Styles, Textural Evolution, and Sulfur Isotope Systematics of Cu-Rich Sulfides from the Cambrian Whalesback Volcanogenic Massive Sulfide Deposit, Central Newfoundland, Canada

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Abstract

The Whalesback Cu-rich volcanogenic massive sulfide deposit in the Newfoundland Appalachians is a highly deformed deposit found on a steep limb of a closed and boundaried overturned fold. The deposit was intensely deformed at low temperature but medium pressure (>175 MPa) during the accretion of the composite Lusis Bight oceanic tract-Dashwoods terrane onto the Humber margin at ca. 480 Ma.

The ore mineralogy consists of chalcopyrite, pyrrhotite, and pyrite with lesser sphalerite and trace Ag, Bi, and Hg tellurides. Four styles of sulfide mineralization are present: (1) disseminated (5%); (2) vein (50%); (3) breccia (25%); and (4) semimassive to massive (20%). Independent of mineralization style, massive pyrite and pyrrhotite (and some chalcopyrite) are commonly parallel to main S2 schistosity in the deposit, whereas late chalcopyrite piercement veins occur at a high angle to S2. The progressive increase in pressure and temperature produced a remobilization sequence wherein sphalerite was the first sulfide phase to cross the brittle-ductile boundary, followed by pyrrhotite and, finally, chalcopyrite. Maximum temperature was not high enough for the pyrite to cross the brittle-ductile boundary. Instead, pyrite grains were incorporated and transported by pyrrhotite and chalcopyrite during the ductile remobilization events, rounding and fracturing them. Remobilization of the sulfides occurred mainly by plastic flow, but some solution transport and recrystallization is locally observed.

In situ secondary ion mass spectrometry sulfur isotope geochemistry of sulfides yielded values of δ34S ranging from 2.7‰ to 4.7‰ for pyrite, 2.1‰ to 4.0‰ for pyrrhotite, and 1.3‰ to 4.7‰ for chalcopyrite. Sulfur isotope modeling suggests that at least 60% of the sulfur was derived from leaching of igneous rocks (i.e., basalts), with the remainder derived from thermochemical sulfate reduction of seawater sulfate during alteration of the basalts by seawater. At the deposit scale, sulfur isotopes retained their original signature and did not reequilibrate during the secondary deformation and remobilization events.

Introduction

The Cu-RICH Whalesback volcanic massive sulfide (VMS) deposit was discovered by the Betts Cove mining company in 1879 (Martin, 1993; Kean et al., 1995). In 1880, the property was sold to the Newfoundland Consolidated Copper Mining Company, which dug numerous trenches and emplaced a 18-m deep shaft in the hanging wall of the deposit, but no mineralization was encountered and exploration of the property stopped until mining rights were granted to the British Newfoundland Exploration Company (BRINEX) in 1957 (MacLean, 1947; Kean et al., 1995). Between 1960 and 1962, extensive exploration programs were jointly undertaken by BRINEX and the Anglo-American Corporation, successfully delineating a 2.7-million tonne resource at 1.8% Cu. The Whalesback deposit entered production in 1963 and produced 3.8 million tonnes at 1% Cu over its nine-year mine life. In July 1972, the production ceased abruptly due to a major cave-in breaching the surface and low Cu prices (Kean et al., 1995). More recently, an increase in the price of copper triggered a third exploration cycle at the Whalesback and adjacent Little Deer properties by Thundermin Resources Inc. To date, the Whalesback deposit has an indicated resource of 797,000 tonnes at 1.67% Cu (CIM/N143-101; Brown, 2012).

The Whalesback deposit is a type example of an Appalachian stringer-dominated Cyprus-type VMS deposit. Globally, Cyprus-type (also known as mafic-type) VMS deposits are commonly Cu-rich strata-bound to stratiform, syngenetic deposits that form on or near the seafloor by precipitation from hydrothermal fluids at temperatures between 200° and 350°C (e.g., Large, 1977; Franklin et al., 1981, 2005; Lydon, 1984, 1988; Hannington, 2014). The ore mineralogy of Cyprus-type deposits commonly consists of pyrite, chalcopyrite, pyrrhotite, and sphalerite with minor amounts of galena, tetrahedrite, tennantite, arsenopyrite, bornite, and magnetite (e.g., Large, 1977, 1992; Eldridge et al., 1983; Lydon, 1988; Ohmoto, 1996; Franklin et al., 2005). They often have metal zoning patterns that were driven by temperature-dependent metal solubility differences with low-temperature Zn-(Pb) deposition followed by higher-temperature Cu deposition, the latter often leading to zone refining of earlier-formed Zn-(Pb) sulfides (Ohmoto, 1996). The Cu-rich sulfides in Cyprus-type deposits, like those at Whalesback, generally precipitate from hotter fluids, often adjacent to or within the footwall feeder conduit or at the base of the sulfide mound, whereas Zn- and Pb-rich sulfides precipitate from cooler hydrothermal fluids at the top and outer margins of the deposits.

Cyprus-type deposits, like all VMS deposits, generally form within extensional geodynamic regimes, with Cyprus-type
systems generally forming at mid-ocean ridges, back-arc basins, and intraoceanic arc rifts (e.g., Swinden, 1991a; Piercey, 2010, 2011; Hannington, 2014). In ancient environments, the extensional stage of tectonic activity is commonly followed by uplift, basin inversion, compressional deformation, and metamorphism of the sequence hosting the massive sulfide deposits, often due to post-VMS formation accretionary tectonics (e.g., McClay, 1995; Nelson, 1997). During this accretionary activity, rheological differences between sulfides and more competent silicate minerals in the host sequence can lead to significant remobilization of the sulfides during deformation, creating distinct deformation and metamorphic textures such as durchbewegung (Cox, 1987; Marshall and Gilligan, 1985, 1989, 1993). Durchbewegung texture, as defined by Marshall and Gilligan (1989), consists of a mixture of secondary tectonic origin composed of angular to rounded clasts of competent materials (e.g., silicates) within a matrix of predominantly less competent material (e.g., sulfides) where the competent clasts are generally contorted and disoriented.

