Depositional setting of the Late Archean Fe oxide- and sulfide-bearing chert and graphitic argillite in the Shaw Dome, Abitibi greenstone belt, Canada

Hiebert R.S. [1, *], Bekker A. [1, 2], Houlé M.G. [3], Rouxel Olivier [4, 5]

[1] Department of Geological Sciences, University of Manitoba, Winnipeg, MB R3T 2N2, Canada
[2] Department of Earth Sciences, University of California, Riverside, CA, 92521, USA
[3] Geological Survey of Canada, Québec, QC G1K 9A9, Canada
[4] IFREMER, Centre de Brest, Unité Géosciences Marines, Plouzané, France
[5] Department of Oceanography, University of Hawaii at Manoa, HI 96822, USA

* Corresponding author : R. S. Hiebert, email address :

Abstract :

Interbedded chert-rich exhalite and graphitic argillite are the only sedimentary rocks deposited in deep-water settings during long-lived hiatuses in mafic to ultramafic volcanism within the Hart area of the Shaw Dome in the Late Archean Abitibi greenstone belt in Canada. The Fe oxide- and sulfide-bearing, but predominantly cherty, exhalite lithological unit in the Hart area can be traced laterally to iron formation elsewhere in the Shaw Dome. Whole-rock as well as Fe and S isotope geochemistry suggest that the exhalite unit was formed as a result of direct precipitation from seawater, distally from hydrothermal centres. Fractionation of Fe isotopes through the precipitation of iron oxyhydroxides in a neutrally buoyant hydrothermal plume removed the heavier isotopes of Fe, resulting in the negative δ^{56}Fe values observed in the exhalite in the Hart area. Archean seawater is generally considered to be anoxic, but moderate Mn enrichments (up to 1.87 weight% MnO) in exhalite along with negative Fe isotope values resulting from partial Fe(II) oxidation suggest the presence of oxygen in the upper part of the water column along the pathway of hydrothermal plumes from their source to the depositional site in the Abitibi greenstone belt. In contrast, the graphitic argillite contains abundant pyrite nodules and bands that exhibit systematic negative Fe isotope values, but does not show Mn enrichment. This unit likely formed in a zone of upwelling of nutrient-rich waters from deeper parts of the basin resulting in high organic productivity. Both exhalite and graphitic argillite have negative Δ^{33}S values, suggesting that sulfur was derived from seawater sulfate, which is consistent with an anoxic atmosphere with sulfate aerosols produced by photochemical reactions. Combined, our data indicates disequilibrium between anoxic atmosphere and partially oxygenated upper part of the water column during periods of volcanic quiescence in the ~2.7 Ga Abitibi greenstone belt supporting the existence of oxidized oases within the Archean ocean.

34   **Introduction**

35   It is widely accepted that the Archean atmosphere contained little or no oxygen (Farquhar et al.,

36   2011), with multiple S isotope data constraining the level of oxygen in the Archean atmosphere to less

37   than 10^{-5} PAL (e.g., Farquhar et al., 2000, 2001; Pavlov and Kasting, 2002). At the same time, multiple

38   studies using trace element and stable isotope data indicate the presence of low oxygen levels, locally or

39   episodically in the Archean ocean (e.g., Anbar et al., 2007; Kaufman et al., 2007; Reinhard et al., 2009;

40   Riding et al., 2014; Fralick and Riding, 2015), in highly productive areas of continental margins (e.g.,

41   Olson et al., 2013; Planavsky et al., 2014), or in continental settings in association with microbial mats

42   (e.g., Lalonde and Konhauser, 2014). The current view of Archean surface redox conditions is that the

43   anoxic atmosphere was in disequilibrium with locally and/or episodically oxidized continental and

44   nearshore oceanic settings (e.g., Lyons et al., 2014). The extent of these oxidized oases, however,

45   remains uncertain and is still debated (e.g., Lalonde and Konhauser, 2014).

46   Evidence in support of locally developed oxidizing environments includes Mn enrichment in

47   Archean sedimentary rocks (Maynard, 2014). Mn enrichment occurs under most modern and

48   Phanerozoic marine redox conditions due to the precipitation of Mn-oxyhydroxides, and their

49   formation, even though bacterially mediated, requires presence of at least low levels of oxygen. As such,

50   sedimentary Mn deposits and Mn enrichments in sediments are rare in the Archean sedimentary record

51   (Maynard, 2014).

52   As previously suggested (Rouxel et al., 2005; von Blanckenburg et al., 2008; Steinhoefel et al.,

53   2009; Tsikos et al., 2010; Planavsky et al., 2012; Busigny et al., 2014; Kurzweil et al., 2016), anoxygenic

54   phototrophic oxidation could have established significant water column Fe concentration gradients –

55   and therefore Fe isotope trends – through ferric Fe removal during upwelling. However, several cases of

56   Archean and early Paleoproterozoic Mn-rich iron formations with highly negative Fe isotope values have

57   been documented recently (e.g., Rouxel et al., 2005; Tsikos et al., 2010; Planavsky et al., 2012; Haugaard

58   et al., 2016; Mendes et al., 2016; Lantink et al., 2018), potentially indicating an extreme degree of Fe

59   depletion in an expanding hydrothermal plume in association with precipitation of iron oxyhydroxides

60   and, ultimately, Mn oxidation. Recently, Ossa Ossa et al. (2016) found Mn to be present in carbonates,

61   orthosilicates, oxides, phyllosilicates, and pyrite in Mn-rich shales and BIFs of the Mesoarchean Mozaan

62   Group within the Pongola Supergroup in South Africa. However, it still remains unknown whether these

63   rare occurrences of Mn-enrichment reflect short-lived periods of atmospheric oxygenation or localized

64   marine oxygen oases.

65   The Hart deposit within the Abitibi greenstone belt is a komatiite-associated Ni-Cu-(PGE)

66   magmatic sulfide deposit that has derived much of the sulfur from the underlying metasedimentary

67   rocks (Hiebert et al., 2016). The predominant sulfur source rock has been considered to be sulfur-rich

68   iron formation (Houlé et al., 2010b), but locally it is significantly more silica-rich, and iron oxide-poor,

69   than the typical iron formation leading to it being referred to as a lean iron formation. This unit also

70   contains zones of significant sulfide accumulation as pyrrhotite- and pyrite-rich bands and lenses.

71   Although this unit is regionally interpreted as a true iron formation, the prevalence of silica-rich, and

72   iron oxide-poor, assemblage, as well as the abundance of sulfides in the vicinity of the Hart deposit

73   suggests that some environmental, depositional, or chemical conditions were different than elsewhere

74   along strike. Additionally, Bekker et al. (2010) argued that true iron formation should not contain

75   significant concentrations of sulfides, and that rocks previously classified as "sulfide-facies iron

76   formations" may be actually sulfide-rich shales or barren sulfide (e.g., lacking base-metal mineralization)

77   exhalative deposits formed from hydrothermal fluids either distally from the vent or under low-

78   temperature conditions.

79   In the Abitibi greenstone belt, periods of widespread sedimentation have been shown to

80   represent long-lived hiatuses in the rapid accumulation of volcanic rocks, during which siliciclastic and

81   chemical sedimentary rocks slowly accumulated (Thurston et al., 2008). These sedimentary rocks thus

82 provide an insight into seawater composition and redox conditions as well as marine processes at the

83 time of magmatic quiescence in the Archean ocean. In this study, we seek to constrain the depositional

84 environment and diagenetic history of the exhalite and graphitic argillite lithologies within the Hart area

85 of the Shaw Dome in the Abitibi greenstone belt through the comparison with two end-member

86 processes. As iron formations are thought to be related to hydrothermal activity (Isley, 1995; Beukes

87 and Gutzmer, 2008; Bekker et al., 2010), purely hydrothermal deposition of exhalative chert, iron oxides,

88 and sulfides is considered as one end-member. The second end-member would be precipitation from

89 ambient seawater directly unrelated to hydrothermal processes and may or may not be aided by

90 biological activity (e.g., Li et al., 2015). We evaluate these two possible end-members using petrographic

91 analysis of the sedimentary unit as well trace element and rare-earth element (REE) geochemistry to

92 determine the chemical nature of the water column, along with multiple isotopes of sulfur and iron to

93 determine the sources of these elements in the Fe-oxides and Fe-sulfides present in the sedimentary

94 rocks. Additionally, we address the possibility that the chert exhalites and graphitic argillites were

95 deposited during volcanic quiescence in the ca. 2.7 Ga Abitibi greenstone belt within a localized, marine

96 oxidized oasis by studying geochemical proxies that constrain atmospheric and local marine redox

97 conditions.

98   **Geological Setting**

99   The volcano-sedimentary succession of the Late Archean Abitibi greenstone belt has been

100 previously subdivided into 9 volcanic and sedimentary episodes, in which long-lived hiatuses in the rapid

101 emplacement of volcanic rocks are represented by slowly accumulated sedimentary deposits (Thurston

102 et al., 2008; Houlé and Lesher, 2011; Thurston et al., 2012). Conventionally, the Abitibi greenstone belt

103 has been interpreted to have been developed autochthonously, with the volcanic sequences tectonically

104 stacked upon each other, with only the younger Temiskaming and Porcupine sequences deposited in

105 transtensional, pull-apart basins (e.g. Thurston and Chivers, 1990). Recently, however, it has been

106 suggested that the volcanic rocks of the Abitibi greenstone belt were formed within a rift environment

107 in which feeder dykes of the younger volcanic units crosscut older units, indicating autochtonous

108 position (Ayer et al., 2002; Ayer et al., 2005; Ketchum et al., 2008; Thurston et al., 2008). Importantly,

109 younger volcanic rocks contain zircon xenocrysts derived from older volcanic rocks suggesting that the

110 volcanic sequences developed on top of each other (Ayer et al., 2002; Ayer et al., 2005; Thurston et al.,

111 2008). In the Shaw Dome, the volcano-sedimentary succession is composed of the following units

112 (Figure 1; Thurston et al., 2008; Houlé and Lesher, 2011; Thurston et al., 2012):

113   1) massive and pillowed, intermediate volcanic rocks and thin, but laterally extensive, iron

114   formations of the 2734–2724 Ma volcanic sequence (Deloro);

115   2) felsic to intermediate, volcaniclastic rocks intercalated with komatiitic dikes, sills, lavas, and

116   less extensive iron formations in the lower part of the 2710 – 2704 Ma volcanic sequence

117   (lower Tisdale);

118   3) intercalated, tholeiitic, mafic, and komatiitic volcanic rocks of the middle part of the 2710 –

119   2704 Ma volcanic sequence (middle Tisdale); and

120   4) calc-alkaline, felsic to intermediate volcanic rocks in the upper part of the 2710–2704 Ma

121   volcanic sequence (upper Tisdale; Houlé et al., 2010a, b; Houlé and Lesher, 2011).

