallogenic synthesis of the New Quebec Orogen (Labrador Trough). Minstère des Ressources naturelles, de la Faune et des Parcs, Québec (MM 2005-01).
- Clark, C.D., Knight, J.K., Gray, J.T., 2000. Geomorphological reconstruction of the Labrador Sector of the Laurentide Ice Sheet. Quat. Sci. Rev. 19, 1343–1366.
- Cook, N., Ciobanu, C.L., George, L., Zhu, Z.-Y., Wade, B., Ehrig, K., 2016. Trace element analysis of minerals in magmatic-hydrothermal ores by laser ablation inductivelycoupled plasma mass spectrometry: Approaches and opportunities. Minerals 6, 111. https://doi.org/10.3390/min6040111.
- Corrigan, D., Pehrsson, S., Wodicka, N., De Kemp, E., 2009. The Palaeoproterozoic Trans-Hudson Orogen: a prototype of modern accretionary processes. In: Geol. Soc. London, Spec. Publ. 327, pp. 457–479.

- Dare, S.A.S., Barnes, S.-J., Prichard, H.M., 2010. The distribution of platinum group elements and other chalcophile elements among sulfides from the Creighton Ni–Cu–PGE sulfide deposit, Sudbury, Canada, and the origin of Pd in pentlandite. Mineral. Deposita 45, 765–793.
- Dare, S.A.S., Barnes, S.-J., Prichard, H.M., Fisher, P.C., 2011. Chalcophile and platinumgroup element (PGE) concentrations in the sulfide minerals from the McCreedy East deposit, Sudbury, Canada, and the origin of PGE in pyrite. Mineral. Deposita 46, 381–407.
- Dare, S.A.S., Barnes, S.-J., Prichard, H.M., Fisher, P.C., 2014. Mineralogy and geochemistry of Cu-rich ores from the McCreedy East Ni-Cu-PGE deposit (Sudbury, Canada): implications for the behavior of platinum group and chalcophile elements at the end of crystallization of a sulfide liquid. Econ. Geol. 109, 343–366.
- Djon, M.L.N., Barnes, S.-J., 2012. Changes in sulphides and platinum-group minerals with the degree of alteration in the Roby, Twilight, and High-Grade Zones of the Lac des Iles Complex, Ontario, Canada. Mineral. Deposita 47, 875–896.
- Dubé-Loubert, H., Daubois, V., Roy, M., 2014a. Géologie des dépôts de surface de la région du lac Saffray (24G). Ministère de l'Énergie et des Ressources naturelles, Québec (RP-2014-06).
- Dubé-Loubert, H., Daubois, V., Roy, M., 2014b. Géologie des dépôts de surface de la région du lac Brisson (24A). Ministère de l'Énergie et des Ressources naturelles, Québec (RP-2016-03).
- Dubé-Loubert, H., Daubois, V., Roy, M., 2016. Géologie des dépôts de surface de la région du lac Henrietta (24H). Ministère de l'Énergie et des Ressources naturelles, Québec (RP-2016-01).
- Duran, C.J., Barnes, S.-J., Corkery, J.T., 2015. Chalcophile and platinum-group element distribution in pyrites from the sulfide-rich pods of the Lac des Iles Pd deposits, Western Ontario, Canada: implications for post-cumulus re-equilibration of the ore and the use of pyrite compositions in exploration. J. Geochem. Explor. 158, 223–242.
- Duran, C.J., Barnes, S.-J., Corkery, J.T., 2016a. Trace element distribution in primary sulfides and Fe–Ti oxides from the sulfide-rich pods of the Lac des Iles Pd deposits, Western Ontario, Canada: constraints on processes controlling the composition of the ore and the use of pentlandite compositions in exploration. J. Geochem. Explor. 166, 45–63.
- Duran, C.J., Barnes, S.-J., Corkery, J.T., 2016b. Geology, petrography, geochemistry, and genesis of sulfide-rich pods in the Lac des Iles palladium deposits, western Ontario, Canada. Mineral. Deposita 51, 509–532.
