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

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Abstract

21

22   The Whalesback Cu-rich VMS deposit in the Newfoundland Appalachians is a

23 highly deformed deposit found on a steep limb of a closed and boudinaged overturned

24 fold. The deposit was intensely deformed at low temperature but medium pressure (>175

25 MPa) during the accretion of the composite Lushs Bight Oceanic Tract-Dashwoods

26 terrane onto the Humber margin at ca. 480 Ma.

27   The ore mineralogy consists of chalcopyrite, pyrrhotite and pyrite with lesser

28 sphalerite and trace Ag-, Bi- and Hg-tellurides. Four styles of sulfide mineralization are

29 present: 1) disseminated (5%); 2) vein (50%); 3) breccia (25%); and 4) semi-massive to

30 massive (20%). Independent of mineralization style, massive pyrite and pyrrhotite (and

31 some chalcopyrite) are commonly parallel to main S_2 schistosity in the deposit, whereas

32 late chalcopyrite piercement veins occur at a high angle to S_2. The progressive increase in

33 pressure and temperature produced a remobilization sequence wherein sphalerite was the

34 first sulfide phase to cross the brittle-ductile boundary, followed by pyrrhotite and finally

35 chalcopyrite. Maximum temperature was not high enough for the pyrite to cross the

36 brittle-ductile boundary. Instead, pyrite grains were incorporated and transported by

37 pyrrhotite and chalcopyrite during the ductile remobilization events, rounding and

38 fracturing them. Remobilization of the sulfides occurred mainly by plastic flow, but some

39 solution transport and re-precipitation is locally observed.

40   *In situ* secondary ion mass spectrometry (SIMS) sulfur isotopes geochemistry of

41 sulfides yielded values of $\delta^{34}S$ ranging from +2.7‰ to 4.7‰ for pyrite, +2.1‰ to 4.0‰

42 for pyrrhotite and +1.3‰ to 4.7‰ for chalcopyrite. Sulfur isotopic modeling suggests

43 that at least 60% of the sulfur was derived from leaching of igneous rocks (i.e., basalts),

44 with the reminder derived from thermochemical sulfate reduction (TSR) of seawater

45 sulfate during alteration of the basalts by seawater. At the deposit scale, sulfur isotopes

46 retained their original signature and did not re-equilibrate during the secondary

47 deformation and remobilization events.

Introduction

49   The Cu-rich Whalesback volcanic massive sulfide (VMS) deposit was discovered

50 by the Betts Cove mining company in 1879 (Martin, 1983; Kean et al., 1995). In 1880,

51 the property was sold to the Newfoundland Consolidated Copper Mining Company who

52 dug numerous trenches and emplaced a 18m deep shaft in the hanging wall of the deposit,

53 but no mineralization was encountered and exploration of the property stopped until

54 mining rights were granted to the British Newfoundland Exploration Company

55 (BRINEX) in 1957 (MacLean, 1947; Kean et al., 1995). Between 1960-1962, extensive

56 exploration programs were jointly undertaken by BRINEX and the Anglo-American

57 Corporation, successfully delineating a 2.7 million tonnes resource at 1.8% Cu. The

58 Whalesback deposit entered production in 1963 and produce 3.8 million tonnes at 1% Cu

59 over its 9 year mine life. In July 1972, the production ceased abruptly due a major cave-in

60 breaching the surface and low Cu prices (Kean et al., 1995). More recently, an increase in

61 the price of copper triggered a third exploration cycle at the Whalesback and adjacent

62 Little Deer properties by Thundermin Resources Inc. To date, the Whalesback deposit

63 has an indicated resource of 797,000 tonnes at 1.67% Cu (CIM/NI43-101; Brown, 2012)

64   The Whalesback deposit is a type example of an Appalachian stringer-dominated

65 Cyprus-type VMS deposit. Globally, Cyprus-type (also known as mafic-type) VMS

66 deposits are commonly Cu-rich stratabound to stratiform, syngenetic deposits that form

67 on or near the seafloor by precipitation from hydrothermal fluids at temperatures between

68 200-350°C (e.g., Large, 1977; Franklin et al., 1981, 2005; Lydon, 1984, 1988;

69 Hannington, 2014). The ore mineralogy of Cyprus-type commonly consists of pyrite,

70 chalcopyrite, pyrrhotite and sphalerite with minor amounts of galena, tetrahedrite,

71 tennantite, arsenopyrite, bornite, and magnetite (e.g., Large, 1977, 1992; Eldridge et al.,

72 1983; Lyndon, 1988; Ohmoto, 1996; Franklin et al., 2005). They often have metal zoning

73 patterns that were driven by temperature-dependent metal solubility differences with low

74 temperature Zn-(Pb) deposition followed by higher temperature Cu deposition; the latter

75 often leading to zone refining of earlier formed Zn-(Pb) sulfides (Ohmoto, 1996). The

76 Cu-rich sulfides in Cyprus-type deposits, and like those at Whalesback, generally

77 precipitate from hotter fluids often adjacent or within the footwall feeder conduit or at the

78 base of the sulfide mound), whereas Zn- and Pb-rich sulfides precipitate from cooler

79 hydrothermal fluids at the top and outer margins of the deposits.

80　　　　Cyprus-type deposits, like all VMS deposits generally form within extensional

81 geodynamic regimes, with Cyprus-type systems generally forming at mid-ocean ridges,

82 back-arc basins, and intra-oceanic arc rifts (e.g., Swinden, 1991a; Piercey, 2010, 2011;

83 Hannington, 2014). In ancient environments, the extensional stage of tectonic activity is

84 commonly followed by uplift, basin inversion, compressional deformation, and

85 metamorphism of the sequence hosting the massive sulfide deposits often due to post-

86 VMS formation accretionary tectonics (e.g., McClay, 1995; Nelson, 1997). During this

87 accretionary activity, rheological differences between sulfides and more competent

88 silicate minerals in the host sequence can lead to significant remobilization of the sulfides

89 during deformation, creating distinct deformation and metamorphic textures such as

90 durchbewegung (Cox, 1987; Marshall and Gilligan, 1987, 1989, 1993). Durchbewegung

91 texture, as defined by Marshall and Gilligan (1989), consists of a mixture of secondary

92 tectonic origin composed of angular to rounded clasts of competent materials (e.g.,

93 silicates) within a matrix of predominantly less competent material (e.g., sulfides) where

94 the competent clasts are generally contorted and disoriented.

95   Despite a sound theoretical understanding of sulfide deformation processes, only

96 a few studies have documented the effects of metamorphism and deformation on sulfide

97 textures, and the primary sulfur isotope distribution in VMS deposits (e.g. Bachinski,

98 1977b; Craig and Vokes, 1993; Cook and Hoefs, 1997; Wagner et al., 2004; Barrie et al.,

99 2010a; Barrie et al., 2010b). The purpose of this investigation is to document the

100 mineralogy, textural relationships and sulfur isotope composition of the major sulfide

101 phases present at the Cyprus-type Whalesback VMS deposit. This deposit is an

102 outstanding natural laboratory to test the effects of deformation on sulfide textures and

103 their potential influence (or lack thereof) on sulfur isotope systematics at low temperature

104 and medium pressure.

105   **Geology**

106 *Regional Geology*

107   The Whalesback VMS deposit is located 11km northeast of the community of

108 Springdale and is situated within the Notre Dame subzone of the Dunnage Zone of the

109 Newfoundland Appalachians, Canada (Fig. 1). The Dunnage Zone is bounded to the west

110   by the Humber Zone and to the east by the Gander Zone (Williams, 1979; Williams et al.,

111   1988; Hibbard et al., 2004). It represents the deformed vestiges of arcs, back arcs, and

112   ophiolite complexes assembled during the closure of the Cambrian to Ordovician Iapetus

113   Ocean (Fig. 1; Swinden et al., 1989; Swinden, 1991b; Kean et al., 1995; van Staal and

114   Colman-Sadd, 1997; Evans and Kean, 2002; Rogers and van Staal, 2002; Rogers et al.,

115   2006; van Staal, 2007; Zagorevski et al., 2010). The Dunnage Zone is divided into the

116   western Notre Dame subzone, which formed near the Laurentian equatorial margin, and

117   the eastern Exploits subzone, which formed on the edge of Gondwana and related

118   microcontinents at mid- to high-southerly latitudes (e.g. Zagorevski et al., 2006; van Staal

119   et al., 2007; Cocks and Torsvik, 2002). The Notre Dame subzone is subdivided into five

120   zones which are, from oldest to youngest: 1) the Late Neoproterozoic–Cambrian ribbon-

121   shaped Dashwoods microcontinent; 2) the 510-501 Ma mafic to ultramafic ophiolitic

122   rocks of the Lushs Bight oceanic tract (LBOT); 3) the 489-477 Ma mafic to ultramafic

123   ophiolitic rocks of the Baie Verte oceanic tract (BVOT); 4) the 488-453 Ma granodioritic

124   to gabbroic Notre Dame magmatic arc; and 5) the 481-460 Ma ophiolite-arc-back arc

125   tectonic collage of the Annieopsquotch accretionary tract (AAT) (Dunning and Krogh,

126   1985; Elliot et al., 1991; Szybinski, 1995; Cawood et al., 1996; Swinden et al., 1997;

127   Waldron and van Staal, 2001; Zagorevski et al., 2006; van Staal, 2007; van Staal et al.,

128   2007; Skulski et al., 2010; van Staal and Barr, 2012).

129   The Whalesback VMS deposit occurs within the LBOT sequence. Obduction of

130   the LBOT sequence onto the western margin of the Dashwoods microcontinent occurred

131   during phase 1 of the Taconic orogeny, which was initiated between 500 and 493 Ma

132   (Szybinski, 1995; Swinden et al., 1997; van Staal and Barr, 2012). The composite LBOT-

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133 Dashwoods terrane was accreted onto the Humber margin at ca. 480 Ma during phase 2

134 of the Taconic orogeny, resulting in the closure of the Taconic seaway and producing

135 high-grade metamorphism and polyphase deformation in large parts of the Notre Dame

136 subzone (van Staal, 2007; van Staal et al., 2007; van Staal and Barr, 2012). Collision of

137 the Notre Dame subzone with the Exploits subzone occurred during phase 3 of the

138 Taconic orogeny (455–450 Ma), initiating the collision of composite Laurentia with

139 Ganderia, in which the peak of deformation occurred during the Salinic orogeny (445–

140 423 Ma; Dunning et al., 1991; van Staal et al., 2003; van Staal, 2007; van Staal and Barr,

141 2012; Zagorevski et al., 2010). Subsequent collision with the Avalon terrane during the

142 Acadian orogeny (421-390 Ma), with the Meguma terrane during the Neoacadian

143 orogeny (ca. 395-340 Ma), and with Gondwana during the Alleghanian orogeny (ca. 340-

144 260 Ma) lead to the formation of the Pangea supercontinent, ending ca. 250 m.y. of

145 convergent tectonism (Hicks et al., 1999; Hatcher, 2002; Keppie et al., 2002; Reynolds et

146 al., 2004; van Staal, 2005; van Staal et al., 2009; van Staal and Barr, 2012).