122   Felsic to intermediate, volcanic and sedimentary rocks of the lower Tisdale sequence, overlain

123 by komatiitic and basaltic lava flows of the middle Tisdale sequence outcrop in the Hart area. At the

124 base of the middle Tisdale volcanic package, komatiitic lava flows have thermomechanically eroded a

125 wide (>200 m) channel into its footwall rocks, which are dominantly composed of felsic to intermediate,

126 volcanic and volcaniclastic rocks with lesser amounts of chert, graphitic argillite, and minor iron

127 formation of the regional lower Tisdale volcanic package (Figure 2; Houlé et al., 2010b). The chert and

128 graphitic argillite appear to be interbedded on a meter-scale at and stratigraphically below the channel

129   in drill cores. For simplicity, the prefix meta- will be omitted in the following description, but all rocks in

130   the study area have been metamorphosed under lower to upper greenschist facies conditions

131   (Thompson, 2005).

132   *Description of Sedimentary Lithologies in the Hart Area*

133   Regionally, the exhalite unit is generally continuous on the scale of several kilometers, and has

134   been mapped and classified as iron formation, although in many locations it is described as a lean or

135   chert-rich iron formation (Houlé et al., 2010b). However, based on the predominance of chert and silica-

136   rich lithologies in the vicinity of the Hart deposit, it has been reclassified as a distal exhalite by Hiebert et

137   al. (2016; Figure 3a), since it is interpreted to have largely been formed through an exhalative process

138   (cf. Ridler, 1971). The exhalite unit typically contains thin laminae of Fe-oxides or sulfides (Figures 3b, c;

139   e.g., sample H11-16-411.4; 86.2% SiO_2, 10.9% Fe_2O_3), but lacks any other sedimentary structures.

140   Locally, the chert or silica-rich lithologies grade into typical banded iron formation (e.g., sample H11-

141   13C-387.2; 41.73% SiO_2, 37.44% Fe_2O_3) or massive sulfide composed of pyrrhotite and pyrite, but these

142   sulfidic lithologies are thought to extend for only a few tens of meters, and cannot be traced between

143   drill holes and outcrops. The sulfides within the exhalite typically contain fine-grained pyrrhotite (0.1 –

144   0.2 mm in size) that appears to have been locally replaced by pyrite (0.25 – 0.6 mm in size), which still

145   contains inclusions of pyrrhotite (Figure 3d). The sulfides form lenses or are found to be replacing Fe-

146   oxide laminae. The unit also contains minor silicates, such as actinolite and chlorite as replacement

147   minerals, and calcite as a replacement mineral and, possibly, as cement.

148   The graphitic argillite is only observed in the drill core in the eastern part of the Hart property.

149   Based on visual estimates with optical microscope and geochemical data, it is composed of 35 – 50%

150   graphite by volume (TOC content is up to 17.6 wt.% with the average of 8.5 wt.%) and 10 – 40% sulfide

151   by volume (TS content is up to 47.4 wt.% with the average of 28.0 wt.%), with variable amounts of

152   metamorphic chlorite, epidote, actinolite, and quartz (10 – 60 wt.% SiO_2; Figures 4a, b). Sulfide in the

153   graphitic argillite takes two forms, large (1 – 1.5 cm in diameter) pyrite nodules and bands (Figure 4c), or

154   finely disseminated pyrite (<0.1 mm in diameter; Figure 4d).

155   **Multiple S and Fe Isotope Background**

156   The majority of earlier research attempted to characterize the processes producing the sulfides

157   in sedimentary rocks using $\delta^{34}S$ values, but the range of sulfur isotope values recorded in Archean

158   supracrustal rocks is much smaller than that in Phanerozoic examples, commonly resulting in near-to-

159   mantle $\delta^{34}S$ values (Ripley, 1999). This can lead to a difficulty in identifying the processes responsible for

160   the origin of these sedimentary sulfides. The values of $\delta^{34}S$ are expressed in parts per thousand (‰ or

161   per mil), and are defined as:

$$\delta^{34}S = 1000 * \left(\frac{\frac{^{34}S}{^{32}S}\,sample}{\frac{^{34}S}{^{32}S}\,V-CDT} - 1\right)$$

162   where V-CDT is a reference scale defined by the isotopic composition of IAEA-S-1, a sulfur reference

163   material distributed by the International Atomic Energy Agency (IAEA, Vienna), and calibrated to have

164     $\delta^{34}S_{IAEA-S-1} \equiv -0.3‰$ based on the historical Canõn Diablo Troilite reference material (Coplen and Krouse,

165   1998). A similar formula is used to calculate $\delta^{56}Fe$, with masses 56 and 54 forming the ratio and IRMM-

166   14 used as the reference standard (see recent review by Dauphas et al., 2017).

167   Under oxygenated Earth's surface conditions, sulfur isotope fractionation is controlled strictly by

168   relative isotope mass differences and, therefore, is a completely mass-dependent process. However, as

169   a result of photochemical reactions in the Archean anoxic atmosphere, atmospherically processed

170   Archean sulfur exhibits widespread mass-independent fractionation that can be characterized by the

171   difference between the $\delta^{33}S$ value expected from normal mass-dependent fractionation and the

172   measured $\delta^{33}S$ value (Farquhar and Wing, 2003). It can be calculated using measured $\delta^{33}S$ and $\delta^{34}S$

173   values (in per mil) as:

174 $$\Delta^{33}S = \delta^{33}S - \left[\left(\frac{\delta^{34}S}{1000} + 1\right)^{\lambda_{RFL}} - 1\right] \times 1000$$

175   where the λ_{RFL} has been defined as the slope of the reference fractionation line for [33]S and [34]S isotopes

176   equal to 0.515.

177   Photochemically fractionated sulfur can then be delivered to seawater and ultimately

178   sediments. Two isotopically distinct sulfur pools were formed by the photochemical reactions in the

179   Archean atmosphere: 1) a reduced pool with positive Δ^{33}S and δ^{34}S values, and 2) an oxidized pool with

180   negative Δ^{33}S and δ^{34}S values (e.g., Farquhar et al., 2002; Ono et al., 2003; Figure 5). The reduced pool is

181   inferred to have been delivered to the Archean ocean as either elemental sulfur (S^0) aerosols or sulfide

182   (S^{2-}), which then reacted with Fe^{2+} dissolved in the anoxic seawater and precipitated as disseminated Fe-

183   sulfide in sediments (Ono et al., 2009; Maynard et al., 2013; Marin-Carbonne et al., 2014). The oxidized

184   sulfur pool, delivered from the atmosphere as sulfate aerosols, is thought to have been either reduced

185   by bacterial metabolism and incorporated into paleosols on the continents (Maynard et al., 2013), or

186   added to seawater as dissolved sulfate (Farquhar et al., 2002). Once delivered to seawater, sulfate was

187   either reduced via bacterial sulfate-reducing metabolism to form eventually pyrite nodules in organic

188   matter-rich sediments during diagenesis, or cycled through submarine hydrothermal systems. Under

189   hydrothermal conditions, seawater sulfate is first precipitated as Ca-sulfate (anhydrite), with a

190   remaining fraction becoming eventually reduced at high temperature and vented at the seafloor as H_2S-

191   rich hydrothermal fluids forming barren massive sulfide lenses distally and base-metal volcanogenic

192   massive sulfide deposits proximally to hydrothermal centers (e.g., Bekker et al. 2009; Jamieson et al.,

193   2013). A significant fraction of anhydrite is redissolved as aging and cooling oceanic crust is transported

194   away from spreading mid-ocean ridges (Alt, 1995).

195   Once in aqueous phase either on the land or in the ocean, the near-to-zero to negative δ^{34}S

196   values of SO_2-derived sulfate could have been further modified by mass-dependent processes; for

197   example, by bacterial or thermochemical seawater sulfate reduction, resulting in nodules or layers of

198   sulfides in sediments with variable $\delta^{34}S$ values, but with consistently negative $\Delta^{33}S$ values (Ono et al.,

199   2003, 2009; Bekker et al., 2009; Marin-Carbonne et al., 2014). Unlike in modern oceans, however,

200   Archean seawater had relatively high iron content, but low sulfate concentrations, less than 80-200

201    $\mu mol\ L^{-1}$ (Habicht et al., 2002; Jamieson et al., 2013), which resulted in small sulfur isotopic

202   fractionations during bacterial sulfate reduction in a closed to semi-closed pore-water system due to

203   much faster sulfate reduction with respect to sulfur transport rates (Brunner and Bernasconi, 2005;

204   Detmers et al., 2001). As a result of nearly complete reduction of seawater sulfate in anoxic, organic

205   matter-rich sediments, Archean pyrite does not exhibit the large variations in $\delta^{34}S$ values seen in

206   modern marine sediments.

207   Iron isotope fractionation is thought to be dominantly controlled by redox reactions. Igneous

208   rocks typically have $\delta^{56}Fe$ values of ~0.1‰ (e.g., Beard et al., 2003; see also recent review by Dauphas et

209   al., 2017), but redox reactions under surface conditions, as recorded by sedimentary rocks with

210   significant authigenic Fe enrichment (e.g., iron formations and black shales), tend to fractionate Fe in

211   oxidized Fe-mineral species towards positive $\delta^{56}Fe$ values (e.g., Planavsky et al., 2012), and in reduced

212   Fe-mineral species towards negative $\delta^{56}Fe$ values (e.g., Rouxel et al., 2005). During oxidative

213   precipitation from fluids containing dissolved Fe^{2+}, redox reactions will preferentially remove the heavier

214   isotopes of Fe with oxidized phases resulting in residual iron in the fluid having a lower $\delta^{56}Fe$ value. For

215   example, precipitation of magnetite corresponds to a fractionation factor $\Delta^{56}Fe_{Fe(II)aq-magnetite}$ ~-1.3‰

216   (Johnson et al., 2005), while precipitation of goethite and ferrihydrite (HFO) results in $\Delta^{56}Fe_{Fe(II)aq-goethite}$ ~-

217   1‰ (Beard et al., 2010) and $\Delta^{56}Fe_{Fe(II)aq-HFO}$ ~-3.2‰, respectively (Wu et al., 2011). The "reservoir" effects

218   during partial Fe^{2+} oxidation have been well demonstrated in biotic and abiotic experimental studies

219   (e.g., Balci et al., 2006; Croal et al., 2004) and in modern redox-stratified aqueous environments (Busigny

220   et al., 2014; Rouxel et al., 2008, 2017). Dissimilatory Fe^{3+} reduction (DIR), which is known to produce

221   isotopically light Fe in diagenetic environments (Crosby et al., 2007; Tangalos et al., 2010; Percak-

222   Dennett et al., 2011), may also produce a Fe^{2+} pool with negative $\delta^{56}Fe$ values. A clear distinction

223   between these two mechanisms (i.e., partial Fe^{2+} oxidation versus partial Fe^{2+} reduction) as the source of

224   isotopically light Fe^{2+} has been generally difficult to draw, even in modern marine or diagenetic

225   environments (Severmann et al., 2008; Chever et al., 2015). Both low and high-temperature alteration of

226   oceanic crust by seawater leads to the preferential release of more soluble Fe^{2+}, resulting in seafloor