Despite a sound theoretical understanding of sulfide deformation processes, only a few studies have documented the effects of metamorphism and deformation on sulfide textures and the primary sulfur isotope distribution in VMS deposits (e.g., Bachinski, 1977b; Craig and Vokes, 1993; Cook and Hoefs, 1997; Wagner et al., 2004; Barrie et al., 2010a, b). The purpose of this investigation is to document the mineralogy, textural relationships, and sulfur isotope composition of the major sulfide phases present at the Cyprus-type Whalesback VMS deposit. This deposit is an outstanding natural laboratory to test the effects of deformation on sulfide textures and their potential influence (or lack thereof) on sulfur isotope systematics at low temperature and medium pressure.

Geology

Regional geology

The Whalesback VMS deposit is located 11 km northeast of the community of Springdale and is situated within the Notre Dame subzone of the Dunnage zone of the Newfoundland Appalachians, Canada (Fig. 1). The Dunnage zone is bounded to the west by the Humber zone and to the east by the Gander zone (Williams, 1979; Williams et al., 1988; Hibbard et al., 2004). It represents the deformed vestiges of arcs, back arcs, and ophiolite complexes assembled during the closure of the Cambrian to Ordovician Iapetus Ocean (Fig. 1; Swinden et al., 1989; Swinden, 1991b; Kean et al., 1995; van Staal and Colman-Sadd, 1997; Evans and Kean, 2002; Rogers and van Staal, 2002; Rogers et al., 2006; van Staal, 2007; Zagorevski et
itic basalt with local boninite and minor dioritic to gabbroic composed of lower greenschist facies metamorphosed tholeiitic rocks of the Lushs Bight oceanic tract, (3) the 459 to 477 Ma mafic to ultramafic ophiolitic rocks of the Baie Verte oceanic tract, (4) the 488 to 453 Ma granodioritic to gabbroic Notre Dame magmatic arc, and (5) the 481 to 460 Ma ophiolite-arc-back arc tectonic collage of the Annieopsquotch accretionary tract (Dunning and Krogh, 1985; Elliott et al., 1991; Szybinski, 1995; Cawood et al., 1996; Swinden et al., 1997; Waldron and van Staal, 2001; Zagorevski et al., 2006; van Staal, 2007; van Staal et al., 2007; Skulski et al., 2010; van Staal and Barr, 2012).

The Whalesback VMS deposit occurs within the Lushs Bight oceanic tract sequence. Obduction of the Lushs Bight oceanic tract sequence onto the western margin of the Dashwoods microcontinent occurred during phase 1 of the Taconic orogeny, which was initiated between 500 and 493 Ma (Szybinski, 1995; Swinden et al., 1997; van Staal and Barr, 2012). The composite Lushs Bight oceanic tract-Dashwoods terrane was accreted onto the Humber margin at ca. 480 Ma during phase 2 of the Taconic orogeny, resulting in the closure of the Taconic seaway and producing high-grade metamorphism and polymorphic deformation in large parts of the Notre Dame subzone (van Staal, 2007; van Staal et al., 2007; van Staal and Barr, 2012). Collision of the Notre Dame subzone with the Exploits subzone occurred during phase 3 of the Taconic orogeny (455–450 Ma), initiating the collision of composite Laurentia with Ganderia, in which the peak of deformation occurred during the Salinic orogeny (445–423 Ma; Dunning et al., 1991; van Staal et al., 2003; van Staal, 2007; Zagorevski et al., 2010; van Staal and Barr, 2012). Subsequent collision with the Avalon terrane during the Acadian orogeny (421–390 Ma), with the Meguma terrane during the Neoacadian orogeny (ca. 395–340 Ma), and with Gondwana during the Alleghanian orogeny (ca. 340–260 Ma) led to the formation of the Pangea supercontinent, ending ca. 250 m.y. of convergent tectonism (Hicks et al., 1999; Hatcher, 2002; Keppie et al., 2002; Reynolds et al., 2004; van Staal, 2005; van Staal et al., 2009; van Staal and Barr, 2012).

Geology of the Springdale Peninsula

Following the stratigraphy established by Szybinski (1995), the Lushs Bight oceanic tract is subdivided into three groups, which are, from oldest to youngest, (1) the late Neoproterozoic-Cambrian ribbon-shaped Dashwoods microcontinent, (2) the 510 to 501 Ma mafic to ultramafic ophiolitic rocks of the Lushs Bight oceanic tract, (3) the 459 to 477 Ma mafic to ultramafic ophiolitic rocks of the Baie Verte oceanic tract, (4) the 488 to 453 Ma granodioritic to gabbroic Notre Dame magmatic arc, and (5) the 481 to 460 Ma ophiolite-arc-back arc tectonic collage of the Annieopsquotch accretionary tract (Dunning and Krogh, 1985; Elliott et al., 1991; Szybinski, 1995; Cawood et al., 1996; Swinden et al., 1997; Waldron and van Staal, 2001; Zagorevski et al., 2006; van Staal, 2007; van Staal et al., 2007; Skulski et al., 2010; van Staal and Barr, 2012).

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At Whalesback, mafic dikes emplaced during D1 deformation are affected by NW-directed high-angle reverse faults (Szybinski, 1995). 