147

148 *Geology of the Springdale Peninsula*

149   Following the stratigraphy established by Szybinski (1995), the LBOT is

150 subdivided into three groups that are, from oldest to youngest: 1) the mafic Lushs Bight

151 Group, 2) the dominantly mafic volcanic with minor felsic volcanic Western Arm Group,

152 and 3) the bimodal volcanic Cutwell Group (Fig. 2; Marten, 1971a, 1971b; Kean, 1973;

153 Kean and Strong, 1975; Kean et al., 1995; Szybinski, 1995). The Whalesback deposit

154 occurs in the Lushs Bight Group (Figs. 2, 3). The Lushs Bight Group is 3-4 km thick and

155 is predominantly composed of lower greenschist facies metamorphosed tholeiitic basalt

156 with local boninite and minor dioritic to gabbroic sheeted intrusions. Rare felsic

157 pyroclastic rocks, jasper and magnetite-bearing chert are also present. The basalts occur

158 as pillowed or massive flows, and can locally be variolitic. In most cases, the variolitic

159 basalts are of boninitic affinity and have quartz-filled amygdules. Areas of VMS

160 mineralization tend to be spatially associated with areas of abundant boninites and felsic

161 pyroclastic rocks (Kean et al., 1995; Szybinski, 1995). The Lushs Bight Group is crosscut

162 by several generations of intrusive rocks, which include gabbro, quartz dacite, plagioclase

163 porphyry, hornblende porphyry, hornblende-plagioclase porphyry, and pyroxene

164 porphyry (Kanehira and Bachinski, 1968; Szybinski, 1995). The Lushs Bight Group is

165 characterized by strong epidote alteration of the basalts, with a general decrease in

166 epidote abundance towards the stratigraphic top of the group, and by locally extensive

167 quartz ± carbonate veins (Kean et al., 1995).

168   The Lushs Bight Group was informally subdivided by Papezik and Fleming

169 (1967) and Fleming (1970), on the basis of alteration, into a spilitic and chlorite altered

170 "St. Patrick-type" and an epidote altered "Whalesback-type". More recently, Szybinski

171 (1995) subdivided the Lushs Bight Group into the basal Indian Head complex dominated

172 by sheeted dikes and the overlying Little Bay Formation dominated by basalt.

173

174 *Structural geology*

175   Szybinski (1995) recorded five stages of deformation in the Notre Dame Bay

176 region. The first phase of deformation (D_1) is a non-penetrative deformation linked with

177 the mylonitization of pre-existing chlorite-rich syn-volcanic faults that were the feeder

178 conduits to VMS mineralization, creating an S_1 foliation. During D_1, these chlorite-rich

179　shear zones accommodated a component of dextral trans-current shearing (Szybinski,

180　1995) related to dextral oblique convergence between the LBOT and Dashwoods micro-

181　continent (Dewey, 2002), and was synchronous with phase 1 of the Taconic orogeny (van

182　Staal, 2007; van Staal and Barr, 2012). The second phase of deformation (D_2) produced a

183　regional penetrative S_2 foliation and tight to isoclinal upright folds with NE-NNE axial

184　planes throughout the Lushs Bight Group. Szybinski (1995) concluded that D_2 was

185　synchronous with the emplacement of the Colchester and Coopers Cove plutons (465 ± 2

186　Ma), and coincident with phase 2 of the Taconic orogeny. At Whalesback, D_2 produced a

187　steep S_2 schistosity trending ~060°N and dipping toward the southeast (Papezik, 1965;

188　West, 1972). The third phase of deformation (D_3) is also a significant regional event that

189　produced many large NE-trending folds and numerous brittle-ductile NE-striking thrust

190　faults related to the emplacement of an alpine-style nappe in the Notre Dame Bay region

191　(Szybinski, 1995). At Whalesback, D_3 resulted in the creation of an open fold with an

192　axial trace trending ~025°N and dipping steeply to the north, deforming the chlorite

193　schists into a major dextral drag fold (West, 1972). The fourth phase of deformation (D_4)

194　is locally evidenced in the Lushs Bight Group as ENE to SE plunging antiforms, folds

195　and thrusts, and is not present near the Whalesback deposit. D_4 reaches its maximum

196　intensity in the vicinity of the Lobster Cove Fault, located approximately 10 km southeast

197　of the study area. The fifth phase of deformation (D_5) represents the third major regional

198　event in the Lushs Bight Group and resulted in the creation of NE-SW trending folds

199　verging to the NW, NNW trending high-angle thrust faults and foreland propagating

200　duplexes of various sizes (Szybinski, 1995). At Whalesback, mafic dykes emplaced

201　during D1 deformation are affected by NW directed high angle reverse faults (Szybinski,

202   1995).

203

204   *Geology of the Whalesback Deposit*

205   The Whalesback deposit is a Cu-rich (Cyprus-type) VMS deposit hosted in mafic

206   volcanic rocks (Kanehira and Bachinski, 1968). It consists of veins, pods, and

207   disseminated sulfides forming 0.3-15m wide mineralized lenses hosted within a 720m

208   long and 120m wide highly chloritized shear zone that strikes 245˚N and dips steeply

209   towards the north (Figs. 3, 4). The Whalesback massive sulfide lenses are located in the

210   central and hanging-wall portions of a chlorite shear zone that plunges southwest at about

211   50˚ (Fig. 4; Kanehira and Bachinski, 1968). These lenses occur at the site of maximum

212   deformation intensity within the chlorite shear zone(s), suggesting extensive

213   remobilization during post VMS-formation deformation events. With increasing

214   proximity to the main shear zone, pillow basalts from the Lushs Bight Group become

215   increasingly sheared and elongated parallel to the shear planes, primary pyroxenes are

216   replaced by secondary chlorite, epidote alteration decreases in intensity, and quartz

217   aggregates replace albite laths (Kanehira and Bachinski, 1968). Barren, weakly altered,

218   regionally metamorphosed, and deformed gabbro, quartz dacite, plagioclase porphyry,

219   hornblende porphyry, hornblende-plagioclase porphyry, and pyroxene porphyry intrude

220   the chlorite altered shear zone and the ore lenses (Kanehira and Bachinski, 1968).

221   The sulfide lenses consist of pyrite, chalcopyrite, pyrrhotite and sphalerite with

222   minor mackinawite, pentlandite, magnetite, cubanite, galena, and ilmenite (Kanehira and

223   Bachinski, 1968). The sulfides assemblages at the Whalesback deposit are spatially zoned

224   with pyrrhotite and chalcopyrite being the dominant sulfides in the Eastern lenses,

225 whereas pyrite, sphalerite and chalcopyrite are the most abundant sulfides in the Western

226 lenses (Fig. 4; West, 1972). Silicate alteration minerals associated with mineralization are

227 predominantly chlorite and quartz with minor muscovite, carbonate, titanite, albite, and

228 epidote (Kanehira and Bachinski, 1968). Alteration of the rocks surrounding the

229 Whalesback deposit within the chlorite-rich shear zone is marked by depletion of Na and

230 Ca and enrichment of Fe, S and K (Bachinski, 1977a), and is typical of VMS alteration

231 systems (e.g. Franklin et al., 2005; Hannington, 2014 and references therein).

Mineralization

233 Detailed drill core logging and conventional optical petrography of mineralized

234 intervals of 13 diamond drill cores acquired from the Western lenses and lower portion of

235 the Eastern lenses, recently drilled by Thundermin Resources Inc., (Fig. 4) allowed the

236 subdivision of the sulfide mineralization into four types: 1) disseminated; 2) veinlet; 3)

237 breccia; and 4) semi-massive to massive. The sulfide minerals consist of chalcopyrite,

238 pyrrhotite, pyrite and sphalerite, and coexist with silicate gangue minerals, which include

239 chlorite (40-100%) with subordinate quartz (<50%), calcite (<40%), muscovite (<30%),

240 epidote (<25%), feldspar (<20%) and titanite (<5%). Trace amounts (<0.01%) of 1-10µm

241 long Ag, Bi and Hg tellurides were identified by scanning electron microscopy within the

242 sulfide matrix.

243

244 *Textures and Distribution of Major Sulfide Phases*

245 *Western lenses.* Sulfides in the Western lenses consist of pyrite (~85%) with

246 subordinate sphalerite (~10%) ± chalcopyrite (~5%) hosted in highly chloritized basalts

247 (Fig. 5ab). Pyrite occurs as euhedral to subrounded grains and is spatially associated with

248 quartz and sphalerite. Sphalerite occurs as small (<1 mm long) euhedral crystal

249 aggregates that are interstitial to and infill fractures of pyrite grains, and commonly

250 contains micro-inclusions of chalcopyrite, i.e., chalcopyrite disease (Barton and Bethke,

251 1987). Greater abundances of sphalerite (up to 20%) are present in the semi-massive and

252 massive pyrite intervals. Chalcopyrite occurs as anhedral grains with no visible individual

253 grain boundaries, forming a matrix that crosscuts and fills fractures in pyrite and

254 sphalerite. The chalcopyrite matrix locally contains 0.1-3 mm long subrounded to

255 rounded pyrite grains.

256   *Eastern lenses*. Sulfides in the deeper portion of the Eastern lenses consist of

257 chalcopyrite (~45%) with lesser pyrrhotite (~40%), pyrite (~15%), and trace sphalerite

258 (<1%). Chalcopyrite and pyrrhotite have no observable internal grain boundaries and

259 form a sulfide matrix that varies between pyrrhotite-rich and chalcopyrite-rich (Fig.

260 5cdef). Chalcopyrite crosscuts and separates pyrrhotite-rich intervals into smaller

261 aggregates, isolating them in its matrix (Figs. 5f, 6d, and 7ad). The chalcopyrite-

262 pyrrhotite matrix contains angular to rounded, 0.1-3 mm long fractured pyrite grains and

263 small aggregates of anhedral sphalerite that contain micro-inclusions of chalcopyrite, i.e.,

264 chalcopyrite disease (Fig. 8a; Barton and Bethke, 1987). When sulfides are massive to

265 semi-massive the chalcopyrite-pyrrhotite matrix fills fractures in pyrite and sphalerite

266 (Figs. 7b, 8bc) and is locally intergrown with fibrous chlorite (Fig. 7b).