227   hydrothermal fluids having $\delta^{56}Fe \leq 0‰$ (Rouxel et al., 2003; Rouxel et al., 2008). As pyrite is often

228   precipitated through a mackinawite ($FeS_{0.9}$) precursor, it preferentially incorporates the lighter isotopes

229   of Fe, resulting in $\delta^{56}Fe$ values of the sulfide to be 0.3 to 0.9‰ lower than residual dissolved Fe^{2+} (Butler

230   et al., 2005; Guilbaud et al., 2011). Further (i.e., partial) conversion to pyrite might also result in

231   additional fractionation, resulting in final values of $\delta^{56}Fe$ that are 1.7 to 3.0‰ lower than the initial

232   dissolved Fe^{2+}. Therefore, Fe delivered to the oceans by hydrothermal fluids, and any Fe-sulfides

233   precipitated from these fluids, typically have slightly negative $\delta^{56}Fe$ values, although heavier values of

234   the hydrothermal Fe flux are expected in the case of extensive Fe-sulfide precipitation in hydrothermal

235   plume environments (Bennett et al., 2009; Rouxel et al., 2016; Lough et al., 2017). There are several

236   notable exceptions of Fe-oxide iron formations of Archean and Paleoproterozoic age with negative Fe

237   isotope values that are typically Mn-enriched and largely deposited in shallow-water settings (e.g.,

238   Rouxel et al., 2005; Tsikos et al., 2010; Planavsky et al., 2012; Haugaard et al., 2016; Mendes et al., 2016;

239   Lantink et al., 2018). Their iron isotope values are considered to be the result of reservoir effects (e.g.

240   Rayleigh distillation) associated with the earlier removal of Fe-oxides and oxyhydroxides resulting in

241   negative $\delta^{56}Fe$ values of the residual Fe in the spreading hydrothermal plume distally from the

242   hydrothermal vents (Planavsky et al., 2012).

243 **Material Analyzed and Analytical Methods**

244 *Sampling Methodology*

245   All samples (n=27) for this project were selected from drill cores and surface trenches produced

246 by Northern Sun Mining Corp. (Table 1). Sampling of drill cores and surface trenches was conducted to

247 obtain a wide range of lithologies from the exhalite and graphitic argillite units.

248 *Major and Trace Element Geochemistry*

249   Samples were analyzed for major, trace, and rare-earth elements in two laboratories: The

250 Ontario Geological Survey Geoscience Laboratories (Geo Labs; Sudbury, Ontario) and the Acme

251 Laboratories (Acme Labs; Vancouver, British Columbia). All the materials were crushed at the Stable

252 Isotopes for Innovative Research (SIFIR) laboratory at the University of Manitoba to a fine powder (200

253 mesh) using an agate puck mill before the pulps were sent to these laboratories for geochemical

254 analysis. At Geo Labs, major elements were determined by mixing sample powder with a borate flux and

255 heating to create a glass bead, which was analyzed by X-ray fluorescence (XRF), and trace, including

256 rare-earth, elements were measured on an inductively coupled plasma-mass spectrometer (ICP-MS)

257 after digestion in a closed vessel using multi-acid technique. At Acme Labs, samples were prepared via a

258 lithium borate fusion and were analyzed for major elements by ICP-ES, and for trace elements by ICP-

259 MS. In both labs, total C and S were determined by oxidation through combustion of the sample in an

260 oxygen-rich environment and detection of CO_2 and SO_2 by infrared absorption (LECO elemental

261 analyzer). Both labs use duplicate analyses of samples and certified reference materials to confirm the

262 precision and accuracy of data.

263 *Bulk Rock S Isotope Analysis*

264   Samples were prepared using the same analytical protocol as that of Hiebert et al. (2015), and

265 analyzed at the Stable Isotope Laboratory of the Department of Earth and Planetary Sciences, McGill

266   University. The sulfur isotope compositions are reported on the V-CDT scale, and the $\Delta^{33}S$ value of

267   reference material IAEA-S-1 is taken to be 0.094‰ based on repeated analysis of the standard at this

268   facility. Repeat analyses throughout the entire analytical procedure returned 2σ uncertainties on $\delta^{34}S$

269   and $\Delta^{33}S$ values that are <0.25 and <0.01‰, respectively.

270   *Fe Isotope Analysis*

271   Aliquots of sample powders were dissolved for Fe isotope analysis using the same method as

272   described in Rouxel et al. (2005) and Hiebert et al. (2015) at the Pôle Spectrométrie Océan, IFREMER

273   (Brest, France). Internal precision of data was determined through duplicate analysis of internal

274   reference standards IF-G (iron formation), BHVO-1 (Hawaiian Island basalt), and DTS-1 (Cr-rich

275   ultramafic rock), and the long-term external reproducibility is 0.08‰ for $\delta^{56}Fe$ values (2σ). Fe isotope

276   values are reported relative to the standard IRMM-14, using the conventional delta notation (Table 1).

277   *Microbeam Analysis*

278   Two samples were selected for analysis on a Cameca SX100 electron microprobe at the

279   University of Manitoba. These samples (H11-13C-387.2 and H11-08-63.9) were analyzed using energy

280   dispersive x-ray spectroscopy (EDS) to determine the mineral(s) that host Mn in exhalite.

281   **Results**

282   *Major and Trace Element Geochemistry*

283   Major element variations generally reflect the lithology and dominant mineralogy, with chert-

284   rich and iron oxide-rich varieties having high SiO_2 and Fe_2O_3 contents (Table 1). Some samples have

285   compositions controlled by the abundance of pyrrhotite and pyrite, with high Fe_2O_3 and SO_2, but low

286   SiO_2. In general, low concentrations of TiO_2 and Al_2O_3 are found in all samples of exhalite, with the

287   exception of high Al_2O_3 (17.01 wt.%) found in a sample of silicate-rich iron formation with high sulfide

288   content. Notably, all exhalite samples are enriched in MnO above the crustal levels of ~0.1 wt. %

289   (Rudnick and Gao, 2014) with values as high as 1.87 wt.%. Graphitic argillite samples have extremely

290   variable compositions depending on the abundance of graphite, pyrite, and silicate minerals.

291   Several trace element concentrations, and rare earth element patterns and anomalies in

292   chemical sediments, including cherts and iron formations, have been used to describe the composition

293   and redox state of the ancient water column in recent publications (e.g., Bolhar et al., 2004; Barrie,

294   2005; Kato et al., 2006; Frei et al., 2008; Bekker et al., 2013; Planavsky et al., 2010; Thurston et al.,

295   2012). Graphitic argillite samples from the Hart area typically have low, but variable, Zn concentration,

296   with the range of values from 3 to 734 ppm. Mo concentrations of 0.3 to 10.9 ppm are also comparable

297   to data for shales of similar age (Scott et al., 2008). Importantly, almost all samples have Mo

298   concentrations above average crustal levels of 1 to 2 ppm and 0.07 ppm/wt.%, respectively (Rudnick and

299   Gao, 2014). In addition, concentrations of U are also very low compared to crustal average: 0.03 to 0.77

300   ppm (with the average of 0.22 ppm) for exhalite, and 0.36 to 0.59 ppm (with the average of 0.47 ppm)

301   for graphitic argillite, which is below various estimates for average crustal levels of 1.5 to 2.8 ppm (see

302   Rudnick and Gao, 2014).

303   The abundances of rare earth elements have been normalized to the Post-Archean average

304   Australian Shale (PAAS) as it is the most commonly used reference for normalizing similar lithologies,

305   allowing for easy comparison to previous work (Figure 6; refer to Table 3 for data and formulas used to

306   calculate anomalies). The exhalite has generally positive anomalies for Eu and Y (Figure 6b). A significant

307   positive Eu anomaly (Eu/Eu*; see Table 3 for method of calculation of REE anomalies), ranging from 1.2

308   to 8.1, is found in all exhalite samples. Exhalite samples have a wide range of Ce anomalies, both

309   positive and negative, with values ranging from 0.41 to 1.30, with positive Ce anomalies not created as

310   an artifact of a positive La anomaly influencing the calculation (Figure 6a; Table 3). Values for Y/Ho ratio

311   have a wide range from 32.6 to 70.0, but are generally superchondritic, similar to those found in

312   seawater (Bolhar et al., 2004). The rare earth element (REE) patterns also show a general heavy-REE

313   (HREE; Figure 6b) enrichment as indicated by normalized Pr/Yb and Gd/Yb ratios ranging from 0.12 to

314   0.99 and 0.51 to 1.76, respectively, similar to modern hydrogenous chemical sediments (Table 1; Bau,

315   1999).

316   The graphitic argillites lack significant anomalies for Ce and Y, but have positive Eu anomalies

317   (1.28 to 2.55; see Figure 7). Values for Y/Ho have a narrow range from 27.3 to 29.0 and are lower than

318   those for modern seawater and close to those of chondrites (~26), indicating limited uptake of REE from

319   seawater. The rare earth element (REE) data for graphitic argillites also shows a predominantly flat

320   pattern (Figure 7b), with only weak HREE enrichment as shown by normalized Pr/Yb and Gd/Yb values

321   ranging from 0.92 to 1.09 and 0.61 to 0.78, respectively (Table 3).

322   *Petrography and Scanning Electron Microscopy (SEM)*

323   High Mn concentrations within the exhalite unit were further investigated to determine the

324   mineral host of Mn. The EDS analyses of exhalite samples found that Mn was hosted predominantly in

325   carbonates, chlorite, and actinolite (Figure 8). No significant Mn enrichment was observed in sulfides

326   and oxides. The presence of Mn in carbonates and metamorphic silicates, without significant

327   enrichments in sulfides and oxides, suggests that Mn was not likely to have been hosted in the

328   oxyhydroxides during early diagenesis, but may have been adsorbed to the surface of clay minerals and

329   later incorporated into diagenetic carbonates.

330   *Stable Isotopes*

331   Sulfur isotope data have been used as a tracer of biological activity in modern and ancient

332   aqueous environments, and, in the case of Archean rocks, also contain a record of atmospheric reactions

333   (e.g., Farquhar et al., 2000; Ono et al., 2003, 2009). On a plot of $\delta^{34}S$ against $\delta^{33}S$ values for sediments

334   from the Hart area, the data forms a trend offset from, but generally parallel to the terrestrial

335   fractionation line (TFL) that follows mass-dependent fractionation (Figure 9a). The offset from the TFL is

336   due to non-mass dependent fractionation in the Archean atmosphere (Farquhar et al., 2000), and the

337   magnitude and consistency of this offset is expressed on a plot of $\delta^{34}S$ against $\Delta^{33}S$, where values along

338   the TFL would plot with $\Delta^{33}S = 0‰$ (Figure 9b).

339   Exhalite samples have a large range of $\delta^{34}S$ values, -11.4 to +7.6‰ (n=24), and an average value

340   of -2.1‰ (Figure 8b; Table 2). The $\Delta^{33}S$ values have a much smaller, and consistently negative, range

341   from -1.37 to -0.34‰, with an average value of -0.62‰.