**Geology of the Whalesback deposit**

The Whalesback deposit is a Cu-rich (Cyprus-type) VMS deposit hosted in mafic volcanic rocks (Kanehira and Bachinski, 1968). It consists of veins, pods, and disseminated sulfides forming 0.3- to 15-m-wide mineralized lenses hosted within a 720-m-long and 120-m-wide highly chloritized shear zone that strikes 245° N and dips steeply toward the north (Figs. 3, 4). The Whalesback massive sulfide lenses are located in the central and hanging-wall portions of a chlorite shear zone that plunges southwest at about 50° (Fig. 4; Szybinski, 1995).
Cu-RICH SULFIDES FROM THE CAMBRIAN WHALESBACK VMS DEPOSIT, NEWFOUNDLAND, CANADA

Kanehira and Bachinski, 1968). These lenses occur at the site of maximum deformation intensity within the chlorite shear zone(s), suggesting extensive remobilization during post-VMS formation deformation events. With increasing proximity to the main shear zone, pillow basalts from the Lushs Bight Group become increasingly sheared and elongated parallel to the shear planes, primary pyroxenes are replaced by secondary chlorite, epidote alteration decreases in intensity, and quartz aggregates replace albite laths (Kanehira and Bachinski, 1968). Barren, weakly altered, regionally metamorphosed, and deformed gabbro, quartz dacite, plagioclase porphyry, hornblende porphyry, hornblende-plagioclase porphyry, and pyroxene porphyry intrude the chlorite-altered shear zone and the ore lenses (Kanehira and Bachinski, 1968).

The sulfide lenses consist of pyrite, chalcopyrite, pyrrhotite, and sphalerite with minor mackinawite, pentlandite, magnetite, cubanite, galena, and ilmenite (Kanehira and Bachinski, 1968). The sulfides assemblages at the Whalesback deposit are spatially zoned, with pyrrhotite and chalcopyrite being the dominant sulfides in the Eastern lenses, whereas pyrite, sphalerite, and chalcopyrite are the most abundant sulfides in the Western lenses (Fig. 4; West, 1972). Silicate alteration minerals associated with mineralization are predominantly chlorite and quartz with minor muscovite, carbonate, titanite, albite, and epidote (Kanehira and Bachinski, 1968). Alteration of the rocks surrounding the Whalesback deposit within the chlorite-rich shear zone is marked by depletion in Na and Ca and enrichment in Fe, S, and K (Bachinski, 1977a), and is typical of VMS alteration systems (e.g., Franklin et al., 2005; Hannington, 2014, and references therein).

Mineralization

Detailed drill core logging and conventional optical petrography of mineralized intervals of 13 diamond drill cores acquired from the Western lenses and lower portion of the Eastern lenses, recently drilled by Thundermin Resources Inc. (Fig. 4), allowed the subdivision of the sulfide mineralization into four types: (1) disseminated, (2) veinlet, (3) breccia, and (4) semimassive to massive. The sulfide minerals consist of chalcopyrite, pyrrhotite, pyrite, and sphalerite, and coexist with silicate gangue minerals, which include chlorite (40–100%), with subordinate quartz (<50%), calcite (<40%), muscovite (<30%), epidote (<25%), feldspar (<20%), and titanite (<5%). Trace amounts (<0.01%) of 1- to 10-μm-long...
Ag, Bi, and Hg tellurides were identified by scanning electron microscopy within the sulfide matrix.

**Textures and distribution of major sulfide phases**

**Western lenses:** Sulfides in the Western lenses consist of pyrite (~85%) with subordinate sphalerite (~10%) ± chalcopyrite (~5%) hosted in highly chloritized basalts (Fig. 5a, b). Pyrite occurs as euhedral to subrounded grains and is spatially associated with quartz and sphalerite. Sphalerite occurs as small (<1-mm-long) euhedral crystal aggregates that are interstitial to and infill fractures of pyrite grains, and commonly contains microinclusions of chalcopyrite, i.e., chalcopyrite disease (Barton and Bethke, 1987). Greater abundances of sphalerite (up to 20%) are present in the semimassive and massive pyrite intervals. Chalcopyrite occurs as anhedral grains with no visible individual grain boundaries, forming a

![Block model of Cu grade of the Whalesback deposit. Also shown are the pierce points of the drill hole examined during this study.](image)
matrix that crosscuts and fills fractures in pyrite and sphalerite. The chalcopyrite matrix locally contains 0.1- to 3-mm-long subrounded to rounded pyrite grains.

**Eastern lenses:** Sulfides in the deeper portion of the Eastern lenses consist of chalcopyrite (~45%) with lesser pyrrhotite (~40%), pyrite (~15%), and trace sphalerite (<1%). Chalcopyrite and pyrrhotite have no observable internal grain boundaries and form a sulfide matrix that varies between pyrrhotite rich and chalcopyrite rich (Fig. 5c-f). Chalcopyrite crosscuts and separates pyrrhotite-rich intervals into smaller aggregates, isolating them in its matrix (Figs. 5f, 6d, 7a, d). The chalcopyrite-pyrrhotite matrix contains angular to rounded, 0.1- to 3-mm-long fractured pyrite grains and small aggregates of anhedral sphalerite that contain microinclusions.

**Fig. 5.** Photographs and photomicrographs of representative samples from the Western lenses and the Eastern lenses. (A) Pyrite-rich sample from the Western lenses. Sample WB-11-103_172.8m. (B) Reflected light image of a massive pyrite layer from (A). Pyrite occurs as euhedral to subrounded grains and is associated with minor sphalerite and chalcopyrite. (C) Pyrrhotite-rich sample from the Eastern lenses. The pyrrhotite-rich zone is crosscut by chalcopyrite. Sample WB-12-105_468.35m. (D) Reflected light image of the pyrrhotite-rich zone from (C). The pyrrhotite-rich zone contains angular to rounded grains of pyrite and small aggregates of sphalerite and chalcopyrite. (E) Chalcopyrite-rich sample from the Eastern lenses. Sample WB-12-108_657.0m. (F) Reflected light image of the chalcopyrite-rich zone from (E). The chalcopyrite-rich zone contains angular to rounded grains of pyrite and small aggregates of sphalerite and pyrrhotite. Abbreviations are as follows: Ccp = chalcopyrite, Chl = chlorite, Po = pyrrhotite, Py = pyrite, RL = reflected light, Sp = sphalerite.
of chalcopyrite (Fig. 8a; Barton and Bethke, 1987). When sulfides are massive to semimassive the chalcopyrite-pyrrhotite matrix fills fractures in pyrite and sphalerite (Figs. 7b, 8b, c) and is locally intergrown with fibrous chlorite (Fig. 7b).