267

268 *Types of mineralization*

12

269   *Disseminated-type*. This mineralization type is dominated by pyrrhotite and pyrite

270   with subordinate chalcopyrite and sphalerite, hosted by chlorite-rich basalt (Fig. 6a-c).

271   Disseminated sulfides occur as discrete grains in proximity to vein-type mineralization

272   (see below) and manifests itself as 1-3 mm long anhedral and asymmetrical grains that

273   are weakly to strongly elongated parallel to sulfide veins. Disseminated sulfides are

274   associated with >95% silicate matrix and account for ~5% of the total sulfide resource at

275   the Whalesback deposit.

276   *Veinlet-type.* This mineralization type consists of chalcopyrite, pyrrhotite and

277   pyrite veinlets that range from 1 to 10 mm in width. The veinlets have an anastomosing

278   texture and commonly surround the angular to rounded fragments of the silicate gangue,

279   usually dominated by quartz, and constitute 10-40% of the host rock (Fig. 6d-f).

280   Pyrrhotite veinlets contain accessory rounded to subrounded pyrite and sphalerite, and are

281   aligned parallel to S_2. In contrast, chalcopyrite veinlets are generally monomineralic and

282   crosscut the pyrrhotite veinlets at a high angle. This type of mineralization accounts for

283   ~50% of the total sulfide resource at the Whalesback deposit.

284   *Breccia-type*. This mineralization type consists of chalcopyrite, with minor

285   pyrrhotite and pyrite. It contains 50-95% angular to subrounded dark chloritized basalt

286   fragments within a 5-50% sulfide matrix (Fig. 6g-i). The breccia-type mineralization

287   accounts for ~25% of the total sulfide resource at the Whalesback deposit.

288   *Semi-massive to massive sulfide*. This mineralization type consists of a mixture of

289   chalcopyrite and subordinate pyrite and pyrrhotite in the Eastern lenses and of a mixture

290   of pyrite and subordinate sphalerite and chalcopyrite in the Western lenses (Fig. 7a-f).

291   Small, 1-5 mm long, subrounded to flattened (parallel to S_2) fragments of silicate

292 minerals, mainly chlorite-altered wall rock, and constitute between 5 and 50% of the rock

293 (Fig. 7ad). In areas with more intense deformation, the flattened fragments are

294 heterogeneously distributed throughout the sulfide matrix, giving this type of

295 mineralization a durchbewegung texture. Small 0.2-3 mm wide chalcopyrite veinlets

296 commonly crosscut the semi-massive to massive sulfide assemblage (Fig. 7d). This type

297 of mineralization accounts for ~20% of the total sulfide resource at the Whalesback

298 deposit.

299   **Sulfur Isotopes**

300   One representative sample of massive sulfide from the Western lenses and five

301 representative samples of massive sulfide (n=2), semi-massive sulfide (n=1), breccia

302 (n=1) and veinlets (n=1) from the Eastern lenses (n=5) were chosen for *in situ* sulfur

303 isotope analysis by secondary ion mass spectrometry (SIMS). Sample mounts were

304 prepared from thin section off cuts by embedding ~1 cm x 1 cm pieces in epoxy in 1 inch

305 diameter aluminum retaining rings. Samples were polished using standard lapidary

306 procedures, and then sputter coated with 300 Å of Au to reduce charging under primary

307 ion bombardment. All analyses were performed using a Cameca IMS 4f SIMS instrument

308 at the MAF-IIC Microanalysis Facility at Memorial University.

309   The δ^{34}S data was collected from pyrite, pyrrhotite, and chalcopyrite using the

310 method described in Toman (2013) and Brueckner et al. (2014). In summary,

311 determinations were performed by bombarding the sample with a primary ion microbeam

312 of 600-850 picoamps (pA) of Cs^+, accelerated through a nominal 10 kiloelectron volt

313 (keV) potential, and focused into a 5–15 µm diameter spot on the sample. To exclude

314 exotic material in the polished surface from analysis, each spot was first pre-sputtered for

315 100 s with a 25 μm square raster applied to the beam. Negatively charged sputtered

316 secondary ions were accelerated into the mass spectrometer of the instrument through a

317 nominal potential of 4.5 keV. A combination of mass resolution (Mass Resolving Power

318 approx. 2975) and energy filtering (sample offset -60 eV with a 40 eV energy window)

319 were used to effectively eliminate isobaric interferences from $^{16}O_2^-$ and $^{33}SH^-$. Signals for

320 $^{32}S^-$, $^{34}S^-$ and a background position at 31.67 Dalton (Da) were obtained by cyclical

321 magnetic peak switching (typically 80 cycles were accumulated for each spot analysis),

322 and detected using an electron multiplier in pulse counting mode. Standard counting

323 times were: 0.5 s at the background position, 2.0 s on $^{32}S^-$, and 6.0 s on $^{34}S^-$. Waiting

324 times of 0.25 s were inserted before each peak counting position to allow for magnet

325 settling. All analyses are reported using the standard δ notation in units of per mil (‰)

326 relative to the international Vienna Canyon Diablo Troilite (VCDT) standard.

327 Internal precision on individual $\delta^{34}S$ analysis is typically better than ± 0.3‰ (1σ),

328 whereas the overall reproducibility is typically better than ± 0.5‰ (1σ). In house

329 standards for pyrite (UL9B), pyrrhotite (PoW1) and chalcopyrite (Norilsk) were used to

330 correct for instrumental mass fractionation for each specific mineral phase.

331

332 *Results*

333 Sulfide minerals from the Whalesback deposit display a relatively narrow range

334 of sulfur isotope compositions. Measured $\delta^{34}S$ of 18 pyrite samples range from +2.7 to

335 +6.6 per mil with an average of +5.0 per mil; 7 pyrrhotite samples range from +2.1 per

336 mil to +4.0 per mil with an average of +3.3 per mil; and 17 chalcopyrite samples range

337   from +1.3 to +4.7 per mil with an average of +2.9 per mil (Figs. 9a-f, 10, 11; Table 1).

338   Within individual samples, the internal variations of $\delta^{34}S$ in pyrrhotite and chalcopyrite

339   are generally low (<0.6 per mil), with a maximum observed variation of 1.0 per mil (Fig.

340   9a-f). Pyrite shows the greatest internal variations, and most of the $\delta^{34}S$ range observed

341   for Whalesback as a whole is present in one sample from the Eastern lenses (e.g., WB-

342   12-106A_561.05m, +4.5 to +6.4 per mil; Fig. 9c; Table 1). However, even for pyrite, the

343   internal variation within individual grain is quite restricted in overall magnitude (3.5 to

344   5.2 per mil; Fig 9c).

345   **Discussion**

346   *Morphology and Metal Zoning of the Whalesback Deposit*

347   The Whalesback deposit consists of a tightly folded and boudinaged deposit

348   dominated by chalcopyrite and pyrrhotite in the Eastern lenses and by pyrite in the

349   Western lenses (Fig. 4; Papezik, 1965; West, 1972; Szybinski, 1995). In most genetic and

350   descriptive models for Cyprus-type VMS deposits, there is a well developed zonation of

351   metals with chalcopyrite and pyrrhotite concentrated at the base and in the core of the

352   deposits, and pyrite and sphalerite concentrated at the top and more distal parts of the

353   deposit (Fig. 12a; e.g. Large, 1977; Franklin, 1981; Lydon, 1984, 1988; Ohmoto, 1996;

354   Franklin et al., 2005; Hannington, 2014). The metal distribution at Whalesback suggests

355   that the pyrite-rich Western lenses represent the top or distal parts of the Whalesback

356   deposit, whereas the chalcopyrite-pyrrhotite-rich Eastern lenses represent the core and

357   base of the deposit, in accordance with a younging direction towards west. Metal zoning

358   projected above the present day surface implies that D_2 deformation produced a closed

359 overturned fold (Fig. 12c). Overturned folds at this location have not been previously

360 documented and have implications for the longer-term exploration of the deposit.

361 Furthermore, it confirms the Whalesback deposit has been highly deformed, folded and

362 boudinaged during D_2 resulting in a closed overturned anticline (Fig. 12bc), and creating

363 the characteristic durchbewegung deformation texture observed at hand specimen scale.

364

365 *Sulfide textural evolution during deformation and remobilization*

366 Durchbewegung textured rocks are generally hosted within durchbewegung

367 structures (Marshall and Gilligan, 1989), which form from the progression of folding and

368 shearing related to the formation of tight to isoclinal folds. In these structures, the silicate

369 layers surrounding the less competent sulfide layers become disrupted, detached and

370 incorporated into the sulfides as they deform ductily. This process results in the creation

371 of detached fold cores and boudins of varying geometry depending on competency

372 contrast between the silicate and sulfide layers (Marshall and Gilligan, 1989). Relatively

373 late piercement (or ductile) veins are commonly associated with the formation of

374 durchbewegung structures. The veins range in size from a few centimeters to a few

375 meters wide and generally form at high angle to the layer interface and fill in extensional

376 planar fractures (Marshall and Gilligan, 1989).

377 At Whalesback, the majority of deformation and remobilization occurred during

378 the D_2 deformation event, as most of the sulfide-rich zones are parallel to the main S_2

379 schistosity (Papezik, 1965; West, 1972; Szybinski, 1995). Remobilization and

380 deformation of sphalerite, pyrrhotite, and chalcopyrite was due to ductile flow, whereas

381 pyrite deformed brittly as demonstrated by its rounded habit and high degree of fracturing

382 (Figs. 7ab, 8a-d). Sphalerite, pyrrhotite, and chalcopyrite fill the fractures in pyrite,

383 supporting their ductile remobilization. Moreover, pyrrhotite and chalcopyrite

384 remobilization incorporated and transported pyrite grains, rounding and fracturing them

385 (Figs. 8cd, 11def). Based on crosscutting relationships, sphalerite was the first sulfide

386 phase to be remobilized followed by pyrrhotite and chalcopyrite, and the latter were

387 followed by the formation of chalcopyrite veins (Fig. 8a-d). The sequence in which the

388 sulfides crossed the brittle-ductile transition zone is indicative of low to medium pressure

389 (>175 MPa) and low temperature deformation conditions, which were insufficient

390 conditions for pyrite to deform ductily (Fig. 13; Marshall and Gilligan, 1987). These

391 conditions are consistent with the lower greenschist grade metamorphism recorded

392 elsewhere in the Lushs Bight Group (Kean et al., 1995).