- Duran, C.J., Barnes, S.-J., Pleše, P., Prašek, M.K., Zientek, M.L., Pagé, P., 2017. Fractional crystallization-induced variations in sulfides from the Noril'sk-Talnakh mining district (polar Siberia, Russia). Ore Geol. Rev. 90, 326–351.
- Fleet, M.E., 2006. Phase equilibria at high temperatures. Rev. Mineral. Geochem. 61, 365-419.
- Franklin, J.M., Gibson, H.L., Jonasson, I.R., Galley, A.G., 2005. Volcanogenic massive sulfide deposits. Econ. Geol., 100th Anniversary vol., 523–560.
- Genna, D., Gaboury, D., 2015. Deciphering the hydrothermal evolution of a VMS system by LA-ICP-MS using trace elements in pyrite: an example from the Bracemac-McLeod deposits, Abitibi, Canada, and implications for exploration. Econ. Geol. 110, 2087–2108.
- George, L.L., Cook, N.J., Crowe, B.B.P., Ciobanu, C.L., 2017. Trace elements in hydrothermal chalcopyrite. Mineral. Mag. https://doi.org/10.1180/minmag.2017.081. 021.
- Gervilla, F., Leblanc, M., 1990. Magmatic ores in high-temperature alpine type lherzolite massifs (Ronda, Spain, and Beni Bousera, Morocco). Econ. Geol. 85, 112–132.
- Godel, B., Barnes, S.-J., 2008. Platinum-group elements in sulfide minerals and the whole rocks of the J-M Reef (Stillwater Complex): implication for the formation of the reef. Chem. Geol. 248, 272–294.
- Godel, B., Barnes, S.-J., Maier, W.D., 2007. Platinum-group elements in sulfide minerals, platinum-group minerals, and whole-rocks of the Merensky Reef (Bushveld Complex, South Africa): implications for the formation of the reef. J. Petrol. 48, 1569–1604.
- Groves, D.I., Bierlein, F.P., 2007. Geodynamic settings of mineral deposit systems. J. Geol. Soc. 164, 19–30.
- Hannington, M.D., De Ronde, C.E.J., Petersen, S., 2005. Sea-floor tectonics and submarine hydrothermal systems. Econ. Geol., 100th Anniversary vol., 111–142.
- Henrique-Pinto, R., Guilmette, C., Bilodeau, C., McNicoll, V., 2017. Evidence for transition from a continental forearc to a collisional pro-foreland basin in the eastern Trans-Hudson Orogen: detrital zircon provenance analysis in the Labrador Trough, Canada. Precambrian Res. 296, 181–194.
- Hoffman, P.F., 1988. United Plates of America, the birth of a craton-Early Proterozoic assembly and growth of Laurentia. Annu. Rev. Earth Planet. Sci. 16, 543–603.
- Houle, P., Perreault, S., 2007. Les orogènes du Nouveau-Québec et des Torngat, la province de Churchill Sud-Est (zone noyau) et l'Orogène de l'Ungava (région administrative 10, Nord-du-Québec). Ministère des Ressources naturelles et de la Faune du Ouébec (DV-2008-01).
- Houlé, M.G., Bédard, M.-P., McNicoll, V.J., Corrigan, D., Huot, F., 2015. Investigations of the mafic and ultramafic intrusive rocks of the Montagnais sills, northern Labrador Trough, Nunavik, Québec. In: Geological Survey of Canada, Open File 7979.
- Jansson, K., Stroeven, A., Kleman, J., 2003. Configuration and timing of Ungava Bay ice streams, Labrador-Ungava, Canada. Boreas 32, 256–262.
- Jochum, K.P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., Hofmann, A.W., 2005. GeoReM: a new geochemical database for reference materials and isotopic standards. Geostand. Geoanal. Res. 29, 333–338.
- Lafrance, I., Simard, M., Bandyayera, D., 2014. Géologie de la région du lac Saffray (SNRC 24G 24F). Ministère des Ressources naturelles (RG 2014-02).