342   Graphitic argillite samples have much more restricted range of $\delta^{34}S$ values than the exhalite,

343   with the range of +1.6 to +5.0‰ (n=3). This positive range, although overlapping with that of the

344   exhalite, has a positive average value of +3.4‰, significantly different from that of the exhalite. The $\Delta^{33}S$

345   values of the graphitic argillite have a small, and consistently negative, range, similar to that of the

346   exhalite, -0.94 to -0.19‰, with an average value of -0.47‰ (Figure 9b). This suggests that sulfur in

347   sulfides in the graphitic argillite was likely derived from the same sulfate source as the exhalite sulfides.

348   The bulk-rock $\delta^{56}Fe$ values of both the exhalite and graphitic argillite are systematically negative.

349   The exhalite exhibits a range of -2.13 to -0.85‰ (n=18), with an average value of -1.69‰. The graphitic

350   argillite exhibits a range of -1.96 to -1.66‰ (n=3), with an average value of -1.82‰ (Figure 10).

351   Considering that co-existing Fe-bearing minerals in such samples may have distinctly different $\delta^{56}Fe$

352   values, it is important to relate bulk-rock $\delta^{56}Fe$ signature and mineralogy. For example, the various

353   proportions of isotopically light pyrite (or isotopically heavy Fe-oxides) and lithogenic components with

354    $\delta^{56}Fe = 0.09‰$ may produce a significant range in bulk $\delta^{56}Fe$ values (e.g., Duan et al., 2010; Severmann

355   et al., 2008; Rouxel et al. 2016). As shown in Figure 11, there is no significant correlation between $\delta^{56}Fe$

356   values and S concentration, suggesting that variations in $\delta^{56}Fe$ are not a result of mixing between

357   isotopically light pyrite and lithogenic components.

358   **Discussion**

359   *Environmental Implications of Major and Trace Element Data*

360   Generally low TiO_2 and Al_2O_3 concentrations in the exhalite unit indicate low detrital input (cf.

361   Slack et al., 2007), and, when plotted against each other (Figure 12a), show no apparent trend. Similarly,

362   Zr versus TiO_2 plot shows no apparent trend (Figure 12b). The trends found within the graphitic argillite

363   data, however, show the expected pattern for detrital contribution to sediments (Figures 12a and b; cf.

364   Pecoits et al., 2009). When recalculated to elemental weight percent, ratios of Fe/Ti and Al/(Al+Fe+Mn)

365   can be used to show a continuum between the exhalite and graphitic argillite units, suggesting

366   precipitation from a mixture of hydrothermal fluids and seawater for exhalite, and some influence of

367   hydrothermal fluids on the predominantly detrital material in the graphitic argillite (Figure 12c; cf.

368   Bonatti et al., 1972; Böstrom et al., 1969; Böstrom, 1973; Pecoits et al., 2009).

369   The trace element concentrations and ratios, and rare-earth element anomalies in the Hart area

370   sediments provide insight into the composition and redox state of the water column at their

371   depositional site (e.g., Bolhar et al., 2004; Kato et al., 2006; Frei et al., 2008; Bekker et al., 2010;

372   Planavsky et al., 2010; Thurston et al., 2012). When compared to data for Precambrian shales (Robbins

373   et al., 2013; Scott et al., 2008; 2013), the low Zn and Mo concentrations in graphitic argillites from the

374   Hart area, and the ratio of Zn (ppm)/Al_2O_3 (wt.%) fall within the range of values compiled by Scott et al.

375   (2008, 2013) for organic-rich shales deposited in the anoxic Archean oceans.

376   Partin et al. (2013a, b) evaluated U concentrations and authigenic U enrichment (U_{auth}=U – Th/3)

377   in the Archean, prior to the rise of atmospheric oxygen, for both iron formations and black shales. In the

378   Archean iron formations, before the rise of atmospheric oxygen between ca. 2.45 and 2.32 Ga (e.g.,

379   Bekker et al., 2004; Gumsley et al., 2017), very low U concentrations and U_{auth} enrichments were found

380   (Partin et al., 2013a), and in the Hart exhalites U concentrations are comparable to the typical values

381   found in the similar Archean deposits (Barrie, 2005; Partin et al., 2013a). In the Archean black shales,

382   Partin et al. (2013b) found average U concentration and U_{auth} enrichment of 3.8 ppm and 0.9 ppm,

383   respectively. Graphitic argillites from the Hart area have U concentrations well below the average value

384   for the Archean shale (Partin et al., 2013b). Low, pre-GOE (Great Oxidation Event) levels are also

385   observed in our samples for other trace elements such as Co (cf. Swanner et al., 2014), and Cr (cf.

386   Konhauser et al., 2011). Combined, this trace element dataset suggests deposition under a generally

387   anoxic water column, although the rapid precipitation of Fe in modern hydrothermal settings (e.g., in

388   distal part of hydrothermal plume where seafloor microbial mats grow) would be also consistent with

389   such signatures (Rouxel et al., 2016, 2017). However, Mn concentrations in exhalite samples are

390   anomalously high for anoxic environments. The possible link between Mn enrichment and localized

391   oxygenated oases in the Archean ocean, proposed in previous studies (cf. Olson et al., 2013; Ossa Ossa

392   et al., 2016; Planavsky et al., 2014), is discussed in more detail below.

393   Positive La, Gd, and Y anomalies have been observed in the modern seawater and have been

394   explained by REE complexation on particle surfaces (e.g., Bolhar et al., 2004). The positive Eu anomalies

395   are common in Archean sediments, and have been interpreted to represent strong influence of high-

396   temperature, hydrothermal, anoxic fluids on seawater composition during that time (e.g., Bau and

397   Dulski, 1996; Bolhar et al., 2004; Slack et al., 2007; Bekker et al., 2010, 2014; Planavsky et al., 2010). By

398   analogy, positive Eu anomalies of the Hart area exhalite indicate influence of hydrothermal fluids on

399   seawater composition at the depositional site and, potentially, relative proximity to high-temperature

400   hydrothermal vents. The rare-earth element (REE) patterns of the Hart area exhalites also show a

401   general heavy-REE (HREE; Figure 6b) enrichment as indicated by normalized Pr/Yb and Gd/Yb values

402   ranging from 0.27 to 0.99 and 0.51 to 1.76, respectively (Table 3). These Pr/Yb values overlap with

403   higher values within the range reported for Abitibi BIFs by Thurston et al. (2012), which were

404   interpreted to characterize BIFs formed in shallower water than those with lower Pr/Yb ratios (Kamber,

405 2010; Thurston et al., 2012). Combined, these REE characteristics of the Hart area exhalites record

406 seawater composition dominated by high-temperature hydrothermal flux.

407 In modern environments, negative Ce anomalies are generated under oxidizing conditions in

408 river waters and seawater, but are dominantly produced by Ce scavenging onto Fe-Mn nodules and

409 crusts in deep, oxygenated ocean waters (Bau and Dulski, 1996; Bau, 1999; Slack et al., 2007). As the

410 deep seawater was unlikely to have been oxygenated during the Archean, fractionation may have

411 occurred locally in environments where REE were scavenged by Fe-Mn particles. The presence of small,

412 true positive and negative Ce anomalies in the exhalite samples could suggest redox cycling of REE

413 coupled to formation and dissolution of Fe-Mn oxyhydroxides. Following the model of German et al.

414 (1991) and Slack et al. (2007), Fe-Mn-rich particles generated in local, shallow oxidized environments

415 (and producing negative Ce anomalies in the upper part of the water column) would have been

416 dissolved below the redoxcline in deeper waters, returning the Ce back to the seawater and erasing any

417 negative Ce anomaly, or even producing a positive Ce anomaly. Whether a similar mechanism could

418 operate in hydrothermal plume-influenced environments remains, however, poorly constrained.

419 The near-chondritic values of Y/Ho for the graphitic argillite are lower than those for the

420 modern seawater and the Hart area exhalites, suggesting that their REE composition is dominated by a

421 detrital signal. Positive Eu anomalies however suggest that significant hydrothermal flux continued

422 during deposition of the graphitic argillite.

423 *Formation of the Graphitic Argillite Unit*

424 The negative δ^{56}Fe values in the graphitic argillite unit are surprising considering the high

425 abundance of detrital/lithogenic material. As mentioned above, the lack of correlation between S and

426 δ^{56}Fe values suggests that the range of δ^{56}Fe values is not solely explained by the contribution of

427 isotopically light Fe-sulfides (i.e., mixing between lithogenic and sulfide components). This likely implies

428 that the Fe incorporated into sulfides and other authigenic (including silicate minerals) phases was

429 derived from water masses with isotopically light Fe as is also envisioned for the exhalite deposits except

430 that there was stronger influence of hydrothermal plumes on water masses from which Fe-

431 oxyhydroxides precipitated to form the exhalite. The abundance of carbon in graphitic argillite unit

432 suggests deposition in an area of high organic productivity, possibly in a zone of upwelling from deeper

433 part of the ocean basin. Low P concentrations, which are lower than expected for modern sediments

434 deposited in areas of high biological productivity, are common to Archean organic matter-rich shales

435 (e.g., Reinhard et al., 2017), suggesting that upwelling zones before the GOE did not receive large

436 amounts of P from deep oceans (Bjerrum and Canfield, 2002).

437 *Formation of the Exhalite Unit*

438 The exhalite unit in the Hart area has many characteristics that distinguish it from typical iron

439 formation. The chert-rich nature with generally low Fe-oxide abundances and abnormally high sulfide

440 and manganese contents suggest that the processes involved in the genesis of the exhalite unit may also

441 differ from those for typical iron formations.

442 As described by Klein (2005), Beukes and Gutzmer (2008), and Bekker et al. (2010), the general

443 model for the genesis of iron formation can be summarized as follows:

444 • Dissolution of Fe from the oceanic crust by hydrothermal fluids and its delivery to the

445 oceans.

446 • Precipitation of Fe-oxyhydroxides, following oxidation of Fe indirectly by oxygenic

447 photosynthesis or directly by anoxygenic photosynthesis, siderite, or Fe-rich clays from

448 ambient waters.

449 • Development of chert hardgrounds via infilling of pores or sediment replacement during

450 early diagenesis at the sediment-water interface when delivery of iron and deposition of

451 iron compounds slowed or stopped.

452   This sequence of events typically produced a combination of geochemical characteristics in iron

453   formations such as: high Y/Ho ratio and positive Eu anomaly, which reflect transport and precipitation

454   from aqueous solutions with a strong hydrothermal input (Bolhar et al., 2004), slight HREE enrichment

455   (Bolhar et al., 2004; Planavsky et al., 2010), and positive δ^{56}Fe values reflecting oxidation of Fe prior to

456   deposition (Rouxel et al., 2005; Bekker et al., 2010; Planavsky et al., 2012). Iron formations should also

457   have little to no synsedimentary sulfide present since iron formations reflect ferruginous rather than

458   euxinic water column conditions (Bekker et al., 2010).