Types of mineralization

**Disseminated type:** This mineralization type is dominated by pyrrhotite and pyrite with subordinate chalcopyrite and sphalerite, hosted by chlorite-rich basalt (Fig. 6a-c). Disseminated sulfides occur as discrete grains in proximity to vein-type mineralization (see below) and manifest themselves as 1- to 3-mm-long anhedral and asymmetrical grains that are weakly to strongly elongated parallel to sulfide veins. Disseminated sulfides are associated with >95% silicate matrix and account for ~5% of the total sulfide resource at the Whalesback deposit.

**Veinlet type:** This mineralization type consists of chalcopyrite, pyrrhotite, and pyrite veinlets that range from 1 to 10 mm in width. The veinlets have an anastomosing texture and commonly surround the angular to rounded fragments of the silicate gangue, usually dominated by quartz, and constitute 10% to 40% of the host rock (Fig. 6d-f). Pyrrhotite veinlets contain accessory rounded to subrounded pyrite and sphalerite, and are aligned parallel to S2. In contrast, chalcopyrite veinlets are generally monomineralic and crosscut the pyrrhotite veinlets at a high angle. This type of mineralization accounts for ~50% of the total sulfide resource at the Whalesback deposit.

**Breccia type:** This mineralization type consists of chalcopyrite, with minor pyrrhotite and pyrite. It contains 50% to 95% angular to subrounded dark chloritized basalt fragments within a 5% to 50% sulfide matrix (Fig. 6g-i). The breccia-type
mineralization accounts for ~25% of the total sulfide resource at the Whalesback deposit.

Semimassive to massive sulfide: This mineralization type consists of a mixture of chalcopyrite and subordinate pyrite and pyrrhotite in the Eastern lenses and of a mixture of pyrite and subordinate sphalerite and chalcopyrite in the Western lenses (Fig. 7a-f). Small, 1- to 5-mm-long, subrounded to flattened (parallel to S2) fragments of silicate minerals, mainly chlorite-altered wall rock, constitute between 5% and 50% of the rock (Fig. 7a-d). In areas with more intense deformation, the flattened fragments are heterogeneously distributed throughout the sulfide matrix, giving this type of mineralization a durchbewegung texture. Small, 0.2- to 3-mm-wide chalcopyrite veinlets commonly crosscut the semimassive to massive sulfide assemblage (Fig. 7d). This type of mineralization accounts for ~20% of the total sulfide resource at the Whalesback deposit.

**Sulfur Isotopes**

One representative sample of massive sulfide from the Western lenses and five representative samples of massive sulfide (n = 2), semimassive sulfide (n = 1), breccia (n = 1), and veinlets (n = 1) from the Eastern lenses (n = 5) were chosen for in situ sulfur isotope analysis by secondary ion mass spectrometry (SIMS). Sample mounts were prepared from thin section off cuts by embedding ~1 × 1 cm pieces in epoxy in 1-inch-diameter aluminum retaining rings. Samples were polished using standard lapidary procedures, and then sputter-coated with 300 Å of Au to reduce charging under primary ion bombardment. All analyses were performed using a Cameca IMS 4f SIMS instrument at the MAF-IIC Microanalysis Facility at Memorial University.

The δ34S data was collected from pyrite, pyrrhotite, and chalcopyrite using the method described in Toman (2013) and Brueckner et al. (2014). In summary, determinations were performed by bombarding the sample with a primary ion microbeam of 600 to 850 picoamps (pA) of Cs+, accelerated through a nominal 10-kiloelectron volt (keV) potential, and focused into a 5- to 15-µm-diameter spot on the sample. To exclude exotic material in the polished surface from analysis, each spot was first presputtered for 100 s with a 25-µm square raster applied to the beam. Negatively charged sputtered secondary ions were accelerated into the mass spectrometer of the instrument through a nominal potential of 4.5 keV. A combination of mass resolution (Mass Resolving Power approx. 2,975) and energy filtering (sample offset –60 eV with a 40-eV energy window) were used to effectively eliminate isobaric interferences from 16O2– and 33SH–. Signals for 32S–, 34S–, and a background position at 31.67 Dalton (Da) were obtained by cyclical magnetic peak switching (typically, 80 cycles were accumulated for each spot analysis) and detected using an electron multiplier in pulse-counting mode. Standard counting times were: 0.5 s at the background position, 2.0 s on 32S–, and 6.0 s on 34S–. Waiting times of 0.25 s were inserted before each peak counting position to allow for magnet settling. All analyses are reported using the standard δ notation in units of ‰ relative to the international Vienna-Canyon Diablo Troilite (V-CDT) standard.

![Fig. 7. Photographs and photomicrographs of the different massive mineralization types. (A) Semimassive-type mineralization showing subrounded pyrite, pyrrhotite, and chalcopyrite crosscutting a subrounded to rounded pyrite and carbonate layer parallel to S2 foliation. Sample WB-12-104_391.5m. (B) Reflected light image of semimassive sulfides consisting of subrounded to rounded pyrite, pyrrhotite, and chalcopyrite. Also shown is pyrrhotite and chalcopyrite intergrowth with fibrous chlorite. Sample WB-12-104_391.5m. (C) Same as (B) under cross-polarized light. (D) Massive-type pyrrhotite and chalcopyrite crosscut by chalcopyrite veinlets. Sample WB-12-108_670.75m. (E) Reflected light image of a massive sulfide consisting of a pyrrhotite-rich matrix overprinted by chalcopyrite, and fragments of chlorite and quartz. Sample WB-12-108_670.75m. (F) Same as (E) under cross-polarized light. Abbreviations are as follows: Cal = calcite, Ccp = chalcopyrite, Chl = chlorite, Po = pyrrhotite, Py = pyrite, Qz = quartz, RL = reflected light, XP = cross-polarized.](image-url)
Internal precision on individual $\delta^{34}S$ analysis is typically better than $\pm 0.3\%$ (1σ), whereas the overall reproducibility is typically better than $\pm 0.5\%$ (1σ). In-house standards for pyrite (UL9B), pyrrhotite (PoW1), and chalcopyrite (Norilsk) were used to correct for instrumental mass fractionation for each specific mineral phase.