- Large, R.R., Danyushevsky, L., Hollit, C., Maslennikov, V., Meffre, S., Gilbert, S., Bull, S., Scott, R., Emsbo, P., Thomas, H., Singh, B., Foster, J., 2009. Gold and trace element zonation in pyrite using a laser imaging technique: implications for the timing of gold in orogenic and carlin-style sediment-hosted deposits. Econ. Geol. 104, 635–668.

- Lawley, C.J.M., Selby, D., Imber, J., 2013. Re-Os molybdenite, pyrite, and chalcopyrite geochronology, lupa goldfield, southwestern Tanzania: tracing metallogenic time scales at midcrustal shear zones hosting orogenic Au deposits. Econ. Geol. 108, 1591–1613.
- Leach, D.L., Sangster, D.F., Kelley, K.D., 2005. Sediment-hosted Pb–Zn deposits: a global perspective. Econ. Geol., 100th Anniversary vol., 561–608.
- Lesher, C.M., Stone, W.E., 1996. Exploration geochemistry of komatiites. In: Wyman, D.A. (Ed.), Igneous Trace Element Geochemistry, Applications for Massive Sulfide Exploration. 12. Geological Association of Canada-Mineralogical Association of Canada, pp. 153–204 (Short Course Notes).
- Livingstone, S.J., Cofaigh, C., Stokes, C.R., Hillenbrand, C.-D., Vieli, A., Jamieson, S.S.R., 2012. Antarctic palaeo-ice streams. Earth Sci. Rev. 111, 90–128.
- Makvandi, S., Ghasemzadeh-Barvarz, M., Beaudoin, G., Grunsky, E.C., McClenaghan, M.B., Duchesne, C., Boutroy, E., 2016. Partial least squares-discriminant analysis of trace element compositions of magnetite from various VMS deposit subtypes: application to mineral exploration. Ore Geol. Rev. 78, 388–408.
- Manéglia, N., Beaudoin, G., Simard, M., 2018. Indicator minerals of the Meliadine orogenic gold deposits, Nunavut (Canada), and application to till surveys. Geochem.: Explor., Environ., Anal. https://doi.org/10.1144/geochem2017-036.
- Margold, M., Stokes, C.R., Clark, C.D., 2015. Ice streams in the Laurentide Ice Sheet: identification, characteristics and comparison to modern ice sheets. Earth Sci. Rev. 143, 117–146.
- Margold, M., Stokes, C.R., Clark, C.D., 2018. Reconciling records of ice streaming and ice margin retreat to produce a palaeogeographic reconstruction of the deglaciation of the Laurentide Ice Sheet. Quat. Sci. Rev. 189, 1–30.
- Maslennikov, V.V., Maslennikova, S.P., Large, R.R., Danyushevsky, L.V., 2009. Study of trace element zonation in vent chimneys from the Silurian Yaman-Kasy volcanichosted massive sulfide deposit (Southern Urals, Russia) using laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS). Econ. Geol. 104, 1111–1141.
- McClenaghan, M.B., 2005. Indicator mineral methods in mineral exploration. Geochem.: Explor., Environ., Anal. 5, 233–245.
- McClenaghan, M.B., Kjarsgaard, B.A., 2007. Indicator mineral and surficial geochemical exploration methods for kimberlite in glaciated terrain: examples from Canada. In: Goodfellow, W.D. (Ed.), Mineral Deposits of Canada: A Synthesis of Major Deposittypes, District Metallogeny, The Evolution of Geological Provinces, and Exploration Methods. Geological Association of Canada, Mineral Deposits Division, Special Publication No. 5, pp. 983–1006.
- McClenaghan, M.B., Paulen, R.C., 2018. Application of till mineralogy and geochemistry to mineral exploration. In: Menzies, J., van der Meer, J.J.M. (Eds.), Past Glacial Environments, Second edition. pp. 689–751.
- McClenaghan, M.B., Averill, S.A., Kjarsgaard, I.M., Layton-Matthews, D., Matile, G., 2011. Indicator mineral signatures of magmatic Ni-Cu deposits, Thompson Nickel Belt, central Canada. In: McClenaghan, B., Peuraniemi, V., Lehtonen, M. (Eds.), Indicator Mineral Methods in Mineral Exploration. Workshop in the 25th International Applied Geochemistry Symposium 2011, 22–26 August 2011 Rovaniemi, Finland. Vuorimiesyhdistys, B92-4, (72 pp.).