459   The geochemistry and petrography of the exhalite unit in the Hart area suggests a somewhat

460   different genesis. The negative, and highly variable, δ^{56}Fe values from all samples, including those that

461   resemble typical iron formation, are more commonly associated with sulfides from Archean organic

462   matter-rich sediments or carbonate-facies iron formations than oxide-facies iron formations (e.g.,

463   Dauphas et al., 2017). Previous studies of Fe isotope fractionation have shown that precipitation of Fe-

464   sulfides from Fe^{2+} dissolved in an aqueous solution produces fractionations between -0.3 and -0.9‰ in

465   the temperature range of 2 to 40°C (Butler et al., 2005). Under hydrothermal conditions, non-

466   equilibrium Fe isotope fractionation between pyrite in hydrothermal chimneys or Fe-sulfides in buoyant

467   hydrothermal plume and hydrothermal fluid has been found to be about -0.9‰ (Rouxel et al., 2008;

468   Bennett et al., 2009; Rouxel et al., 2016). This suggests that the observed δ^{56}Fe values of -2.0‰ in

469   graphitic argillite and -2.1‰ in exhalite were formed as a result of an additional pathway to decrease

470   the δ^{56}Fe value of the water prior to precipitation of Fe-oxides in the exhalite unit, and are unlikely to

471   have been formed just by equilibrium or kinetic isotope fractionation during mineral precipitation in an

472   open aqueous system. Two mechanisms have been proposed to produce isotopically light Fe^{2+} in

473   solution, which could be recorded by Archean sedimentary rocks: 1) dissimilatory iron reduction in pore

474   waters by bacteria (Yamaguchi et al., 2005; Archer and Vance, 2006; Heinman et al., 2010), and 2)

475   reservoir effect resulting in Rayleigh-type fractionation due to the early precipitation of isotopically

476   heavy Fe-oxides (Rouxel et al., 2005; Planavsky et al., 2012). A similar model based on Rayleigh

477   fractionation of Si isotopes was proposed by van den Boorn et al. (2010) to explain isotopic patterns in

478   some Archean cherts.

479   On a plot of Mn/Fe versus δ^{56}Fe (Figure 13), no significant correlation is observed within the

480   Hart data alone. However, when plotted with data from other Archean and early Paleoproterozoic iron

481   formations (e.g., Tsikos et al., 2010; Planavsky et al., 2012, 2014), the exhalite data fits to a general

482   pattern with Mn-enriched samples (Mn/Fe > 0.01) having essentially negative δ^{56}Fe values, and Mn-

483   depleted samples (Mn/Fe < 0.001) having positive δ^{56}Fe values. The apparent dichotomy in δ^{56}Fe values

484   between Mn-enriched and Mn-depleted samples is observed throughout several Archean to

485   Paleoproterozoic units and is also observed in modern seafloor hydrothermal deposits (Rouxel et al.,

486   2017). Although mechanisms for separation of Mn and Fe and for Fe isotope fractionation could have

487   differed between pre-GOE and post-GOE deposits, the observed relationships between Mn/Fe and δ^{56}Fe

488   values might be attributed to the increasing oxidation potential of the water column, leading to

489   significant oxidation of Fe first and then Mn. An increase in oxidation potential could explain why Mn/Fe

490   ratios negatively correlate with δ^{56}Fe values, which might reflect extensive precipitation of isotopically

491   heavy Fe-oxides in less oxidized settings. This process has been invoked for modern Fe-rich

492   hydrothermal systems associated with volcanic seamounts such as Loihi (Rouxel et al., 2017).

493   Additionally, although Eu anomalies are relatively large, the observed Eu anomalies in the Hart area are

494   lower than the highest values recorded for BIFs and cherts from the Abitibi greenstone belt (as high as

495   31 in Thurston et al., 2012). As these Eu anomalies are generally attributed to the influence of

496   hydrothermal input (e.g., Bolhar et al., 2004), the exhalite in the Hart area likely formed distally from the

497   hydrothermal source relative to some of the BIFs sampled by Thurston et al. (2012).

498   Applying this model to the Hart deposit exhalite unit (Figure 14) would suggest that both Fe-

499   oxides and Fe-sulfides formed in distal hydrothermal plume environments, after significant iron

500   depletion from solution. Precipitation of a relatively small amount of Fe-rich minerals with highly

501   negative Fe isotope values, along with deposition of a small amount of clay minerals enriched in Mn-

502   oxyhydroxides and Mn-oxides that were later reacted with organic matter to form Mn-carbonates, was

503   followed by formation of chert hardgrounds developed in pores at or below the sediment-water

504   interface and as a replacement of sediments. The observed positive anomalies for La, Gd, and high Y/Ho

505   ratios all suggest precipitation from seawater, whereas both positive and negative Ce anomalies,

506   pronounced positive Eu anomaly, high Fe/Ti, and low Al/(Al+Fe+Mn) ratios together suggest variable

507   redox conditions in a deep-water setting straddling the redoxcline with strong hydrothermal input at the

508   time of deposition (cf. Bolhar et al., 2004; Pecoits et al., 2009).

509   Petrographic evidence suggests that, following precipitation of chert, locally Fe-rich laminae

510   were replaced by sulfides, as indicated by variable magnetite and pyrrhotite contents along laminae

511   over 5 – 10 mm length. However, individual grains of magnetite do not show textures suggesting

512   replacement by sulfides. This could suggest that sulfides replaced the primary Fe-oxyhydroxides prior to

513   transformation of Fe-oxyhydroxides to magnetite during late diagenesis or metamorphism. The negative

514    $\Delta^{33}S$ values and variable $\delta^{34}S$ values indicate that sulfides were formed through reduction, potentially

515   bacterial, of sulfate likely derived from a nearly homogenous seawater reservoir. Considering the sign of

516   the MIF anomaly, such sulfate reservoir was likely derived from sulfate formed via photochemical

517   reactions in the Archean oxygen-free atmosphere (Ono et al., 2003). The formation of the sulfide phase

518   in these Fe-rich laminae should have been limited by the availability of H_2S, not Fe, and as such,

519   pyrrhotite formed instead of pyrite, as is the case in modern environments where availability of S is the

520   limiting factor (Kao et al., 2004; Larrasoana et al., 2007). Importantly, the pyrrhotite, or amorphous Fe

521   monosulfide precursor to pyrrhotite, did not form at the same time as the exhalite precipitated, but are

522   diagenetic products that must have crystallized before or at approximately the same time as chert

523   precipitated, occluding permeability and porosity and halting bacterial sulfate reduction. Subsequent

524   reaction, and recrystallization, of pyrrhotite to form pyrite could have occurred anaerobically under

525   conditions of increased S availability or Fe-loss (Qian et al., 2011).

526   **Conclusions and Basin Scale Implications**

527   The low concentrations of Zn, U, and U_{auth}, and non-zero $\Delta^{33}S$ values all suggest that exhalite

528   deposition in the Hart area of the Neoarchean Abitibi greenstone belt took place prior to the rise of

529   atmospheric oxygen (cf. Farquhar et al., 2003; Scott et al., 2008, 2013; Partin et al., 2013a, b; Gumsley et

530   al., 2017). However, Mn enrichment and highly negative Fe isotope values in both the exhalite and

531   graphitic argillite require presence of oxygen at least in the upper part of the water column throughout

532   the spreading path of the hydrothermal plume in a deep-water setting. Trace element data and $\delta^{56}Fe$

533   values indicate that the exhalite formed with the significant influence of a hydrothermal fluid on water

534   composition, although distally from the hydrothermal source with the regionally mapped BIF occurring

535   more proximal to the hydrothermal source.

536   The presence of the interbedded exhalite and graphitic argillite suggests that these rocks were

537   deposited in a relatively deep-water environment, as shown by their fine-grain size and absence of

538   sedimentary structures indicative of deposition above the fair-weather and storm-wave base, possibly at

539   the upslope transition from iron formation to black shales in the basinal profile proposed by Klein

540   (2005), Beukes and Gutzmer (2008), and Bekker et al. (2010), representing shallower water depth than

541   the stratigraphically equivalent BIFs elsewhere in the region. Fractionation of Fe isotopes during

542   precipitation of Fe-oxyhydroxides could have resulted in the heavier isotopes being removed via

543   deposition of iron formations in deeper parts of the basin, as represented by iron formations mapped at

544   the correlative stratigraphic level elsewhere in the Shaw Dome (Houlé et al., 2010b; Figure 14). The

545   basin margins sustained high organic productivity, as indicated by the abundance of carbon in the

546   graphitic argillite. Due to deposition of the exhalite distally to the hydrothermal centres, the iron

547   formation and exhalite in the Hart area are unusually chert-rich, with lower concentration of Fe-oxides,

548   Fe-carbonates, and Fe-silicates than in typical iron formations. Early diagenetic bacterial sulfate

549   reduction at the depositional site of exhalite led to the formation of significant amounts of sulfides,

550   however, the limited availability of sulfur with respect to iron during deposition of the exhalite unit

551   could have resulted in the formation of pyrrhotite instead of pyrite as the primary sulfide mineral. Our

552   study indicates spatial and temporal variability of seawater redox conditions and chemical composition

553   in Archean deep-water settings at ~2.7 Ga, during a time when atmosphere stayed persistently anoxic.

565   **References**

566   Alibo, D.S., Nozaki, Y. 1999. Rare earth elements in seawater: particle association, shale-normalization,

567   and Ce oxidation. Geochimica et Cosmochimica Acta 63, 363-372.

568   Alt, J.C. 1995. Sulfur isotopic profile through the oceanic crust: Sulfur mobility and seawater-crustal

569   sulfur exchange during hydrothermal alteration. Geology 23, 585-588.

570   Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., Kaufman, A.J., Gordon, G.W.,

571   Scott, C., Garvin, J., Buick, R. 2007. A whiff of oxygen before the great oxidation event? Science

572   317, 1906-1906.

573   Archer, C., Vance, D. 2006. Coupled Fe and S isotope evidence for Archean microbial Fe(III) and sulfate

574   reduction. Geology 42, 153-156.

575   Ayer, J., Amelin, Y., Corfu, F., Kamo, S., Ketchum, J., Kwok, K., Trowell, N. 2002. Evolution of the southern

576   Abitibi greenstone belt based on U–Pb geochronology: autochthonous volcanic construction

577   followed by plutonism, regional deformation and sedimentation. Precambrian Research 115, 63-

578   95.

579   Ayer, J.A., Thurston, P.C., Bateman, R., Dubé, B., Gibson, H.L., Hamilton, M.A., Hathway, B., Hocker, S.M.,

580   Houlé, M.G., Hudak, G., Ispolatov, V.O., Lafrance, B., Lesher, C.M., MacDonald, P.J., Péloquin,

581   A.S., Piercey, S.J., Reed, L.E., Thompson, P.H. 2005. Overview of results from the Greenstone

582   Architecture Project: Discover Abitibi Initiative; Ontario Geological Survey, Open File Report

583   6154, 146 p.

584   Balci, N., Bullen, T.D., Witte-Lien, K., Shanks, W.C., Motelica, M., Mandernack, K.W. 2006. Iron isotope

585   fractionation during microbially stimulated Fe(II) oxidation and Fe(III) precipitation. Geochimica

586   et Cosmochimica Acta 70, 622-639.