**Results**

Sulfide minerals from the Whalesback deposit display a relatively narrow range of sulfur isotope compositions. Measured $\delta^{34}S$ of 18 pyrite samples range from 2.7 to 6.6‰ with an average of 5.0‰; seven pyrrhotite samples range from 2.1 to 4.0‰ with an average of 3.3‰; and 17 chalcopyrite samples range from 1.3 to 4.7‰ with an average of 2.9‰ (Figs. 9a-f, 10, 11; Table 1). Within individual samples, the internal variations of $\delta^{34}S$ in pyrrhotite and chalcopyrite are generally low (<0.6‰), with a maximum observed variation of 1.0‰ (Fig. 9a-f). Pyrite shows the greatest internal variations, and most of the $\delta^{34}S$ range observed for Whalesback as a whole is present in one sample from the Eastern lenses (e.g., WB-12-106A_561.05m, 4.5–6.4‰; Fig. 9c; Table 1). However, even for pyrite, the internal variation within individual grains is quite restricted in overall magnitude (3.5–5.2‰; Fig 9c).

**Discussion**

**Morphology and metal zoning of the Whalesback deposit**

The Whalesback deposit consists of a tightly folded and boudinaged deposit dominated by chalcopyrite and pyrrhotite in the Eastern lenses and by pyrite in the Western lenses (Fig. 4; Papezik, 1965; West, 1972; Szybinski, 1995). In most genetic and descriptive models for Cyprus-type VMS deposits, there is a well-developed zonation of metals with chalcopyrite and pyrrhotite concentrated at the base and in the core of the deposits, and pyrite and sphalerite concentrated at the top and more distal parts of the deposit (Fig. 12a; e.g., Large, 1977; Franklin et al., 1981, 2005; Lydon, 1984, 1988; Ohmoto, 1996; Hannington, 2014). The metal distribution at Whalesback suggests that the pyrite-rich Western lenses represent the top or distal parts of the Whalesback deposit, whereas the chalcopyrite-pyrrhotite–rich Eastern lenses represent the core and base of the deposit, in accordance with a younging direction toward west. Metal zoning projected above the present-day surface implies that D2 deformation produced a closed overturned fold (Fig. 12c). Overturned folds at this location have not been previously documented and have implications for the longer-term exploration of the deposit. Furthermore, it confirms the Whalesback deposit has been highly deformed, folded, and boudinaged during D2, resulting in a closed overturned anticline (Fig. 12b, c), and creating the characteristic durchbewegung deformation texture observed at hand-specimen scale.

**Sulfide textural evolution during deformation and remobilization**

Durchbewegung-textured rocks are generally hosted within durchbewegung structures (Marshall and Gilligan, 1989), which form from the progression of folding and shearing related to the formation of tight to isoclinal folds. In these structures, the silicate layers surrounding the less competent
Fig. 9. SIMS analysis location and results. (A) Rounded to subrounded pyrite in a chalcopyrite matrix from a massive sulfide layer within the Western lenses. Sample WB-11-102_163.9m. (B) Subrounded pyrite and aggregates of pyrrhotite in a chalcopyrite matrix from a highly deformed veinlet-type sulfide within the Eastern lenses. Sample WB-12-109_578.6m. (C) Rounded to subrounded fractured pyrite in a chalcopyrite matrix from breccia-type mineralization from the Eastern lenses. Sample WB-12-106A_561.05m. (D) Rounded to subrounded pyrite in a pyrrhotite and chalcopyrite matrix from a semi-massive sulfide layer within the Eastern lenses. Pyrrhotite and chalcopyrite are intergrown with fibrous chlorite (in black). Sample WB-12-104_391.5m. (E) Rounded to subrounded pyrite and pyrrhotite matrix crosscut by chalcopyrite pentacement veins within a massive sulfide layer from the Eastern lenses. Sample WB-12-108_670.75m. (F) Subrounded pyrite grains in a quartz-chlorite matrix coexisting with a chalcopyrite-rich area within a massive sulfide layer of the Eastern lenses. Sample WB-12-111_452.5m. Abbreviations and sample location colors are as follows: Ccp = chalcopyrite (red circle), Po = pyrrhotite (blue circle), Py = pyrite (green circle), RL = reflected light.
sulfide layers become disrupted, detached, and incorporated into the sulfides as they deform ductilely. This process results in the creation of detached fold cores and boudins of varying geometry, depending on competency contrast between the silicate and sulfide layers (Marshall and Gilligan, 1989). Relatively late piercement (or ductile) veins are commonly associated with the formation of durchbewegung structures. The veins range in size from a few centimeters to a few meters wide and generally form at high angle to the layer interface and fill in extensional planar fractures (Marshall and Gilligan, 1989).