- McClenaghan, M.B., Plouffe, A., McMartin, I., Campbell, J.E., Spirito, W.A., Paulen, R.C., Garrett, R.G., Hall, G.E.M., 2013. Till sampling and geochemical analytical protocols used by the Geological Survey of Canada. Geochem.: Explor., Environ., Anal. 13, 285–301
- Application of indicator mineral methods to mineral exploration. In: McClenaghan, M.B., Plouffe, A., Layton-Matthews, D. (Eds.), Geological Survey of Canada Open File 7553.
- McClenaghan, M.B., Paulen, R.C., Rice, J.M., Campbell, H.E., Pyne, M.D., 2017a. Gold grains in till samples from the southern Core Zone, Quebec and Newfoundland and Labrador (NTS 23-P and 23-I): potential for undiscovered mineralization. In: Geological Survey of Canada Open File 8222.
- McClenaghan, M.B., Paulen, R.C., Kjarsgaard, I.M., Fortin, R., 2017b. Rare earth element indicator minerals: an example from the Strange Lake deposit, Quebec and Labrador, eastern Canada. In: McClenaghan, M.B., Layton-Matthews, D. (Eds.), Application of Indicator Mineral Methods to Bedrock and Sediments; Geological Survey of Canada Open File 8345.
- McClenaghan, M.B., Paulen, R.C., Oviatt, N.M., 2018. Geometry of indicator mineral and till geochemistry dispersal fans from the Pine Point Mississippi Valley-type Pb-Zn district, Northwest Territories, Canada. J. Geochem. Explor. 190, 69–86.
- Naldrett, A.J., Craig, J.R., Kullerud, G., 1967. The central portion of the Fe-Ni-S system and its bearing on pentlandite exsolution in iron-nickel sulfide ores. Econ. Geol. 62, 826–847.

Neal, H.E., 2000. Iron deposits of the Labrador Trough. Explor. Min. Geol. 9, 113–121. Nikkarinen, M., Kallio, E., Lestinen, P., Ayräs, M., 1984. Mode of occurrence of Cu and Zn

- in till over three mineralized areas in Finland. J. Geochem. Explor. 21, 239–247. Oberthür, T., Melcher, F., 2005. PGE and PGM in the supergene environment: a case study of persistence and redistribution in the main sulphide zone on the Great Dyke, Zimbabwe. In: Mungall, J.E. (Ed.), Exploration for platinum-group elements deposits. Mineralogical Association of Canada Short Course 35. pp. 97–111.
- Öhlander, B., Land, M., Ingri, J., Winderlund, A., 1996. Mobility of rare earth elements during weathering of till in northern Sweden. Appl. Geochem. 11, 93–99.
- Paton, C., Hellstrom, J., Paul, B., Woodhead, J., Hergt, J., 2011. Iolite: freeware for the visualisation and processing of mass spectrometric data. J. Anal. At. Spectrom. 26, 2508–2518.
- Patten, C.G.C., Pitkairn, I.K., Teagle, D.A.H., Harris, M., 2016. Sulphide mineral evolution and metal mobility during alteration of the oceanic crust: insights from ODP Hole 1256D. Geochim. Cosmochim. Acta 193, 132–159.
- Paulen, R.C., Stokes, C.R., Fortin, R., Rice, J.M., Dubé-Loubert, H., McClenaghan, M.B., 2017. Dispersal trains produced by ice streams: an example from Strange Lake, Labrador, Canada. In: Tschirhart, V., Thomas, M.D. (Eds.), Proceedings of Exploration

 Sixth Decennial International Conference on Mineral Exploration, pp. 871–875.
Peuraniemi, V., 1982. Geochemistry of till and mode of occurrence of metals in some moraine types in Finland. In: Geological Survey of Finland, Bulletin. 322 (75 pp.).

- Peuraniemi, V., 1984. Weathering of sulphide minerals in till in some mineralized areas of Finland. In: Prospecting in Areas of Glaciated Terrain. Institution of Mining and Metallurgy, London, pp. 127–135.