587   Barrie, C.T. 2005. Geochemistry of exhalites and graphitic argillites near VMS and gold deposits: Ontario

588   Geological Survey Miscellaneous Release Data 173, 126 p.

589   Bau, M. 1999. Scavenging of dissolved yttrium and rare earths by precipitation iron oxyhydroxide:

590   Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect.

591   Geochimica et Cosmochimica Acta 63, 67-77.

592   Bau, M., Dulski, P. 1996. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-

593   formations, Transvaal Supergroup, South Africa. Precambrian Research 79, 37-55.

594 Beard, B., Handler, R.M., Scherer, M.M., Wu, L., Czaja, A.D., Heimann, A., Johnson, C.M. 2010. Iron

595   isotope fractionation between aqueous ferrous iron and goethite. Earth and Planetary Science

596   Letters 295, 241-250.

597 Beard, B.L., Johnson, C.M., Skulan, J.L., Nealson, K.H., Cox, L., Sun, H. 2003. Application of Fe isotopes to

598   tracing the geochemical and biological cycling of Fe. Chemical Geology 195, 87-117.

599 Bekker, A., Holland, H.D., Wang, P.-L., Rumble III, D., Stein, H.J., Hannah, J.L., Coetzee, L., Beukes, N.J.

600   2004. Dating the rise of atmospheric oxygen. Nature 427, 117-120.

601 Bekker, A., Barley, M.E., Fiorentini, M.L., Rouxel, O.J., Rumble, D., Beresford, S.W. 2009. Atmospheric

602   sulfur in Archean komatiite-hosted nickel deposits. Science 326, 1086-1089.

603 Bekker, A., Slack, J.F., Planavsky, N., Krapež, B., Hofmann, A., Konhauser, K.O., Rouxel, O.J. 2010. Iron

604   formation: the sedimentary product of a complex interplay among mantle, tectonic, oceanic,

605   and biospheric processes. Economic Geology 105, 467-508.

606 Bekker, A., Planavsky, N., Krapež, B., Rasmussen, B., Hofmann, A., Slack, J.F., Rouxel, O.J., Konhauser,

607   K.O. 2013, Iron Formations: Their Origins and Implications for Ancient Seawater Chemistry,

608   Treatise of Geochemistry, Elsevier, v. 9, p. 561-628.

609 Bennett, S.A., Rouxel, O., Schmidt, K., Garbe-Schonberg, D., Statham, P.J., German, C.R. 2009. Iron

610   isotope fractionation in a buoyant hydrothermal plume, 5 degrees S Mid-Atlantic Ridge.

611   Geochimica et Cosmochimica Acta 73, 5619-5634.

612 Beukes, N.J., Gutzmer, J. 2008. Origin and paleoenvironmental significance of major iron formations at

613   the Archean–Paleoproterozoic boundary; in Banded iron formation-related high-grade iron ore,

614   Society of Economic Geologists, Reviews in Economic Geology 15, 5-47.

615 Bjerrum, C.J., Canfield, D.E. 2002. Ocean productivity before about 1.9 Gyr ago limited by phosphorus

616   adsorption onto iron oxides. Nature 417, 159-162.

617   Bolhar, R., Kamber, B.S., Moorbath, S., Fedo, C.M., Whitehouse, M.J. 2004. Characterization of early

618   Archaean chemical sediments by trace element signatures. Earth and Planetary Science Letters

619   222, 43-60.

620   Bonatti, E., Kraemer, T, Rydell, H.S. 1972. Classification and genesis of submarine iron-manganese

621   deposits. In: Ferromanganese deposits on the ocean floor. IDOE, Columbia Univ. N.Y. p.149–166.

622   Böstrom, K., Peterson, M.N.A., Joensuu, O., Fisher, D.E. 1969. Aluminum-poor ferromanganoan

623   sediments on active oceanic ridges. Journal of Geophysical Research 74, 3261.

624   Böstrom, K., Kraemer, T., Gartner, S. 1973. Provenance and accumulation rates of opaline silica, Al, Ti,

625   Fe, Mn, Cu, Ni and Co in Pacific pelagic sediments. Chemical Geology 11, 123-148.

626   Brunner, B., Bernasconi, S.M. 2005. A revised isotope fractionation model for dissimilatory sulfate

627   reduction in sulfate reducing bacteria. Geochimica et Cosmochimica Acta 69, 4759-4771.

628   Busigny, V., Planavsky, N.J., Jezequel, D., Crowe, S., Louvat, P., Moureau, J., Viollier, E., Lyons, T.W. 2014.

629   Iron isotopes in an Archean ocean analogue. Geochimica et Cosmochimica Acta 133, 443-462.

630   Butler, I.B., Archer, C., Vance, D., Oldroyd, A., Rickard, D. 2005. Fe isotope fractionation on FeS formation

631   in ambient aqueous solution. Earth and Planetary Science Letters 236, 430-442.

632   Byrne, R.H., Sholkovitz, E.R. 1996. Chapter 158. Marine chemistry and geochemistry of the lathanides. In:

633   Gschneidner Jr., K.A., LeRoy, E. (Eds.). Handbook on the Physics and Chemistry of the Rare

634   Earths. Elsevier, pp. 497-593.

635   Chever, F., Rouxel, O., Croot, P.L., Ponzevera, E., Wuttig, K., Auro, M. 2015. Total dissolvable and

636   dissolved iron isotopes in the water column of the Peru upwelling regime. Geochimica et

637   Cosmochimica Acta, 162, 66–82.

638   Coplen, T.B., Krouse, H.R. 1998. Sulphur isotope data consistency improved. Nature 392, 32.

639   Croal, L.R., Johnson, C.M., Beard, B.L., Newman, D.K. 2004. Iron isotope fractionation by Fe(II)-oxidizing

640   photoautotrophic bacteria. Geochimica et Cosmochimica Acta 68, 1227-1242.

641   Crosby, H.A., Roden, E.E., Johnson, C.M., Beard, B.L. 2007. The mechanisms of iron isotope fractionation

642   produced during dissimilatory Fe(III) reduction by Shewanella putrefaciens and Geobacter

643   sulfurreducens. Geobiology 5, 169-189.

644   Dauphas, N., John, S., Rouxel, O. 2017. Iron Isotope Systematics. Reviews in Mineralogy & Geochemistry

645   82 415 - 510.

646   Detmers, J., Bruchert, V., Habicht, K.S., Kuever, J. 2001. Diversity of sulfur isotope fractionation by

647   sulfate-reducing prokaryotes. Applied and Environmental Microbiology, 67, 888-894.

648   Duan, Y., Severmann, S., Anbar, A.D., Lyons, T.W., Gordon, G.W., Sageman, B.B. 2010. Isotopic evidence

649   for Fe cycling and repartitioning in ancient oxygen-deficient settings: Examples from black shales

650   of the mid-to-late Devonian Appalachian basin. Earth and Planetary Science Letters 290, 244-

651   253.

652   Farquhar, J., Wing, B.A. 2003. Multiple sulfur isotopes and the evolution of the atmosphere. Earth and

653   Planetary Science Letters 213, 1-13.

654   Farquhar, J., Bao, H., Thiemens, M. 2000. Atmospheric influence of Earth's earliest sulfur cycle. Science

655   289, 756-758.

656   Farquhar, J., Savarino, J., Airieau, S., Thiemens, M.H. 2001. Observation of wavelength-sensitive mass-

657   independent sulfur isotope effects during SO_2 photolysis: Implications for the early atmosphere.

658   Journal of Geophysical Research 106, 32829-32839.

659   Farquhar, J., Wing, B.A., McKeegan, K.D., Harris, J.W., Cartigny, P., Thiemens, M.H. 2002. Mass-

660   independent sulfur of inclusions in diamond and sulfur recycling on early earth. Science 298,

661   2369-2372.

662   Fralick, P., Riding, R. 2015. Steep Rock Lake: Sedimentology and geochemistry of an Archean carbonate

663   platform. Earth-Science Reviews 151, 132-175.

664   German, C.R., Holliday, B.P., Elderfield, H. 1991. Redox cycling of rare earth elements in the suboxic zone

665   of the Black Sea. Geochimica et Cosmochimica Acta 55, 3553-3558.

666   Guilbaud, R., Butler, I.B., Ellam, R.M. 2011. Abiotic Pyrite Formation Produces a Large Fe Isotope

667   Fractionation. Science 332, 1548-1551.

668   Gumsley, A.P., Chamberlain, K.R., Bleeker, W., Söderlund, U., de Kock, M.O., Larsson, E.R., Bekker, A.

669   2017. Timing and tempo of the great oxidation event. Proceedings of the National Academy of

670   the Sciences 114, 1811-1816.

671   Habicht, K.S., Gade, M., Thamdrup, B., Berg, P., Canfield, D.E. 2002. Calibration of the sulfate levels in

672   the Archean ocean. Science 298, 2372-2374.

673   Haogaard, R., Ootes, L., Konhauser, K. 2017. Neoarchaean banded iron formation within a ~2620 Ma

674   turbidite-dominated deep water basin, Slave craton, NW Canada. Precambrian Research 292,

675   130-151.

676   Heimann, A., Johnson, C.M., Beard, B.L., Valley, J.W., Roden, E.E., Spicuzza, M.J., Beukes, N.J. 2010. Fe, C,

677   and O isotope compositions of banded iron formation carbonates demonstrate a major role for

678   dissimilatory iron reduction in ~2.5 Ga marine environments. Earth and Planetary Science Letters

679   294, 8-18.

680   Hiebert, R.S., Bekker, A., Wing, B.A., Rouxel, O.J. 2013. The role of paragneiss assimilation in the origin of

681   the Voisey's Bay Ni-Cu sulfide deposit, Labrador: multiple S and Fe isotope evidence. Economic

682   Geology 108, 1459-1469.

683   Hiebert, R.S., Bekker, A., Houlé, M.G., Wing, B.A., Rouxel, O.J. 2016. Tracing sources of crustal

684   contamination using multiple S and Fe isotopes in the Hart komatiite-associated Ni-Cu-(PGE)

685   sulphide deposit, Abitibi greenstone belt, Ontario, Canada. Mineralium Deposita 51, 919-935.

686   Houlé, M.G., Lesher, C.M. 2011. Komatiite-associated Ni-Cu-(PGE) deposits, Abitibi greenstone belt,

687   Superior Province, Canada; in Magmatic Ni-Cu and PGE deposits: geology, geochemistry, and

688   genesis. Society of Economic Geologists, Reviews in Economic Geology 17, 89-121.