At Whalesback, the majority of deformation and remobilization occurred during the D2 deformation event, as most of the sulfide-rich zones are parallel to the main S2 schistosity (Papezik, 1965; West, 1972; Szybinski, 1995). Remobilization and deformation of sphalerite, pyrrhotite, and chalcopyrite were due to ductile flow, whereas pyrite deformed brittlely, as demonstrated by its rounded habit and high degree of fracturing (Figs. 7a, b, 8a-d). Sphalerite, pyrrhotite, and chalcopyrite fill the fractures in pyrite, supporting their ductile remobilization. Moreover, pyrrhotite and chalcopyrite remobilization incorporated and transported pyrite grains, rounding and fracturing them (Figs. 8c, d, 11d-f). Based on crosscutting relationships, sphalerite was the first sulfide phase to be

**Fig. 10.** Notched whisker plots for sulfur isotope data for chalcopyrite, pyrrhotite, and pyrite. The width of the notches is proportional to the half-width (HW = [75th percentile – 25th percentile] × 1.57 / √N), where N is the population size). The central portion of the notch is the median and is represented by a line across the whisker box. The whiskers represent the extent of the dataset. Statistically, the chalcopyrite and pyrrhotite represent one population while the pyrite represents a different population.

**Fig. 11.** Spatial distribution of δ34S samples within the Whalesback deposit. Also shown is the range in the δ34S values obtained on pyrite and chalcopyrite mineral separates from the former Whalesback mine (Bachinski, 1977b).
remobilized, followed by pyrrhotite and chalcopyrite, and the latter were followed by the formation of chalcopyrite veins (Fig. 8a-d). The sequence in which the sulfides crossed the brittle-ductile transition zone is indicative of low to medium pressure (>175 MPa) and low-temperature deformation conditions, which were insufficient conditions for pyrite to deform ductilely (Fig. 13; Marshall and Gilligan, 1987). These conditions are consistent with the lower greenschist grade metamorphism recorded elsewhere in the Lushs Bight Group (Kean et al., 1995).

The main transport mechanism of ductile sulfides at Whalesback, during peak metamorphism conditions, is interpreted to have been plastic flow, with minor solution transport and precipitation. Cox (1987) showed that the intergrowth of sulfides with fibrous phyllosilicates in low-grade metamorphic environments, like those observed at Whalesback, indicates that some material remobilization occurred by dissolution, solution transport, and precipitation. However, since the intergrowth of fibrous chlorite with massive pyrrhotite and chalcopyrite is only observed locally (Figs. 7h, i, 8b), it is assumed that plastic flow was likely the dominant transport mechanism.

The occurrence, as well as likely late remobilization, of chalcopyrite in high-angle veins relative to S_2 across the sulfide assemblages is very common and expected in durchbewegung structures (Marshall and Gilligan, 1989), and suggests that the late chalcopyrite veins are a direct consequence of the structural evolution of the durchbewegung structure hosting the Whalesback deposit. Close folding and boudinage of Cu-rich ore (Fig. 4) also support a structural evolution within a durchbewegung structure.

<table>
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<th>Mineralization style</th>
<th>δ^{34}S (‰)</th>
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Note: See Sulfur Isotopes section for analytical details
Influence of deformation on $\delta^{34}$S distribution

Only a few studies have investigated the effect of metamorphism on the primary sulfur isotope composition of sulfide minerals in VMS deposits (e.g., Bachinski, 1977b; Craig and Vokes, 1993; Crowe, 1994; Cook and Hoefs, 1997; Wagner et al., 2004). Most of these studies were undertaken in areas affected by classic Barrovian-style metamorphism, i.e., where the temperature and the pressure gradually increase together, and all concluded, except Crowe (1994), that the original

**Influence of deformation on $\delta^{34}$S distribution**

Fig. 13. Metamorphic pressure-temperature diagram with superposed brittle-ductile behavior boundaries. Mechanical behavior of common base metal sulfides at the brittle-ductile transitions at 5% ductile strain before faulting, and at strain rates on the order of $7.2 \times 10^{-5}$ s$^{-1}$ (diagram modified from Marshall and Gilligan, 1987). The general ductile remobilization sequence at Whalesback is depicted by the arrow and starts in the sphalerite ductile domain, followed by the sphalerite-pyrrhotite ductile domain, and ends in the sphalerite-pyrrhotite-chalcopyrite ductile domain. This sequence is only possible for temperatures below 150°C (gray highlighted area). Abbreviations are as follows: Ccp = chalcopyrite, Gn = galena, Po = pyrrhotite, Py = pyrite, Sp = sphalerite.
sulfur isotope composition of individual sulfide phases was preserved during metamorphism. Bachinski (1977b) investigated the sulfur isotope composition of VMS deposits within the Lushs Bight Group, including the former Whalesback mine, and reached a similar conclusion.

The $\delta^{34}S$ values recorded from all sulfide phases during this study display a narrow range of 1.3 to 6.6‰ and are heterogeneously distributed at the scale of the Whalesback deposit (Figs. 9a-f, 10, 11; Table 1). Pyrrhotite is the most consistent sulfide mineral with a range of only 1.9‰, followed by chalcopyrite with a range of 3.4‰ and pyrite with a range of 3.9‰. Equilibrium temperatures derived from coexisting sulfides phases (chalcopyrite-pyrite, chalcopyrite-pyrrhotite, and pyrrhotite-pyrite) using Kajiwara and Krouse (1971) fractionation factors yield temperatures between 27° and 526°C (Fig. 14a-c), with one additional sample yielding a temperature of 4,605°C, above normal hydrothermal fluids and metamorphism temperature range. In addition, one sample had a $\Delta_{\text{Sr}_{\text{py}-\text{cp}}}$ of ~0.6 that could not be solved using the equilibrium temperature equations of Kajiwara and Krouse (1971), indicating isotopic disequilibrium. Overall, most derived equilibrium temperatures are below the 200°C isotherm, which is lower than the typical Cu-rich VMS deposits formation temperature (250°–350°C; Large, 1977; Franklin et al., 1981, 2005; Lydon, 1984, 1988; Hannington, 2014). These low equilibrium temperatures can be due to a partial to complete reequilibration of the sulfide phases at low temperature during the deformation and associated metamorphism (isotopic equilibrium), the product of primary precipitation of coexisting sulfide phases at different temperature yielding a low “apparent” equilibrium temperature (isotopic disequilibrium), or the result of isotopic heterogeneity of the mineralizing fluids through time induced by sulfur extraction from more than one source (isotopic disequilibrium).