393   The main transport mechanism of ductile sulfides at Whalesback, during peak

394 metamorphism conditions, is interpreted to have been plastic flow, with minor solution

395 transport and precipitation. Cox (1987) showed that the intergrowth of sulfides with

396 fibrous phyllosilicates in low-grade metamorphic environments, like those observed at

397 Whalesback, indicates that some material remobilization occurred by dissolution,

398 solution transport and precipitation. However, since the intergrowth of fibrous chlorite

399 with massive pyrrhotite and chalcopyrite is only observed locally (Figs. 7hi, 8b), it is

400 assumed that plastic flow was likely the dominant transport mechanism.

401   The occurrence, and likely late remobilization, of chalcopyrite in high angle veins

402 relative to S_2 across the sulfide assemblages, is very common and expected in

403 durchbewegung structures (Marshall and Gilligan, 1989), and suggests that the late

404 chalcopyrite veins are a direct consequence of the structural evolution of the

405 durchbewegung structure hosting the Whalesback deposit. Close folding and boudinage

406 of Cu-rich ore (Fig. 4) also support a structural evolution within a durchbewegung

407 structure.

408

409 *Influence of Deformation on $\delta^{34}S$ Distribution*

410   Only a few studies have investigated the effect of metamorphism on the primary

411 sulfur isotopic composition of sulfide minerals in VMS deposits (e.g. Bachinski, 1977b;

412 Craig and Vokes, 1993; Crowe, 1994; Cook and Hoefs, 1997; Wagner et al., 2004). Most

413 of these studies were undertaken in areas affected by classic Barrovian-style

414 metamorphism, i.e., where the temperature and the pressure gradually increase together,

415 and all concluded, except Crowe (1994), that the original sulfur isotopic composition of

416 individual sulfide phases was preserved during metamorphism. Bachinski (1977b)

417 investigated the sulfur isotopic composition of VMS deposits within the Lushs Bight

418 Group, including the former Whalesback mine, and reached a similar conclusion.

419   The $\delta^{34}S$ values recorded from all sulfide phases during this study display a

420 narrow range of +1.3 to +6.6 per mil and are heterogeneously distributed at the scale of

421 the Whalesback deposit (Figs. 9a-f, 10, 11; Table 1). Pyrrhotite is the most consistent

422 sulfide mineral with a range of only 1.9 per mil, followed by chalcopyrite with a range of

423 3.4 per mil and pyrite with a range of 3.9 per mil. Equilibrium temperature derived from

424 coexisting sulfides phases (chalcopyrite-pyrite, chalcopyrite-pyrrhotite, and pyrrhotite-

425 pyrite) using Kajiwara and Krouse (1971) fractionation factors yield temperatures

426 between 27 and 526°C (Fig. 14a-c) with one additional sample yielding a temperature of

427 4605°C, above normal hydrothermal fluids and metamorphism temperature range. In

428   addition, one sample had a $\Delta^{34}S_{Py-Ccp}$ of -0.6 that could not be solved using the

429   equilibrium temperature equations of Kajiwara and Krouse (1971), indicating isotopic

430   disequilibrium. Overall, most derived equilibrium temperatures are below the 200°C

431   isotherm, which is lower than the typical Cu-rich VMS deposits formation temperature

432   (250-350°C; Large, 1977; Franklin et al., 1981, 2005; Lydon, 1984, 1988; Hannington,

433   2014). These low equilibrium temperatures can be due to a partial to complete re-

434   equilibration of the sulfide phases at low temperature during the deformation and

435   associated metamorphism (isotopic equilibrium), the product of primary precipitation of

436   coexisting sulfide phases at different temperature yielding a low "apparent" equilibrium

437   temperature (isotopic disequilibrium), or the result of isotopic heterogeneity of the

438   mineralizing fluids through time induced by sulfur extraction from more than one source

439   (isotopic disequilibrium).

440   Paragenetic relationships of sulfide phases at Whalesback suggest that the

441   increase in pressure and temperature during D_2 produced a remobilization and

442   deformation sequence wherein sphalerite crossed the brittle-ductile transition first,

443   followed by pyrrhotite and by chalcopyrite. This remobilization may have lead to partial

444   to complete re-equilibration of the sulfides. If complete isotopic equilibration was

445   attained, each sulfide phases within the deformation zone should have a homogenous

446   composition (i.e., all chalcopyrite should have similar $\delta^{34}S$ values) and the derived

447   equilibrium temperatures should be constant throughout the deposit, which is not the case

448   at the Whalesback deposit (Figs. 10, 14a-c). Partial equilibration at hand sample scale is

449   also unlikely as samples containing more than one sulfide pairs yield a wide range of

450   equilibrium temperatures (Fig. 14a-c). It is therefore suggested that the sulfides are not in

451 isotopic equilibrium and at least partly retained their original isotopic composition, as

452 previously proposed by Bachinski (1977b). However, given that the isotopic

453 compositions of the ductile phases (pyrrhotite and chalcopyrite) are more homogeneous

454 that the pyrite, it is suggested that some local homogenization may have occurred.

455   Using the fractionation factors of Ohmoto and Rye (1979), the maximum

456 expected variation in $\delta^{34}S$ between for a sulfide pair that precipitated from the same

457 fluids, but at different temperatures (250-350°C), is 1.4 per mil for the pyrite-chalcopyrite

458 pair, 0.3 per mil for the pyrrhotite-chalcopyrite pair, and 1.2 per mil the pyrite-pyrrhotite

459 pair. These variations are not sufficient to explain the $\delta^{34}S$ variation at Whalesback.

460 Therefore, we suggest that variation in primary precipitation temperature of the

461 coexisting sulfide phases is not important at the Whalesback deposit and that the

462 provenance of sulfur is the main controlling factor on the $\delta^{34}S$ distribution.

463

464 *Origin of sulfur*

465   The sulfur in VMS deposits may originate from multiple sources, including: 1)

466 sulfur derived from thermochemical sulfate reduction (TSR) of seawater sulfate via the

467 partial reduction of oxidized seawater to isotopically lighter H_2S during seawater

468 alteration of basement rocks. This process commonly results in sulfur in VMS sulfides

469 that is ~17 to 25 per mil lighter than coexisting seawater sulfate (e.g., Sangster, 1968;

470 Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997; Huston, 1999; Shanks, 2001;

471 Seal, 2000, 2006); seawater sulfate itself has varied greatly through geological time (+4

472 to +34.5 per mil; $\delta^{34}S_{Cambrian}$= +34.5 per mil; Claypool et al., 1980; Canfield et al., 2004;

473 Kampschulte and Strauss, 2004; Paytan and Grey, 2012); 2) sulfur derived from anoxic

474   seawater with a sulfide isotopic composition 15 to 60 per mil lighter than sulfate derived

475   from oxidized seawater (-25.5 to +19.5 per mil for Cambrian anoxic seawater; Goldhaber

476   and Kaplan, 1975), and wherein the magnitude of the fractionation is related to

477   sedimentation rates. Low sedimentation rates are associated with slower rate of sulfate

478   reduction and larger fractionation, and high sedimentation rates are associated with faster

479   rates of sulfate reduction and small fractionation. Sediments in anoxic environment are

480   generally associated with elevated concentration of organic matter and sulfide minerals in

481   which pyrite commonly display a framboidal texture (Goldhaber and Kaplan, 1975); 3)

482   sulfide sulfur sourced by direct leaching from the basaltic rocks of the Lushs Bight Group

483   underlying the mineralized stratigraphic horizons. In the case of submarine mafic

484   volcanic hosted Cu-rich deposits, like Whalesback, the $\delta^{34}S_{Sulfides}$ of basalt ranges from

485   +0.3 to +0.7 per mil (Torssander, 1992); 4) magmatic sulfur with $\delta^{34}S_{Reservoir} \approx +0 \pm 2$ per

486   mil (Hoef, 2009). At temperatures above 300°C the dominant sulfur species is SO_2, but at

487   lower temperatures the magmatic SO_2 disproportionates rapidly to form H_2S and H_2SO_4.

488   This latter reaction is accompanied by a large isotopic fractionation that produces

489   negative $\delta^{34}S_{H2S}$ values often resulting in sulfides that have negative $\delta^{34}S$ (Rye, 1993;

490   Huston et al., 2011); and 5) bacteriogenic reduction of sulfate in marine or pore waters.

491   Precipitation of sulfide by bacteria is associated with a strong fractionation, ranging from

492   24 to 71 per mil and averaging 51 ± 10 per mil, depending on the sulfate availability of

493   the system (Ohmoto and Rye, 1979; Canfield and Teske, 1996; Ohmoto and Goldhaber,

494   1997; Canfield, 2001; Seal, 2006). In the case of the Cambrian Whalesback deposit, $\delta^{34}S$

495   values ranging between -36.5 and +10.5 per mil with an average of -16.5 ± 10 per mil are

496   expected for sulfide minerals derived from biogenic reduction of seawater sulfate during

497   the Cambrian (Kampschulte and Strauss, 2004).

498   The absence of negative δ^{34}S values, pyrite framboids, and the narrow positive

499   range of δ^{34}S obtained from the Whalesback deposit during this study (Table 1) suggest

500   that biogenic sulfur input was insignificant. Furthermore, a significant component of

501   magmatic sulfur is also highly unlikely, given these restricted positive δ^{34}S values (i.e.,

502   no evidence of sulfur disproportionation; Rye, 1993; Huston et al., 2011), and the

503   absence of other features that are common to VMS deposits formed from magmatic fluid

504   input, i.e. Au-Ag-enrichment, intermediate- to high-sulfidation ore mineral assemblages,

505   and aluminous alteration assemblages (e.g., Sillitoe et al., 1996; Hannington et al., 1999;

506   Dubé et al., 2007). Anoxic sulfur is also an unlikely sulfur source as carbonaceous and

507   sulfur-rich sediments are rare in the vicinity of the Whaleback deposit. Moreover, the

508   basalts of the Lushs Bight Group near the Whalesback deposit contain hematitized pillow

509   lava with common to extensive magnetite-bearing red cherts (Kean et al., 1995),

510   consistent with deposition in oxidized seawater.