- Peuraniemi, V., Eskola, T., 2013. Glacial dispersal and mode of occurrence of metals in till and esker gravel at Kumpuselkä, northern Finland. Geochem.: Explor., Environ., Anal. 13, 195–203.
- Piña, R., Gervilla, F., Barnes, S.-J., Ortega, L., Lunar, R., 2012. Distribution of platinumgroup and chalcophile elements in the Aguablanca Ni–Cu sulfide deposit (SW Spain): evidence from a LA-ICP-MS study. Chem. Geol. 302–303, 61–75.
- Piña, R., Gervilla, F., Barnes, S.-J., Ortega, L., Lunar, R., 2013. Platinum-group elementsbearing pyrite from the Aguablanca Ni-Cu sulphide deposit (SW Spain): a LA-ICP-MS study. Eur. J. Mineral. 25, 241–252.
- Piña, R., Gervilla, F., Barnes, S.-J., Ortega, L., Lunar, R., 2015. Liquid immiscibility between arsenide and sulfide melts: evidence from a LA-ICP-MS study in magmatic deposits at Serranía de Ronda (Spain). Mineral. Deposita 50, 265–279.
- Piña, R., Gervilla, F., Barnes, S.-J., Oberthür, T., Lunar, R., 2016. Platinum-group element concentrations in pyrite from the Main Sulfide Zone of the Great Dyke of Zimbabwe. Mineral. Deposita 51, 853–872.
- Pisiak, L.K., Canil, D., Lacourse, T., Plouffe, A., Ferbey, T., 2017. Magnetite as an indicator mineral in the exploration of porphyry deposits: a case study in till near the Mount Polley Cu-Au deposit, British Columbia, Canada. Econ. Geol. 112, 919–940.
- Plouffe, A., McClenaghan, M.B., Paulen, R.C., McMartin, I., Campbell, J.E., Spirito, W.A., 2013. Processing of glacial sediments for the recovery of indicator minerals: protocols used at the Geological Survey of Canada. Geochem.: Explor., Environ., Anal. 13, 301–316.
- Primmer, S., Bell, T., Batterson, B., 2015. The Role of Ice Dynamics on Drift Dispersal in the Newfoundland Ice Cap: Preliminary Investigations. Current Research. Geological Survey, Report 15-1 Department of Natural Resources, Newfoundland and Labrador, pp. 277–285.
- Reed, M.H., Palandri, J., 2006. Sulfide mineral precipitation from hydrothermal fluids. Rev. Mineral. Geochem. 61, 609–631.
- Reich, M., Deditius, A., Chryssoulis, S., Li, J.-W., Ma, C.-Q., Parada, M.A., Barra, F., Mittermayr, F., 2013. Pyrite as a record of hydrothermal fluid evolution in a porphyry copper system: a SIMS/EMPA trace element study. Geochim. Cosmochim. Acta 104, 42–62.
- Revan, M.K., Genç, Y., Maslennikov, V.V., Maslennikova, S.P., Large, R.R., Danyushevsky, L.V., 2014. Mineralogy and trace-element geochemistry of sulfide minerals in hydrothermal chimneys from the Upper Cretaceous VMS deposits of the eastern Pontide orogenic belt (NE Turkey). Ore Geol. Rev. 63, 129–149.
- Ripley, E.M., Li, C., 2003. Sulfur isotope exchange and metal enrichment in the formation of magmatic Cu-Ni-(PGE) deposits. Econ. Geol. 98, 635–641.
- Robertson, J., Ripley, E.M., Barnes, S.J., Li, C., 2015. Sulfur liberation from country rocks and incorporation in mafic magmas. Econ. Geol. 110, 1111–1123.
- Rosso, K.M., Vaughan, D.J., 2006. Reactivity of sulfide mineral surfaces. Rev. Mineral. Geochem. 61, 557–607.
- Roy, M., Hemming, S.H., Parent, M., 2009. Sediment sources of northern Québec and

Labrador glacial deposits and the northeastern sector of the Laurentide Ice Sheet during ice-rafting events of the last glacial cycle. Quat. Sci. Rev. 28, 3236–3245.