Paragenetic relationships of sulfide phases at Whalesback suggest that the increase in pressure and temperature during $D_2$ produced a remobilization and deformation sequence wherein sphalerite crossed the brittle-ductile transition first, followed by pyrrhotite and chalcopyrite. This remobilization may have led to partial to complete reequilibration of the sulfides. If complete isotopic equilibration was attained, each sulfide phases within the deformation zone should have a homogeneous composition (i.e., all chalcopyrite should have similar $\delta^{34}S$ values) and the derived equilibrium temperatures should be constant throughout the deposit, which is not the case at the Whalesback deposit (Figs. 10, 14a-c). Partial equilibration at hand sample scale is also unlikely as samples containing more than one sulfide pair yield a wide range of equilibrium temperatures (Fig. 14a-c). It is therefore suggested that the sulfides are not in isotopic equilibrium and at least partly retained their original isotopic composition, as previously proposed by Bachinski (1977b). However, given that the isotopic compositions of the ductile phases (pyrrhotite and chalcopyrite) are more homogeneous than the pyrite, it is suggested that some local homogenization may have occurred.

Using the fractionation factors of Ohmoto and Rye (1979), the maximum expected variation in $\delta^{34}S$ for a sulfide pair that precipitated from the same fluids, but at different temperatures (250°–350°C), is 1.4‰ for the pyrite-chalcopyrite pair, 0.3‰ for the pyrrhotite-chalcopyrite pair, and 1.2‰ for the
pyrite-pyrrhotite pair. These variations are not sufficient to explain the $\delta^{34}S$ variation at Whalesback. Therefore, we suggest that variation in primary precipitation temperature of the coexisting sulfide phases is not important at the Whalesback deposit and that the provenance of sulfur is the main controlling factor on the $\delta^{34}S$ distribution.

**Origin of sulfur**

The sulfur in VMS deposits may originate from multiple sources, including the following:

1. Sulfur derived from thermochemical sulfate reduction (TSR) of seawater sulfate via the partial reduction of oxidized seawater to isotopically lighter $H_2S$ during seawater alteration of basement rocks: This process commonly results in sulfur in VMS sulfides that is $-17$ to $25\%e$ lighter than coexisting seawater sulfate (e.g., Sangster, 1968; Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997; Huston, 1999; Seal et al., 2000; Shanks, 2001; Seal, 2006); seawater sulfate itself has varied greatly through geologic time (4–34.5‰; $\delta^{34}S_{Cambrian}$ is $34.5\%e$; Claypool et al., 1980; Canfield, 2004; Kampschulte and Strauss; 2004, Paytan and Gray, 2012).

2. Sulfur derived from anoxic seawater with a sulfide isotopic composition 15 to $60\%e$ lighter than sulfate derived from oxidized seawater (–25.5 to +19.5 ‰ for Cambrian anoxic seawater; Goldhaber and Kaplan, 1975), and wherein the magnitude of the fractionation is related to sedimentation rates: Low sedimentation rates are associated with slower rate of sulfate reduction and larger fractionation, and high sedimentation rates are associated with faster rates of sulfate reduction and small fractionation. Sediments in anoxic environment are generally associated with elevated concentration of organic matter and sulfide minerals in which pyrite commonly displays a framboidal texture (Goldhaber and Kaplan, 1975).

3. Sulfide sulfur sourced by direct leaching from the basaltic rocks of the Lushs Bight Group overlying the mineralized stratigraphic horizons: In the case of submarine mafic volcano-hosted Cu-rich deposits, like Whalesback, the $\delta^{34}S_{sulfides}$ of basalt ranges from 0.3 to 0.7‰ (Torsander, 1992).

4. Magmatic sulfur with $\delta^{34}S_{reservoir} = 0 \pm 2\%e$ (Hoef, 2009); at temperatures above 300°C the dominant sulfur species is $SO_2$, but at lower temperatures the magmatic $SO_2$ disproportionates rapidly to form $H_2S$ and $H_2SO_3$. This latter reaction is accompanied by a large isotopic fractionation that produces negative $\delta^{34}S_{H_2S}$ values, often resulting in sulfides that have negative $\delta^{34}S$ (Rye, 1993; Huston et al., 2011).

5. Bacteriogenic reduction of sulfate in marine or pore waters: Precipitation of sulfide by bacteria is associated with a strong fractionation, ranging from 24 to 71‰, and averaging 51 ± 10‰e, depending on the sulfate availability of the system (Ohmoto and Rye, 1979; Canfield and Teske, 1996; Ohmoto and Goldhaber, 1997; Canfield, 2001; Seal, 2006). In the case of the Cambrian Whalesback deposit, $\delta^{34}S$ values ranging between –36.5 and $+10.5\%e$ with an average of $-16.5 \pm 10\%e$ are expected for sulfide minerals derived from biogenic reduction of seawater sulfate during the Cambrian (Kampschulte and Strauss, 2004).

The absence of negative $\delta^{34}S$ values, pyrite framboids, and the narrow positive range of $\delta^{34}S$ obtained from the Whalesback deposit during this study (Table 1) suggest that biogenic sulfur input was insignificant. Furthermore, a significant component of magmatic sulfur is also highly unlikely, given these restricted positive $\delta^{34}S$ values (i.e., no evidence of sulfur disproportionation; Rye, 1993; Huston et al., 2011) and the absence of other features that are common to VMS deposits formed from magmatic fluid input, i.e., Au-Ag enrichment, intermediate to high sulfidation ore mineral assemblages, and aluminous alteration assemblages (e.g., Sillitoe et al., 1996; Hanington et al., 1999; Dubé et al., 2007). Anoxic sulfur is also an unlikely sulfur source as carbonaceous and sulfur-rich sediments are rare in the vicinity of the Whaleback deposit. Moreover, the basals of the Lushs Bight Group are the Whalesback deposit contain hematitized pillow lava with common to extensive magnetite-bearing red cherts (Kean et al., 1995), consistent with deposition in oxidized seawater.