511   To evaluate the relative roles of leaching from igneous host rocks and TSR,

512   modeling was undertaken using the method described in Brueckner et al. (2014) using the

513   equations outlined in Ohmoto and Rye (1979), Ohmoto and Goldhaber (1997), and Seal

514   (2006). Thermochemical sulfate reduction (TSR) of seawater sulfate was modeled on the

515   basis of three assumptions: 1) Cambrian seawater sulfate had a δ^{34}S $\approx$ +34.5 per mil

516   (Claypool et al., 1980; Canfield et al., 2004; Kampschulte and Strauss, 2004; Paytan and

517   Grey, 2012); 2) TSR occurred at ~300°C (or higher), based on the observation of

518   chalcopyrite-pyrrhotite assemblages in the sulfides; and 3) the system was open and was

519   continuously replenished as the available heavy sulfate (SO_4) was reduced to lighter H_2S,

520 producing H_2S with $\delta^{34}S_{H2S(300°C)} \approx +12.7$ per mil during TSR (i.e., assuming that $f = 1$,

521 where f is the fraction of SO_4 remaining in solution at site of reduction reaction). The

522 fluid was then cooled from $300°C$ and various sulfide phases were precipitated, with most

523 minerals precipitated at temperatures > 250-$300°C$ given the chalcopyrite-rich

524 assemblages at the Whalesback deposit. Figure 15 illustrates the sulfide isotopic

525 composition as a function of cooling for the interpreted temperatures of deposition for

526 sulfide solely derived from TSR. The model shows that TSR alone cannot generate the

527 $\delta^{34}S$ range determined for the sulfide phases at the Whalesback deposit. Even at the

528 modeled temperature of $250°C$, TSR-derived sulfides would still have $\delta^{34}S$ substantially

529 heavier than the range observed at Whalesback. This implies that sulfur from leaching of

530 igneous rocks must be an important contributor to the overall sulfur budget of the deposit.

531   Binary mixing proportions of sulfur sourced from mafic host rock leached H_2S at

532 $300°C$ ($\delta^{34}S_{py} \sim +1.2$ per mil, $\delta^{34}S_{po} = +0.3$ per mil, $\delta^{34}S_{ccp} = -0.2$ per mil) and sulfur

533 derived from TSR at $300°C$ can be calculated using the following equation:

534 $$\delta^{34}S_{sample} = X\delta^{34}S_{TSR} + (1-X)\delta^{34}S_{leached} \qquad (1),$$

535 where $\delta^{34}S$ is the measured sulfur isotopic signature of the sample, $\delta^{34}S_{TSR} = \delta^{34}S$ derived

536 from TSR calculation at $300°C$ for a given mineral phase, $\delta^{34}S_{leached} = \delta^{34}S$ of igneous-

537 derived sulfur in a given mineral phase at $300°C$, and X is a proportionality factor that is

538 1 when 100% of the sulfur is from TSR and 0 when there is 0% TSR (i.e., 100% leaching

539 of igneous sulfur). The results show that sulfur derived from TSR at $300°C$ accounts for a

540 maximum of ~40% of the sulfur budget of the Whalesback deposit, whereas between 60-

541 90% has been derived from leaching from the surrounding footwall rocks (Fig. 16a-c).

542 This result is expected given the high temperature nature of the mineralization at the

543 Whalesback deposit (i.e., Cu-rich assemblages) and the relatively restricted range of

544 measured δ^{34}S values, further arguing that leaching from nearby footwall rocks was the

545 most important source for sulfur in the Whalesback deposit. Since the Lushs Bight Group

546 is 3-4 km in thickness (Kean et al., 1995), there is no restriction for the depth at which the

547 sulfur and metals present at Whalesback were extracted. However, given that copper

548 solubility is low below 225°C and greatly increase with increasing temperature

549 (Hannington et al., 2014), it is suggested that the sulfur and the metals were leached from

550 the lower portion of the mafic Lushs Bight Group. This single mafic source for the

551 extraction of the metals is also reflected in the simple mineralogy (chalcopyrite, pyrite,

552 pyrrhotite, and subordinate sphalerite) encountered at the Whalesback deposit.

553 **Conclusions**

554   The Whalesback deposit is a Cu-rich VMS deposit hosted within a closed,

555 boudinaged and overturned fold located within a durchbewegung structure. Intense

556 deformation of the Whalesback deposit occurred at low temperature and medium

557 pressure (>175 MPa) during the accretion of the LBOT-Dashwoods composite terrane

558 onto the Humber margin at ca. 480 Ma (D_2). The increase in pressure and temperature

559 produced a remobilization sequence where sphalerite was the first sulfide phase to cross

560 the brittle-ductile transition, followed by pyrrhotite and subsequently by chalcopyrite.

561 The maximum metamorphic temperature was not high enough for pyrite to deform

562 ductily. Instead, pyrite grains were incorporated and transported during the ductile

563 remobilization of less competent sulfide phases (pyrrhotite and chalcopyrite). This led to

564 the rounding and fracturing of the pyrite grains. Remobilization of sulfides occurred

565 primarily by plastic flow but some evidence of dissolution, solution transport and

566 precipitation was observed locally.

567   Sulfur isotopes retained their original signatures and did not re-equilibrate during

568 the remobilization events. The dominant source of sulfur was determined to be from

569 sulfides leached from surrounding basalts, with a lesser component derived from

570 thermochemical sulfate reduction of seawater sulfate during alteration of the basalts.

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880   Abbreviations: BBL = Baie Verte Brompton Line; DBL = Dog Bay Line; DF = Dover

881   Fault; GBF = Green Bay Fault; LCF = Lobster Cove Fault; LRF = Lloyds River Fault;

882   RIL = Red Indian Line.

883

884   ; LR = Long Range; LRF = Lloyds River Fault; PP = Pipestone Pond Complex; RIL =

885   Red Indian Line; SA = St. Anthony; TP = Tally Pond Belt; TU = Tulks Volcanic Belt;

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892   Papezik and Fleming (1967); Fleming (1970) and Kean et al. (1995)).

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895   points of the drill hole examined during this study.

896

897   Figure 5. Photographs and photomicrographs of representative samples from the Western

898   lenses and the Eastern lenses. (A) Pyrite-rich sample from the Western lenses. Sample

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900 occurs are euhedral to subrounded grains and are associated with minor sphalerite and

901 chalcopyrite. (C) Pyrrhotite-rich sample from the Eastern lenses. The pyrrhotite-rich zone

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904 grains of pyrite and small aggregates of sphalerite and chalcopyrite. (E) Chalcopyrite-rich

905 sample from the Eastern lenses. Sample WB-12-108_657.0m. (F) Reflected light image

906 of the chalcopyrite-rich zone from (E). The chalcopyrite-rich zone contains angular to

907 rounded grains of pyrite and small aggregates of sphalerite and pyrrhotite.

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920 fibrous chlorite. Sample Wb-12-109_442.2m. (I) Same as (H) under cross-polarized light.

921 Abbreviations are as follow: Cal = calcite, Ccp = chalcopyrite, Chl = chlorite, Po =

922   pyrrhotite, Qz = quartz, Sp = sphalerite, Ttn = titanite, RL: reflected light and XP: cross-

923   polar.

924

925   Figure 7. Photographs and photomicrographs of the different massive mineralization

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927   chalcopyrite crosscutting a subrounded to rounded pyrite and carbonate layer parallel to

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934   overprinted by chalcopyrite, and fragments of chlorite and quartz. Sample WB-12-

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936   Cal = calcite, Ccp = chalcopyrite, Chl = chlorite, Po = pyrrhotite, Py = pyrite, Qz =

937   quartz, RL: reflected light and XP: cross-polar.

938

939   Figure 8. Photomicrographs of Whalesback sulfide deformation textures. (A) Sphalerite

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941   (brittle). Sample WB-12-108_669.8m; (B) Sphalerite with injected arms of pyrrhotite and

942   chalcopyrite. Sample WB-12-108_670.4m; (C) Pyrrhotite with subrounded to rounded

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946   109_578.6m. Abbreviations are as follow: Ccp = chalcopyrite, Po = pyrrhotite, Py =

947   pyrite, Sp = sphalerite, RL: reflected light and XP: cross-polar.

948

949   Figure 9. SIMS analysis location and results. (A) Rounded to subrounded pyrite in a

950   chalcopyrite matrix from a massive sulfide layers within the Western lenses. Sample

951   WB-11-102_163.9m. (B) Subrounded pyrite and aggregates of pyrrhotite in a

952   chalcopyrite matrix from a highly deformed veinlet type sulfide within the Eastern lenses.

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954   chalcopyrite matrix from breccia-type mineralization from the Eastern lenses. Sample

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956   chalcopyrite matrix from a semi-massive sulfide layer within the Eastern lenses.

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959   chalcopyrite piercement veins within a massive sulfide layer from the Eastern lenses.

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961   coexisting with a chalcopyrite-rich area within a massive sulfide layer of the Eastern

962   lenses. Sample WB-12-111_452.5m. Abbreviations and sample location colors are as

963   follow: Ccp = chalcopyrite (red circle), Po = pyrrhotite (blue circle) and Py = pyrite

964   (green circle). RL = Reflected light.

965

966   Figure 10. Notched whisker plots for sulfur isotopic data for chalcopyrite, pyrrhotite and

967   pyrite. The width of the notches is proportional to the half width (HW = [75th Percentile

968 – 25th Percentile] $\times 1.57/[\sqrt{N}]$, where N is the population size). The central portion of

969 the notched is the median and is represented by a line across the whisker box. The whisks

970 represent the extent of the dataset. Statistically, the chalcopyrite and pyrrhotite represents

971 one population while the pyrite represents a different population.

972

973 Figure 11. Spatial distribution of $\delta^{34}S$ samples within the Whalesback deposit. Also

974 shown is range in the $\delta^{34}S$ values obtained on pyrite and chalcopyrite mineral separates

975 from the former Whalesback mine (Bachinski, 1977).

976

977 Figure 12. Schematic representation of the evolution of the Whalesback deposit (A-C) at

978 the deposit scale and (D-F) at the micro-section scale. (A and D) Formation stage. The

979 Whalesback deposit is deposited near and/or on the seafloor and displays a spatial

980 zonation of metals with chalcopyrite- and pyrrhotite-rich sulfides at the base and in the

981 core of the deposit and pyrite-rich sulfides at the top and more distal parts of the deposit.

982 The chalcopyrite- and pyrrhotite-rich zone contains of euhedral pyrite while the pyrite-

983 rich zone is composed of euhedral pyrite and sphalerite with minor pyrrhotite and

984 chalcopyrite. (B and E) Early D_2 deformation stage. The deposit is compressed along the

985 lateral axis, creating the main S_2 schistosity in the basalt host rock and ductily deforming

986 and remobilizing sphalerite and pyrrhotite, and rounding the pyrite grains. Chalcopyrite-

987 rich lenses were aligned parallel to main S_2 schistosity during that stage. (C and F).

988 Present day disposition of the Whalesback deposit showing a closed and boudinaged

989 overturned fold configuration. The late stage of deformation ductily remobilized

990 chalcopyrite and incorporated fragments of ductile pyrrhotite and brittle pyrite,

44

991 continuing the mechanical rounding of the pyrite grains. Late chalcopyrite veins crosscut

992 all the previously formed mineral assemblages.