689   Houlé, M.G., Lesher, C.M., Gibson, H.L., Ayer, J.A., Hall, L.A.F. 2010a. Localization of komatiite-associated

690   Ni-Cu-(PGE) deposits in the Shaw Dome, Abitibi greenstone belt, Superior Province. In:

691   Abstracts, 11th International Platinum Symposium, 21–24 June 2010, Sudbury, Ontario, Canada,

692   Ontario Geological Survey, Miscellaneous Release—Data 269.

693   Houlé, M.G., Lesher, C.M., Préfontaine, S., Ayer, J.A., Berger, B.R., Taranovic, V., Davis, P.C., Atkinson, B.

694   2010b. Stratigraphy and physical volcanology of komatiites and associated Ni-Cu-(PGE)

695   mineralization in the western Abitibi greenstone belt, Timmins area, Ontario: a field trip for the

696   11th International Platinum Symposium; Ontario Geological Survey, Open File Report 6255, 99p

697   Isley, A. 1995. Hydrothermal plumes and the delivery of iron to banded iron formations. Journal of

698   Geology 103, 169-185.

699   Jamieson, J.W., Wing, B.A., Farquhar, J., Hannington, M.D. 2013. Neoarchean seawater sulphate

700   concentrations from sulphur isotopes in massive sulphide ore. Nature Geoscience 6, 61-64.

701   Johnston, D.T., Farquhar, J., Wing, B.A., Kaufman, A.J., Canfield, D.E., Habicht, K.S. 2005. Multiple sulfur

702   isotope fractionations in biological systems: A case study with sulfate reducers and sulfur

703   disproportionators. American Journal of Science 305, 645-660.

704   Kamber, B.S. 2010. Archean mafic-ultramafic volcanic landmasses and their effect on ocean-atmosphere

705   chemistry. Chemical Geology 274, 19-28.

706   Kao, S.-J., Horng, C.-S., Roberts, A.P., Liu, K.-K. 2004. Carbon-sulfur-iron relationships in sedimentary

707   rocks from southwestern Taiwan: influence of geochemical environment on greigite and

708   pyrrhotite formation. Chemical Geology 203, 153-168.

709   Kaufman, A.J., Johnston, D.T., Farquhar, J., Masterson, A.L., Lyons, T.W., Bates, S., Anbar, A.D., Arnold,

710   G.L., Garvin, J., Buick, R. 2007. Late Archean biospheric oxygenation and atmospheric evolution.

711   Science 317, 1900-1903.

712   Kato, Y., Yamaguchi, K.E., Ohmoto, H. 2006. Rare earth elements in Precambrian banded iron

713   formations: Secular changes of Ce and Eu anomalies and evolution of atmospheric oxygen.

714   Geological Society of America Memoir 198, 269-289.

715   Ketchum, J.W.F., Ayer, J.A., Van Breemen, O. 2008. Pericontinental Crustal Growth of the southwestern

716   Abitibi Subprovince, Canada: U-Pb, Hf, and Nd Isotopic Evidence. Economic Geology 103, 1151-

717   1184.

718   Klein, C. 2005. Some Precambrian banded iron-formations (BIFs) from around the world: Their age,

719   geologic setting, mineralogy, metamorphism, geochemistry, and origin. American Mineralogist

720   90, 1473-1499.

721   Konhauser, K.O., Lalonde, S.V., Planavsky, N.J., Pecoits, E., Lyons, T.W., Mojzsis, S.J., Rouxel, O.J., Barley,

722   M.E., Rosiere, C., Fralick, P.W., Kum, L.R., Bekker, A. 2011. Aerobic bacterial pyrite oxidation and

723   acid rock drainage during the Great Oxidation Event. Nature 478, 369-373.

724   Kurzweil, F., Wille, M., Gantert, N., Beukes, N.J., Schoenberg, R. 2016. Manganese oxide shuttling in pre-

725   GOE oceans – evidence from molybdenum and iron isotopes. Earth and Planetary Science

726   Letters 452, 69-78.

727   Lalonde, S.V., Konhauser, K.O. 2015. Benthic perspective on Earth's oldest evidence for oxygenic

728   photosynthesis. Proceedings of the National Academy of Sciences 112, 995-1000.

729   Lantink, M.L., Oonk, P.B.H., Floor, G.H., Tsikos, H., Mason, P.R.D. 2018. Fe isotopes of a 2.4 Ga hematite-

730   rich IF constrain marine redox conditions around the GOE. Precambrian Research 305, 218-235.

731   Larrasoana J.C., Roberts, A.P., Musgrave, R.J., Gracia, E., Pinero, E., Vega, M., Martinez-Ruiz, F. 2007.

732   Diagenetic formation of greigite and pyrrhotite in gas hydrate marine sedimentary systems.

733   Earth and Planetary Science Letters 261, 350-366.

734   Li, W.Q., Beard, B.L., Johnson, C.M. 2015. Biologically recycled continental iron is a major component in

735   banded iron formations. Proceedings of the National Academy of Sciences of the United States

736   of America 112, 8193-8198.

737   Lough, A.J.M., Klar, J.K., Homoky, W.B., Comer-Warner, S.A., Milton, J.A., Connelly, D.P., James, R.H.,

738   Mills, R.A. 2017. Opposing authigenic controls on the isotopic signature of dissolved iron in

739   hydrothermal plumes. Geochimica et Cosmochimica Acta 202, 1-20.

740   Lyons, T.W., Reinhard, C.T., Planavsky, N.J. 2014. The rise of oxygen in Earth's early ocean and

741   atmosphere. Nature 506, 307-315.

742   Marin-Carbonne, J., Rollion-Bard, C., Bekker, A., Rouxel, O., Agangi, A., Cavalazzi, B., Wohlgemuth-

743   Ueberwasser, C.C. 2014. Coupled Fe and S isotope variations in pyrite nodules from Archean

744   shale. Earth and Planetary Science Letters 392, 67-79.

745   Maynard, J.B., 2010. The chemistry of manganese ores through time: a signal of increasing diversity of

746   earth-surface environments. Economic Geology 105, 535–552.

747   Maynard, J.B., Sutton, S.J., Rumble III, D., Bekker, A. 2013. Mass-independently fractionated sulfur in

748   Archean paleosols: a large reservoir of negative $\Delta^{33}S$ anomaly on the early Earth. Chemical

749   Geology 362, 74-81.

750   Mendes, M., Lobato, L.M., Kunzmann, M., Halverson, G.P., Rosiere, C.A. 2016. Iron isotope and REE+Y

751   composition of the Caue banded iron formation and related iron ores of the Quadrilaero

752   Ferrifero, Brazil. Mineralium Deposita published online.

753   Olson, S.L., Kump, L.R., Kasting, J.F. 2013. Quantifying the areal extent and dissolved oxygen

754   concentrations of Archean oxygen oases. Chemical Geology 362, 35-43.

755   Ono, S., Eigenbrode, J.L., Pavlov, A.A., Kharecha, P., Rumble III, D., Kasting, J.F., Freeman, K.H. 2003. New

756   insights into Archean sulfur cycle from mass-independent sulfur isotope records from the

757   Hamersley Basin, Australia. Earth and Planetary Science Letters 213, 15-30.

758   Ono, S., Beukes, N.J., Rumble, D. 2009. Origin of two distinct multiple-sulfur isotope compositions of

759   pyrite in the 2.5 Ga Klein Naute Formation, Griqualand West Basin, South Africa. Precambrian

760   Research 169, 48-57.

761   Ossa Ossa, F., Hofmann, A., Vidal, O., Kramers, J.D., Belyanin, G., Cavalazzi, B. 2016. Unusual manganese

762   enrichment in the Mesoarchean Mozaan Group, Pongola Supergroup, South Africa. Precambrian

763   Research 281, 414-433.

764   Partin, C.A., Bekker, A., Planavsky, N.J., Scott, C.T., Gill, B.C., Podkovyrov, V., Maslov, A., Konhauser, K.O.,

765   Lalonde, S.V., Love, G.D., Poulton, S.W., Lyons, T.W. 2013a. Large-scale fluctualtions in

766   Precambrian atmospheric and oceanic oxygen levels from the record of U in shales. Earth and

767   Planetary Science Letters 369-370, 284-293.

768   Partin, C.A., Lalonde, S.V., Planavsky, N.J., Bekker, A., Rouxel, O.J., Lyons, T.W., Konhauser, K.O. 2013b.

769   Uranium in iron formations and the rise of atmospheric oxygen. Chemical Geology 362, 82-90.

770   Pavlov, A.A., Kasting, J.F. 2002. Mass-Independent Fractionation of Sulfur Isotopes in Archean

771   Sediments: Strong Evidence for an Anoxic Archean Atmosphere. Astrobiology 2, 27-41.

772   Pecoits, S., Gingras, M.K., Barley, M.E., Kappler, A., Posth, N.R., Konhauser, K.O. 2009. Petrography and

773   geochemistry of the Dales Gorge banded iron formation: Paragenetic sequence, source and

774   implications for palaeo-ocean chemistry. Precambrian Research 172, 163-187.

775   Percak-Dennett, E.M., Beard, B.L., Xu, H., Konishi, H., Johnson, C.M., Roden, E.E. 2011. Iron isotope

776   fractionation during microbial dissimilatory iron oxide reduction in simulated Archaean

777   seawater. Geobiology 9, 205–220.

778   Planavsky, N., Bekker, A., Rouxel, O.J., Kamber, B., Hofmann, A., Knudsen, A., Lyons, T.W. 2010. Rare

779   Earth Element and yttrium compositions of Archean and Paleoproterozoic Fe formations

780   revisited: New perspectives on the significance and mechanisms of deposition. Geochimica et

781   Cosmochimica Acta 74, 6387-6405.

782   Planavsky, N., Rouxel, O.J., Bekker, A., Hofmann, A., Little, C.T.S., Lyons, T.W. 2012. Iron isotope

783   composition of some Archean and Proterozoic iron formations. Geochimica et Cosmochimica

784   Acta 80, 158-169.

785   Planavsky, N.J., Asael, D., Hofmann, A., Reinhard, C.T., Lalonde, S.V., Knudsen, A., Wang, X., Ossa Ossa,

786   F., Pecoits, E., Smith, A.J.B., Beukes, N., Bekker, A., Johnson, T.M., Konhauser, K.O., Lyons, T.W.,

787   Rouxel, O.J. 2014. Evidence for oxygenic photosynthesis half a billion years before the Great

788   Oxidation Event. Nature Geosciences 7, 283-286.

789   Qian, G., Xia, F., Brugger, J., Skinner, W.M., Bei, J., Chen, G., Pring, A. 2011. Replacement of pyrrhotite by

790   pyrite and marcasite under hydrothermal conditions up to 220°C: An experimental study of

791   reaction textures and mechanisms. American Mineralogist 96, 1878-1893.

792   Reinhard, C.T., Raiswell, R., Scott, C., Anbar, A.D., Lyons, T.W., 2009. A late Archean sulfidic sea

793   stimulated by early oxidative weathering of the continents. Science 326, 713-716.