- Rukhlov, A.S., Plouffe, A., Ferbey, T., Mao, M., Spence, J., 2016. Application of traceelement compositions of detrital apatite to explore for porphyry deposits in central British Columbia. In: Geological Fieldwork 2015. British Columbia Geological Survey Paper 2016-1 British Columbia Ministry of Energy and Mines, pp. 145–179.
- Salvi, S., Williams-Jones, A.E., 1995. Zirconosilicate phase relations in the Strange Lake (Lac Brisson) Pluton, Quebec-Labrador, Canada. Am. Mineral. 80, 1031–1040.
- Samalens, N., Barnes, S.-J., Sawyer, E.W., 2017. The role of black shales as a source of sulfur and semimetals in magmatic nickel-copper deposits: example from the Partridge River Intrusion, Duluth Complex, Minnesota, USA. Ore Geol. Rev. 81, 173–187.
- Sarala, P., Peuraniemi, V., 2007. Exploration using till geochemistry and heavy minerals in the ribbed moraine area of southern Finnish Lapland. Geochem.: Explor., Environ., Anal. 7, 195–205.
- Sillitoe, R.H., Thompson, J.F.H., 1998. Intrusion-related vein gold deposits: types, tectono-magmatic settings and difficulties of distinction from orogenic gold deposits. Resour. Geol. 48, 237–250.
- Stokes, C.R., Clark, C.D., 2001. Palaeo-ice streams. Quat. Sci. Rev. 20, 1437-1457.
- Storrar, R.D., Stokes, C.R., Evans, D.J.A., 2013. A map of large Canadian eskers from Landsat satellite imagery. J. Maps 9, 456–473.
- Thomas, H.V., Large, R.R., Bull, S.W., Maslennikov, V., Berry, R.F., Fraser, R., Froud, S., Moye, R., 2011. Pyrite and pyrrhotite textures and composition in sediments, laminated quartz veins, and reefs at Bendigo gold mine, Australia: insights for ore genesis. Econ. Geol. 106, 1–31.
- Tomkins, A.G., Grundy, C., 2009. Upper temperature limits of orogenic gold deposit formation: constraints from the granulite-hosted Griffin's Find deposit, Yilgarn Craton. Econ. Geol. 104, 669–685.
- Tomkins, A.G., Frost, R.B., Pattison, D.R.M., 2006. Arsenopyrite melting during metamorphism of sulfide ore deposits. Can. Mineral. 44, 1045–1062.
- Van der Leeden, J., Bélanger, M., Danis, D., Girard, R., Martelain, J., 1990. Lithotectonic domains in the high-grade terrain east of the Labrador Trough (Quebec). In: Lewry, J.F., Stauffer, M.R. (Eds.), The Early Proterozoic TransHudson Orogen. Geological Association of Canada, Special Paper 37pp. 371–386.
- Vaughan, D.J., 2006. Sulfide mineralogy and geochemistry: introduction and overview. Rev. Mineral. Geochem. 61, 1–5.
- Vaughan, D.J., Craig, J.R., 1978. Mineral Chemistry of Metal Sulfides. Cambridge University Press, Cambridge (512 pp.).
- Veillette, J., Dyke, A.S., Roy, M., 1999. Ice-fow evolution of the Labrador Sector of the Laurentide Ice Sheet: a review, with new evidence from northern Quebec. Quat. Sci. Rev. 18, 993–1019.
- Wardle, R.J., James, D.T., Scott, D.J., Hall, J., 2002. The southeastern Churchill Province: synthesis of a Paleoproterozoic transpressional orogen. Can. J. Earth Sci. 39, 639–663.
- Wickham, H., 2009. ggplot2: Elegant Graphics for Data Analysis. Springer, New York, pp. 213.
- Wilson, S.A., Ridley, W.I., Koenig, A.E., 2002. Development of sulfide calibration standards for the laser ablation inductively-coupled plasma mass spectrometry technique. J. Anal. At. Spectrom. 17, 406–409.