To evaluate the relative roles of leaching from igneous host rocks and TSR, modeling was undertaken using the method described in Brueckner et al. (2014) using the equations outlined in Ohmoto and Rye (1979), Ohmoto and Goldhaber (1997), and Seal (2006). Thermochemical sulfate reduction of seawater sulfate was modeled on the basis of three assumptions: (1) Cambrian seawater sulfate had a $\delta^{34}S = 34.5\%e$ (Claypool et al., 1980; Canfield, 2004; Kampschulte and Strauss; 2004, Paytan and Gray, 2012); (2) TSR occurred at ~300°C (or higher), based on the observation of chalcopyrite-pyrrhotite assemblages in the sulfides; and (3) the system was open and was continuously replenished as the available heavy sulfate ($SO_4$) was reduced to lighter $H_2S$, producing $H_2S$ with $\delta^{34}S_{H_2S(300\degree C)} = 12.7\%e$ during TSR (i.e., assuming that $f = 1$, where $f$ is the fraction of $SO_4$ remaining in solution at site of reduction reaction). The fluid was then cooled from 300°C and various sulfide phases were precipitated, with most minerals precipitated at temperatures >250°C to 300°C, given the chalcopyrite-rich assemblages at the Whalesback deposit. Figure 15 illustrates the sulfide isootope composition as a function of cooling for the interpreted temperatures of deposition for sulfide solely derived from TSR. The model shows that TSR alone cannot generate the $\delta^{34}S$ range determined for the sulfide phases at the Whalesback deposit. Even at the modeled temperature of 250°C, TSR-derived sulfides would still have $\delta^{34}S$ substantially heavier than the range observed at Whalesback. This implies that sulfur from leaching of igneous rocks must be an important contributor to the overall sulfur budget of the deposit.

Binary mixing proportions of sulfur sourced from mafic host rock leached $H_2S$ at 300°C ($\delta^{34}Sp = -1.2\%e$, $\delta^{34}Sp = 0.3\%e$, $\delta^{34}S_{leached} = -0.2\%e$) and sulfur derived from TSR at 300°C can be calculated using the following equation:

$$\delta^{34}S_{sample} = X \delta^{34}S_{TSR} + (1-X)\delta^{34}S_{leached}$$

(1)

where $\delta^{34}S$ is the measured sulfur isotope signature of the sample, $\delta^{34}S_{TSR}$ is $\delta^{34}S$ derived from TSR calculation at 300°C for a given mineral phase, $\delta^{34}S_{leached}$ is $\delta^{34}S$ of igneous-derived sulfur in a given mineral phase at 300°C, and $X$ is a proportionality factor that is 1 when 100% of the sulfur is from TSR and 0 when there is 0% TSR (i.e., 100% leaching of igneous sulfur). The results show that sulfur derived from TSR at 300°C accounts for a maximum of ~40% of the sulfur budget of the Whalesback deposit, whereas between 60% and 90% has been derived from leaching from the surrounding footwall rocks (Fig. 16a-c). This result is expected given the
Fig. 15. Sulfur isotope composition for sulfide derived solely from thermochemical sulfate reduction of seawater sulfate at 250°, 300°, and 350°C. (A) Pyrite, (B) pyrrhotite, and (C) chalcopyrite. Also shown is the range in sulfur isotope composition of sulfide phases observed during this study.

Fig. 16. Modeled sulfide isotopic composition of (A) chalcopyrite, (B) pyrrhotite, and (C) pyrite deposited at 250°, 300°, and 350°C in relation to the proportion of TSR and igneous sulfide required to produce them. The range of TSR proportion required to produce the observed sulfide isotopic composition at Whalesback is highlighted in the shaded area. Also shown is the range in sulfur isotope composition of sulfide phases observed during this study.
high-temperature nature of the mineralization at the Whalesback deposit (i.e., Cu-rich assemblages) and the relatively restricted range of measured δ34S values, further arguing that leaching from nearby footwall rocks was the most important source for sulfur in the Whalesback deposit. Because the Lushs Bight Group is 3 to 4 km in thickness (Kean et al., 1995), there is no restriction for the depth at which the sulfur and metals present at Whalesback were extracted. However, given that copper solubility is low below 225°C and greatly increases with increasing temperature (Hannington, 2014), it is suggested that the sulfur and the metals were leached from the lower portion of the mafic Lushs Bight Group. This single mafic source for the extraction of the metals is also reflected in the simple mineralogy (chalcopyrite, pyrite, pyrrhotite, and subordinate sphalerite) encountered at the Whalesback deposit.

Conclusions

The Whalesback deposit is a Cu-rich VMS deposit hosted within a closed, boudinaged, and overturned fold located within a dextral shearing structure. Intense deformation of the Whalesback deposit occurred at low temperature and medium pressure (>175 MPa) during the accretion of the Lushs Bight oceanic tract-Dashwoods composite terrane onto the Humber margin at ca. 480 Ma (D2). The increase in pressure and temperature produced a remobilization sequence where sphalerite was the first sulfide phase to cross the brittle-ductile transition, followed by pyrrhotite and, subsequently, by chalcopyrite. The maximum metamorphic temperature was not high enough for pyrite to deform ductily. Instead, pyrite grains were incorporated and transported during the ductile remobilization of less competent sulfide phases (pyrrhotite and chalcopyrite). This led to the rounding and fracturing of the pyrite grains. Remobilization of sulfides occurred primarily by plastic flow, but some evidence of dissolution, solution transport, and precipitation was observed locally.

Sulfur isotopes retained their original signatures and did not reequilibrate during the remobilization events. The dominant source of sulfur was determined to be from sulfides leached from surrounding basals, with a lesser component derived from thermochemical sulfate reduction of seawater sulfate during alteration of the basals.

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