993

994 Figure 13. Metamorphic pressure-temperature diagram with superposed brittle-ductile

995 behavior boundaries. Mechanical behavior of common base-metal sulfides at the brittle-

996 ductile transitions at 5% ductile strain before faulting, and at strain rates in the order of

997 $7.2 \times 10\text{-}5 \text{ s}^{-1}$ (diagram modified from Marshall and Gilligan, 1987). The general ductile

998 remobilization sequence at Whalesback is depicted by the arrow and starts in the

999 sphalerite ductile domain, followed by sphalerite-pyrrhotite ductile domain and ends in

1000 the sphalerite-pyrrhotite-chalcopyrite ductile domain. This sequence is only possible for

1001 temperature below 150ºC (grey highlighted area). Abbreviations are as follow: Ccp =

1002 chalcopyrite, Gn = galena, Po = pyrrhotite, Py = pyrite, Sp = sphalerite.

1003

1004 Figure 14. $\delta^{34}S$ vs $\delta^{34}S$ plots of coexisting sulfide phases: (A) pyrite-chalcopyrite, (B)

1005 pyrrhotite-chalcopyrite, and (C) pyrite-pyrrhotite. Isotherms were calculated for

1006 temperatures between 100 to 750ºC using the fraction factors of Kajiwara and Krouse

1007 (1971). Also shown are the isotopic equilibrium temperatures (in italic).

1008

1009 Figure 15. Sulfur isotopic composition for sulfide derived solely from thermochemical

1010 sulfate reduction of seawater sulfate (TSR) at 250, 300 and 350°C. (A) Chalcopyrite, (B)

1011 pyrrhotite, and (C) pyrite. Also shown is the range in sulfur isotopic composition of

1012 sulfide phases observed during this study.

1013

1014   Figure 16. Modeled sulfide isotopic composition of (A) pyrite, (B) pyrrhotite and (C)

1015   chalcopyrite deposited at 250, 300 and 350°C in relation to the proportion of TSR and

1016   igneous sulfide required to produce them. The range of TSR proportion required to

1017   produce the observed sulfide isotopic composition at Whalesback is highlighted in the

1018   shaded area. Also shown is the range in sulfur isotopic composition of sulfide phases

1019   observed during this study.

1020

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1023 Table 1. SIMS δ^{34}S stable isotopic data for pyrite, pyrrhotite and chalcopyrite phases

1024 from the Whalesback deposit. (See sulfur isotopes section for analytical details).
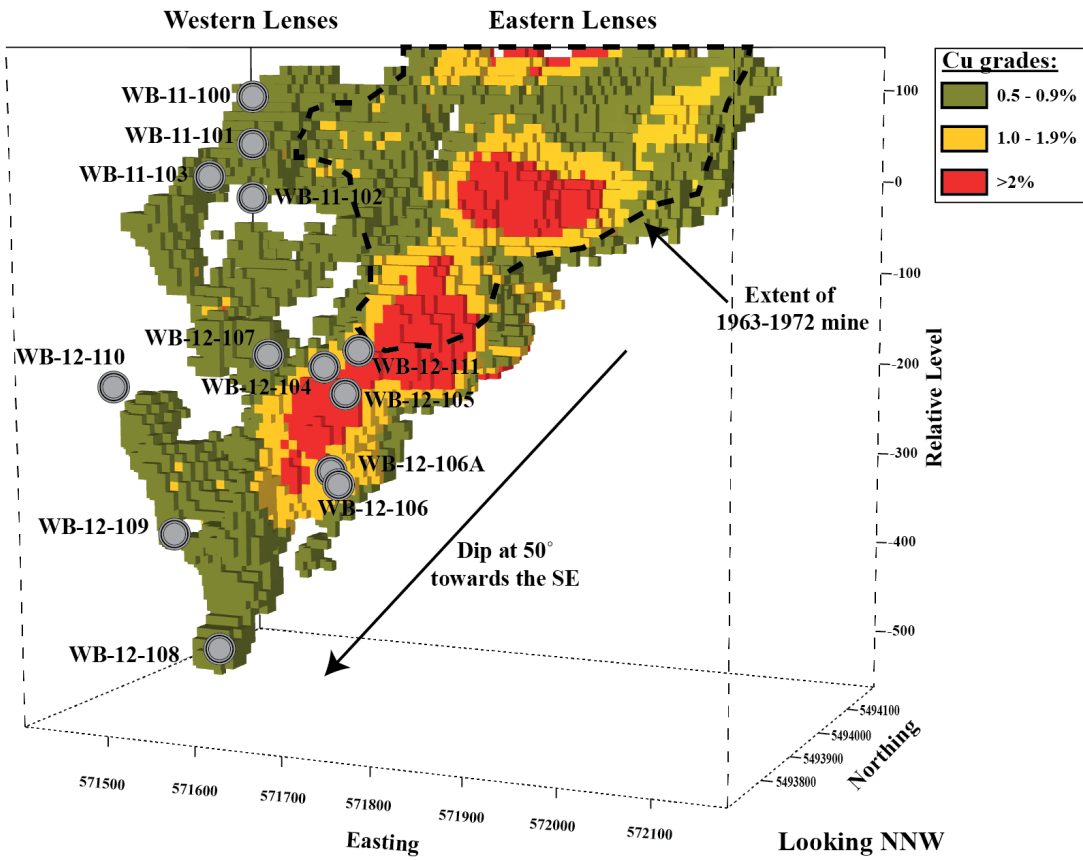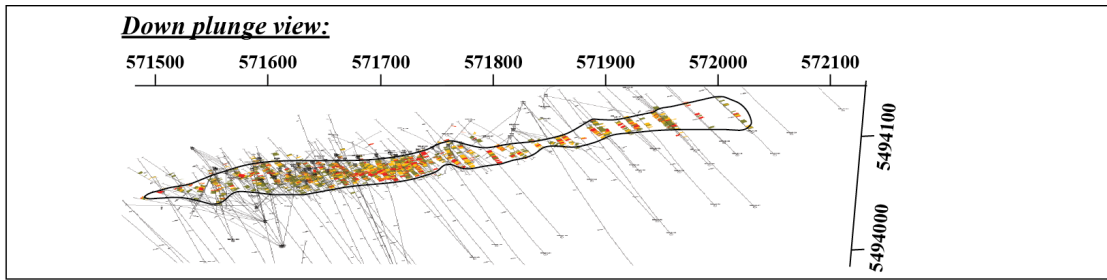
1025

1026

1027　　Figure 1

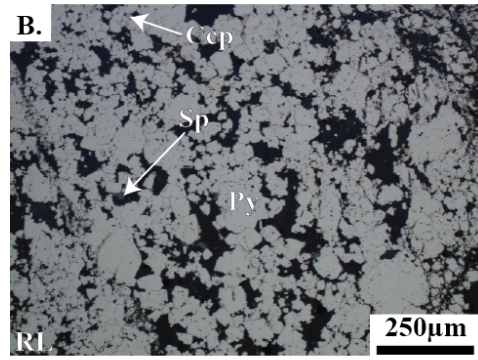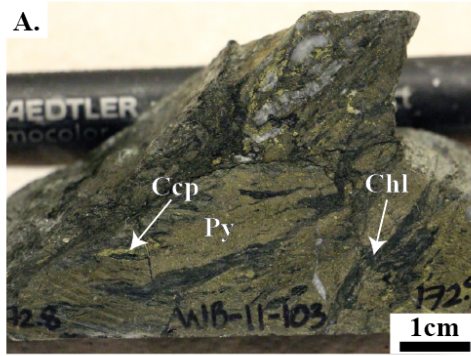1028

1029

1030   Figure 2

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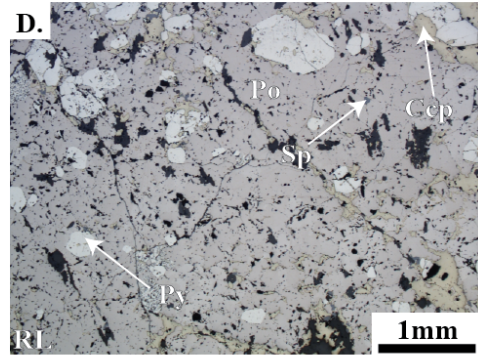
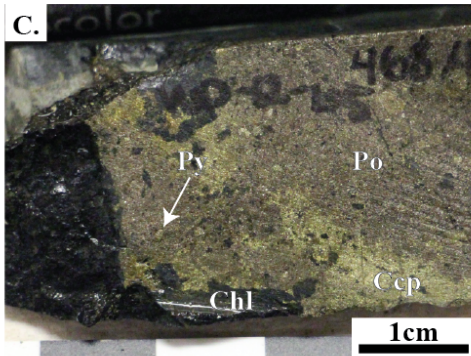1032

1033   Figure 3

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1036   Figure 4

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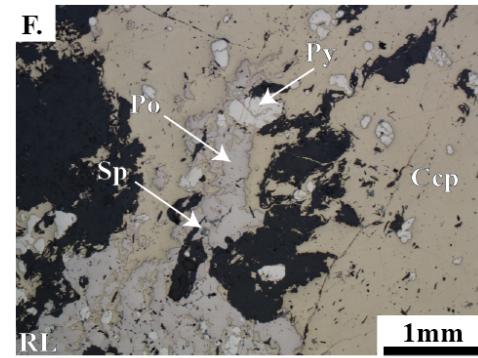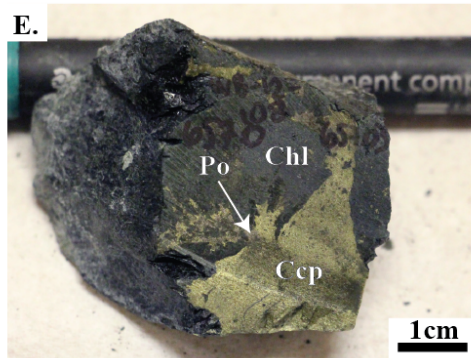
Western lenses

Pyrite-rich

Eastern lenses

Pyrrhotite-rich

Chalcopyrite-rich

1038

1039　Figure 5

1040
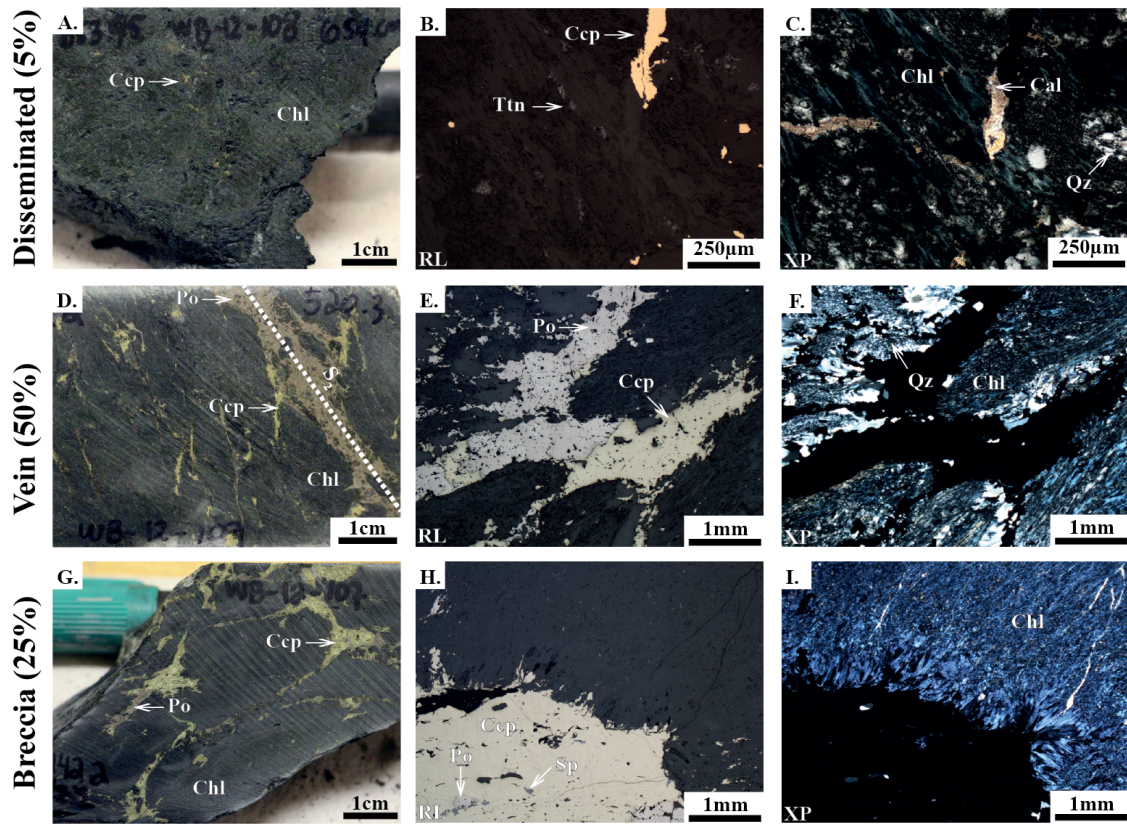
1041

1042   Figure 6

1043
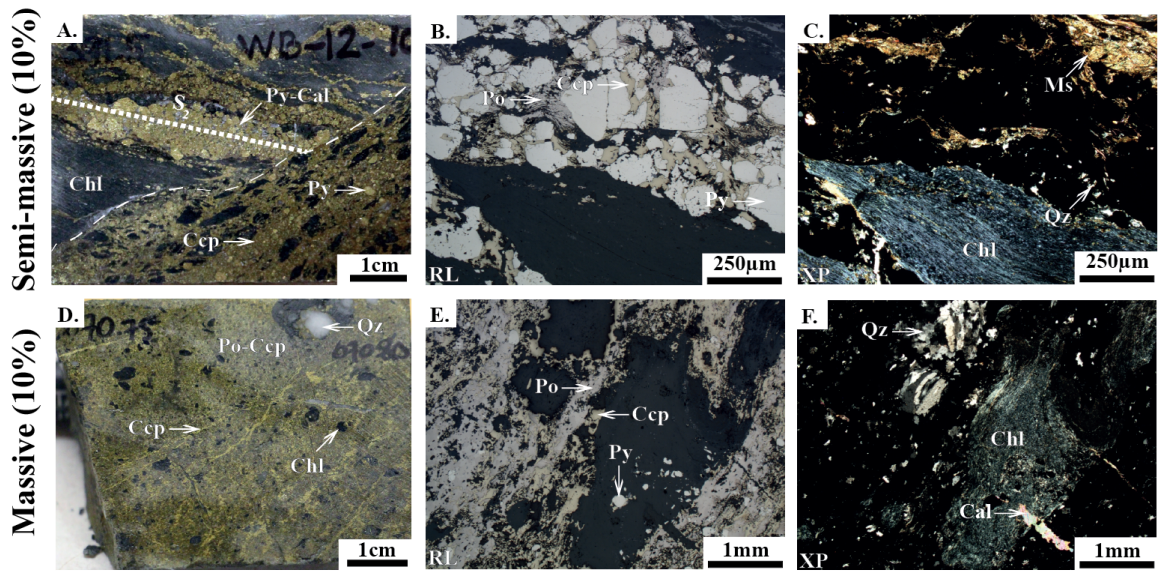
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1045   Figure 7

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1048   Figure 8

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A. Western lenses Massive Sulfide
- Ccp1: +2.5‰
- Py3: +3.3‰
- Py2: +4.8‰
- Ccp2: +2.3‰

B. Eastern lenses Veinlet
- Po1: +3.7‰
- Ccp3: +2.8‰
- Ccp2: +2.8‰
- Ccp1: +2.5‰
- Py2: +4.8‰
- Po2: +4.0‰

C. Eastern lenses Breccia
- Py9: +6.4‰
- Ccp2: +4.0‰
- Py2: +4.8‰
- Py3: +5.2‰
- Py1: +3.5‰
- Py4: +4.5‰
- Ccp1: +4.4‰
- Py6: +6.3‰
- Py7: +6.3‰
- Ccp3: +4.1‰

D. Eastern lenses Semi-massive Sulfide
- Ccp1: +4.5‰
- Ccp3: +4.7‰
- Py2: +5.9‰
- Po1: +3.7‰
- Ccp2: +3.7‰
- Py1: +5.5‰
- Po2: +3.1‰

E. Eastern lenses Massive Sulfide
- Po2: +2.3‰
- Py2: +5.0‰
- Ccp1: +1.3‰
- Po1: +2.1‰
- Py1: +2.7‰
- Ccp2: +1.3‰
- Py3: +4.0‰

F. Eastern lenses Massive Sulfide
- Py1: +5.1‰
- Ccp2: +2.9‰
- Po2: +3.9‰
- Ccp1: +2.2‰

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1051   Figure 9

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1054   Figure 10

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Western lenses **Eastern lenses**

WB-11-102_168.9m
Py: +3.3‰ to +4.8‰ (n=2)
Ccp: +2.3‰ to +2.5‰ (n=2)

Bachinski (1977) δ³⁴S range
Py: +1.2‰ to +7.2‰ (n=16)
Ccp: +2.5‰ to +7.4‰ (n=2)

WB-12-104_391.5m
Py: +5.5‰ to +5.9‰ (n=2)
Po: +3.1‰ to +3.7‰ (n=2)
Ccp: +3.7‰ to +4.5‰ (n=3)

WB-12-111_452.5m
Py: +5.1‰ to +5.5‰ (n=2)
Po: +3.9‰ (n=1)
Ccp: +2.2‰ to +2.9‰ (n=3)

WB-12-109_578.6m
Py: +4.8‰ (n=1)
Po: +3.7‰ to +4.0‰ (n=2)
Ccp: +2.5‰ to +3.8‰ (n=3)

WB-12-106A_561.05m
Py: +4.5‰ to +6.3‰ (n=8)
Ccp: +4.0‰ to +4.4‰ (n=3)

WB-12-108_675.75m
Py: +2.7‰ to +5.0‰ (n=3)
Po: +2.1‰ to +2.3‰ (n=2)
Ccp: +1.3‰ (n=3)

Extent of
1963-1972 mine

Cu grades:
- - - - **0.5 - 0.9%**
——— **1.0 - 1.9%**
━━━ **>2%**

Relative Level
100
0
-100
-200
-300
-400
-500

Northing
5494100
5494000
5493900
5493800

Easting
571500 571600 571700 571800 571900 572000 572100

Looking NNW

1056

1057   Figure 11

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58

Formation Stage

Early D₂

Present day

A.

Basalt (Above mineralization)

Py-rich

Ccp-Po-rich

Chlorite-rich

Mudstone (Above mineralization)

Basalt (Host)

B.

Basalt (Above mineralization)

Py-rich

Ccp-Po-rich

Chlorite-rich

Basalt (Host)

C.

Surface

Py-rich

Ccp-Po-rich

Chlorite-rich

Basalt

100m

D.

Py-rich zone

Ccp-Po-rich zone

250μm

E.

Py-rich zone

Ccp-Po-rich zone

250μm

F.

Py-rich zone

Ccp-Po-rich zone
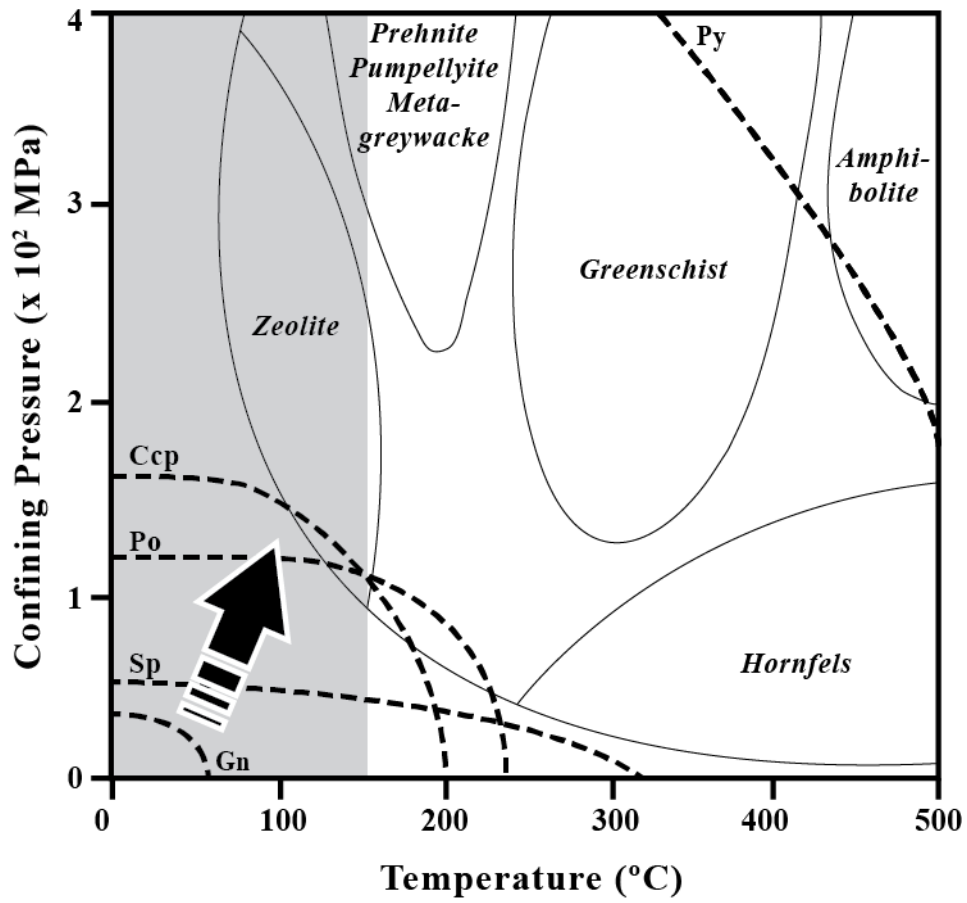
250μm

Legend: ☐ Pyrite ☐ Sphalerite ☐ Pyrrhotite ☐ Chalcopyrite ☐ Chalcopyrite (late; vein-type)

Figure 12

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1063   Figure 13

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Figure 15. δ34S plots with isotherm lines for pyrite-chalcopyrite, pyrrhotite-chalcopyrite, and pyrite-pyrrhotite pairs.

Legend:

Veinlet-Type Sulfide:
+ WB-12-109_578.6m

Breccia-Type Sulfide:
▼ WB-12-106A_561.05m

Semi-massive Sulfide:
● WB-12-104_391.5m

Massive Sulfide:
■ WB-11-102_168.9m (Western lenses)
■ WB-12-108_670.75m
■ WB-12-111_452.5m
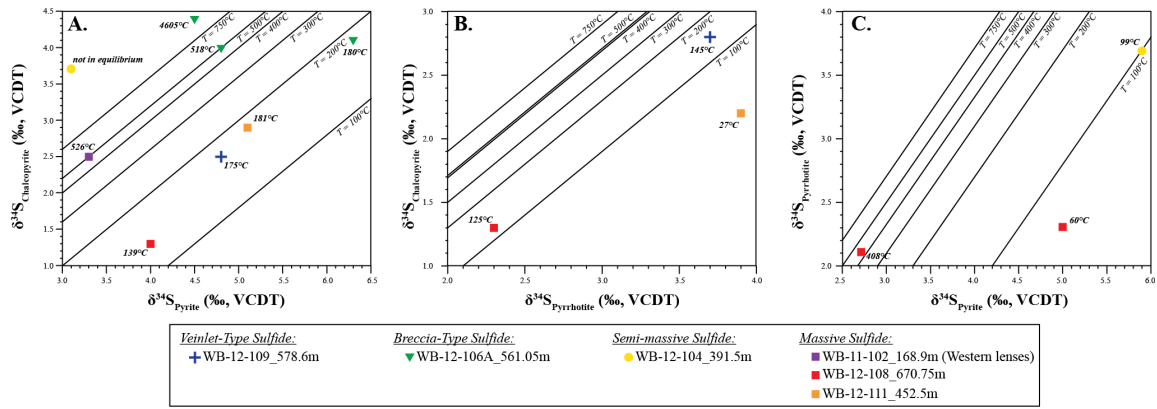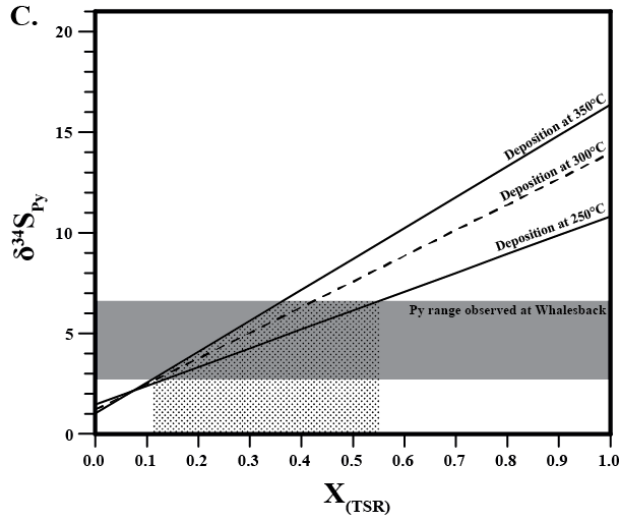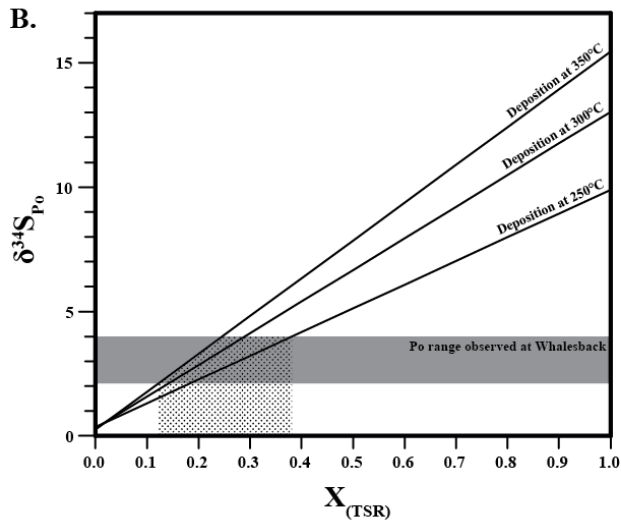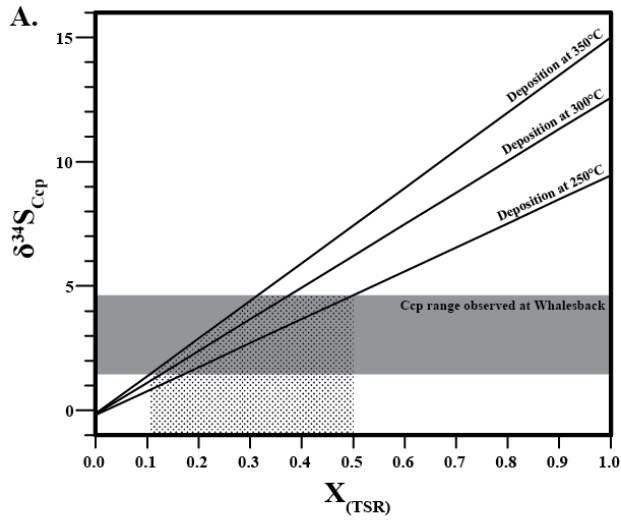
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1066   Figure 15

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1069   Figure 16

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Table 1. SIMS δ^{34}S stable isotopic data for pyrite, pyrrhotite and chalcopyrite phases from the Whalesback deposit. (See sulfur isotopes section for analytical details)

Sample Name	Mineralized Zone	Mineralization Style	δ^{34}S (‰)	1σ
Pyrite:				
WB-11-102_163.9m_Py2	Western lenses	Massive	4.8	0.4
WB-11-102_163.9m_Py3	Western lenses	Massive	3.3	0.3
WB-12-104_391.5m_Py1	Eastern lenses	Semi-Massive	5.5	0.2
WB-12-104_391.5m_Py2	Eastern lenses	Semi-Massive	5.9	0.2
WB-12-106A_561.05m_Py1	Eastern lenses	Breccia	3.5	0.2
WB-12-106A_561.05m_Py2	Eastern lenses	Breccia	4.8	0.2
WB-12-106A_561.05m_Py3	Eastern lenses	Breccia	5.2	0.3
WB-12-106A_561.05m_Py4	Eastern lenses	Breccia	4.5	0.2
WB-12-106A_561.05m_Py6	Eastern lenses	Breccia	6.3	0.3
WB-12-106A_561.05m_Py7	Eastern lenses	Breccia	6.3	0.3
WB-12-106A_561.05m_Py9	Eastern lenses	Breccia	6.4	0.2
WB-12-108_670.75m_Py1	Eastern lenses	Massive	2.7	0.2
WB-12-108_670.75m_Py2	Eastern lenses	Massive	5.0	0.3
WB-12-108_670.75m_Py3	Eastern lenses	Massive	4.0	0.2
WB-12-109_578.6m_Py2	Eastern lenses	Veinlets	4.8	0.3
WB-12-111_452.5m_Py1	Eastern lenses	Massive	5.1	0.2
WB-12-111_452.5m_Py2	Eastern lenses	Massive	5.5	0.2
Pyrrhotite:				
WB-12-104_391.5m_Po1	Eastern lenses	Semi-Massive	3.7	0.3
WB-12-104_391.5m_Po2	Eastern lenses	Semi-Massive	3.1	0.4
WB-12-108_670.75m_Po1	Eastern lenses	Massive	2.3	0.2
WB-12-108_670.75m_Po2	Eastern lenses	Massive	2.1	0.2
WB-12-109_578.6m_Po1	Eastern lenses	Veinlets	3.7	0.2
WB-12-109_578.6m_Po2	Eastern lenses	Veinlets	4.0	0.2
WB-12-111_452.5m_Po2	Eastern lenses	Massive	3.9	0.3
Chalcopyrite:				
WB-11-102_163.9m_Ccp1	Western lenses	Massive	2.5	0.2
WB-11-102_163.9m_Ccp2	Western lenses	Massive	2.3	0.4
WB-12-104_391.5m_Ccp1	Eastern lenses	Semi-Massive	4.5	0.7
WB-12-104_391.5m_Ccp2	Eastern lenses	Semi-Massive	4.7	0.4
WB-12-104_391.5m_Ccp3	Eastern lenses	Semi-Massive	3.7	0.3

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Table 1. (continued)

Sample Name	Mineralized Zone	Mineralization Style	δ^{34}S (‰)	1σ
WB-12-106A-561.05m_Ccp1	Eastern lenses	Breccia	4.4	0.3
WB-12-106A-561.05m_Ccp2	Eastern lenses	Breccia	4.0	0.3
WB-12-106A-561.05m_Ccp3	Eastern lenses	Breccia	4.1	0.3
WB-12-108_670.75m_Ccp1	Eastern lenses	Massive	1.3	0.3
WB-12-108_670.75m_Ccp2	Eastern lenses	Massive	1.3	0.3
WB-12-108_670.75m_Ccp3	Eastern lenses	Massive	1.3	0.3
WB-12-109_578.6m_Ccp1	Eastern lenses	Veinlet	2.5	0.4
WB-12-109_578.6m_Ccp2	Eastern lenses	Veinlet	2.8	0.4
WB-12-109_578.6m_Ccp3	Eastern lenses	Veinlet	2.8	0.3
WB-12-111_452.5m_Ccp1	Eastern lenses	Massive	2.2	0.3
WB-12-111_452.5m_Ccp2	Eastern lenses	Massive	2.9	0.2
WB-12-111_452.5m_Ccp3	Eastern lenses	Massive	2.0	0.6

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