794   Reinhard, C.T., Planavsky, N.J., Gill, B.C., Ozaki, K., Robbins, L.J., Lyons, T.W., Fischer, W.W., Wang, C.J.,

795   Cole, D.B., Konhauser, K.O. 2017. Evolution of the global phosphorus cycle. Nature 541, 386-389.

796   Riding, R., Fralick, P., Liang, L. 2014. Identification of an Archean marine oxygen oasis. Precambrian

797   Research 251, 232-237.

798   Ridler, R.H. 1971. Analysis of Archean volcanic basins in the Canadian Shield using the exhalite concept.

799   Bulletin of the Canadian Institute of Mining and Metallurgy 64, 20.

800   Ripley, E.M. 1999. Systematics of sulphur and oxygen isotopes in mafic igneous rocks and Cu-Ni-PGE

801   mineralization; in Dynamic processes in magmatic ore deposits and their application in mineral

802   exploration. Geological Association of Canada, Short Course Notes, v.13, p.111-158.

803   Robbins, L.J., Lalonde, S.V., Saito, M.A., Planavsky, N.J., Mloszewska, A.M., Pecoits, E., Scott, C., Dupont,

804   C.L., Kappler, A., Konhauser, K.O. 2013. Authigenic iron oxide proxies for marine zinc over

805   geological time and implications for eukaryotic metallome evolution. Geobiology 11, 295-306.

806   Rouxel, O., Dobbek, N., Ludden, J., Fouquet, Y. 2003. Iron isotope fractionation during oceanic crust

807   alteration. Chemical Geology 202, 155-182.

808   Rouxel, O.J., Bekker, A., Edwards, K.J. 2005. Iron isotope constraints of the Archean and

809   Paleoproterozoic ocean redox state. Science 307, 1088-1091.

810   Rouxel, O., Shanks III, W.C., Bach, W. and Edwards, K.J. 2008. Integrated Fe- and S-isotope study of

811   seafloor hydrothermal vents at East Pacific Rise 9-10°N. Chemical Geology 252, 214-227

812   Rouxel, O., Sholkovitz, E., Charette, M., Edwards, K.J. 2008. Iron isotope fractionation in subterranean

813   estuaries. Geochimica et Cosmochimica Acta, 72, 3413-3430.

814   Rouxel, O., Toner, B.M., Manganini, S.J., German, C.R. 2016. Geochemistry and iron isotope systematics

815   of hydrothermal plume fall-out at East Pacific Rise 9 degrees 50 ' N. Chemical Geology 441, 212-

816   234.

817   Rouxel, O., Toner, B., Germain, Y., Glazer, B. 2017. Geochemical and iron isotopic insights into

818   hydrothermal iron oxyhydroxide deposit formation at Loihi Seamount. Geochimica et

819   Cosmochimica Acta, in revision.

820   Rudnick, R.L., Gao, S. 2014. Composition of the Continental Crust. Treatise on Geochemistry (Second

821   Edition) 4, 1-51.

822   Scott, C., Lyons, T.W., Bekker, A., Shen, Y., Poulton, S.W., Chu, X., Anbar, A.D. 2008. Tracing the stepwise

823   oxygenation of the Proterozoic ocean. Nature 452, 456-459.

824   Scott, C., Planavsky, N.J., Dupont, C.L., Kendall, B., Gill, B.C., Robbins, L.J., Husband, K.F., Arnold, G.L.,

825   Wing, B.A., Poulton, S.W., Bekker, A., Anbar, A.D., Konhauser, K.O., Lyons, T.W. 2013.

826   Bioavailability of zinc in marine systems through time. Nature Geoscience 6, 125-128.

827   Severmann, S., Lyons, T.W., Anbar, A., McManus, J., Gordon, G. 2008. Modern iron isotope perspective

828   on the benthic iron shuttle and the redox evolution of ancient oceans. Geology 36, 487-490.

829   Slack, J.F., Grenne, T., Bekker, A., Rouxel, O.J., Lindberg, P.A. 2007. Suboxic deep seawater in the late

830   Paleoproterozoic: Evidence from hematitic chert and iron formation related to seafloor-

831   hydrothermal sulfide deposits, central Arizona, USA. Earth and Planetary Science Letters 255,

832   243-256.

833   Steinhoefel, G., Horn, I., von Blanckenburg, F. 2009. Micro-scale tracing of Fe and Si isotope signatures in

834   banded iron formation using femtosecond laser ablation. Geochimica et Cosmochimica Acta 60,

835   4957-4963.

836   Swanner, E.D., Planavsky, N.J., Lalonde, S.V., Robbins, L.J., Bekker, A., Rouxel, O.J., Saito, M.A., Kappler,

837   A., Mojzsis, S.J., Konhauser, K.O. 2014. Cobalt and marine redox evolution. Earth and Planetary

838   Science Letters 390, 253-263.

839   Swanner, E.D., Wu, W.F., Schoenberg, R., Byrne, J., Michel, F.M., Pan, Y.X., Kappler, A. 2015.

840   Fractionation of Fe isotopes during Fe(II) oxidation by a marine photoferrotroph is controlled by

841   the formation of organic Fe-complexes and colloidal Fe fractions. Geochimica et Cosmochimica

842   Acta,, 165, 44-61.

843   Tangalos, G.E., Beard, B.L., Johnson, C.M., Alpers, C.N., Shelobolina, E.S., Xu, H., Konishi, H., Roden, E.E.

844   2010. Microbial production of isotopically light iron(II) in a modern chemically precipitated

845   sediment and implications for isotopic variations in ancient rocks. Geobiology 8, 197-208.

846 Thompson, P.H. 2005. A new metamorphic framework for gold exploration in the Timmins–Kirkland Lake

847   area, western Abitibi greenstone belt: Discover Abitibi Initiative; Ontario Geological Survey,

848   Open File Report 6162, 104p.

849 Thurston, P.C., Chivers, K.M. 1990. Secular variation in greenstone sequence development emphasizing

850   Superior Province, Canada. Precambrian Research 46, 21-58.

851 Thurston, P.C., Ayer, J.A., Goutier, J., Hamilton, M.A. 2008. Depositional gaps in Abitibi greenstone belt

852   stratigraphy: a key to exploration for syngenetic mineralization. Economic Geology 103, 1097-

853   1134.

854 Thurston, P.C., Kamber, B.S., Whitehouse, M. 2012. Archean cherts in banded iron formation: insight

855   into Neoarchean ocean chemistry and depositional processes. Precambrian Research 214-215,

856   227-257.

857 Tsikos, H., Matthews, A., Erel, Y., Moore, J.M. 2010. Iron isotopes constrain biochemical redox cycling of

858   iron and manganese in a Palaeoproterozoic stratified basin. Earth and Planetary Science Letters

859   298, 125-134.

860 van den Boorn, S.H.J.M., van Bergen, M.J., Vroon, P.Z., de Vries, S.T., Nijman, W. 2010. Silicon isotope

861   and trace element constraints on the origin of ~3.5 Ga cherts: Implications for Early Archaean

862   marine environments. Geochimica et Cosmochimica Acta 74, 1077-1103.

863 von Blanckenburg, F., Mamberti, M., Schoenberg, R., Kamber, B.S., Webb, G.E. 2008. The iron isotope

864   composition of a microbial carbonate. Chemical Geology 249, 113-128.

865 Wu, L.L., Beard, B.L., Roden, E.E., Johnson, C.M. 2011. Stable Iron Isotope Fractionation Between

866   Aqueous Fe(II) and Hydrous Ferric Oxide. Environ. Sci. Technol., 45, 1847-1852.

867 Yamaguchi, K.E., Johnson, C.M., Beard, B.L., Ohmoto, H. 2005. Biogeochemical cycling of iron in the

868   Archean-Paleoproterozoic Earth: Constraints from iron isotope variations in sedimentary rocks

869   from the Kaapvaal and Pilbara Cratons. Chemical Geology 218, 135-169.

871 **Figure Captions**

872 **Figure 1**: Geological map of the Shaw Dome, Abitibi greenstone belt (modified from Houlé et al., 2010a, b).

873 **Figure 2**: Geologic map of the Hart deposit area (modified from Houlé et al., 2010b). Drill hole collar locations are indicated.

874 Locations of sampled surface trenches are indicated by the green bars.

875 **Figure 3: a-b** Outcrop photographs of the exhalite unit, taken along strike from the Hart area; chert (a) and iron formation (b)

876 lithologies. The coin is 18 mm in diameter on figures a and b. **c-d** Reflected light photomicrographs of exhalite in the footwall of

877 the Hart deposit: oxide-rich laminae in chert (c: sample H11-13C-363) and fine pyrrhotite grains replaced by coarse pyrite grains

878 containing inclusions of pyrrhotite (circled) in a barren sulfide lens within the exhalite unit (d: sample H11-08-58.3).

879 **Figure 4: a** Core photo of graphitic argillite, showing nodules and bands of pyrite intercalated with chert-rich exhalite above

880 and below. The coin is 18 mm in diameter. **b** Photomicrographs of graphitic argillite in plane-polarized light, showing quartz

881 (white) and chlorite (grey), and opaque graphite and pyrite (sample H11-13C-357.1). **c** Photomicrograph in reflected light of

882 pyrite nodule in graphitic argillite, showing growth in concentric bands (sample H11-13C-357.1). **d** Photomicrograph of graphitic

883 argillite unit in reflected light (sample H11-13C-366.1), showing minor disseminated pyrite (bright grains), opaque mineral

884 (graphite), and silicates (light grey).

885 **Figure 5:** Approximate fields of Δ^{33}S and δ^{34}S values for the different volcanic, atmospheric, and seawater S pools in the

886 Archean. Purple oval represents composition of mantle-derived volcanic sulfur; blue oval and red circle represent composition

887 of reduced sulfur (S_8) and oxidized sulfur (SO_4^{2-}), respectively. Orange dashed line represents the most likely range in

888 composition of sulfides formed by sulfate-reducing bacteria (SRB) that resulted in a horizontal shift in seawater sulfate

889 composition to higher δ^{34}S values (red oval; fields are after Ono et al. 2003).

890 **Figure 6:** Ce anomalies (a), and rare earth element patterns (b) of exhalite samples (see Table 3 for method of calculation of Ce

891 and La anomalies).

892 **Figure 7:** Ce anomalies (a), and rare earth element patterns (b) for graphitic argillite samples (see Table 3 for method of

893 calculation of Ce and La anomalies).

894 **Figure 8:** Back-scattered electron image of exhalite sample H11-08-63.9, showing the Mn-bearing minerals and the EDS spectra.

895 Chl: chlorite, Act: actinolite, and Cal: calcite. White minerals on image are dense Fe-oxide and sulfide minerals.

896 **Figure 9:** Sulfur isotope signature of the Hart area exhalite and graphitic argillite. Red line in (a) indicates terrestrial

897 fractionation line (TFL; Farquhar and Wing, 2003). Terrestrial fractionation line corresponds to Δ^{33}S=0‰ jn (b).

898 **Figure 10:** Fe-isotope composition of the lithologies present in the Hart deposit area. Orange represents the minimum and

899 maximum values of the mantle range (Beard et al., 2003).

900 **Figure 11:** Plot of S concentration vs. δ^{56}Fe values shows no correlation, indicating that Fe isotope values are not controlled by

901 sulfide content.

902 **Figure 12:** Diagrams designed to test the significance of detrital input on composition of sedimentary rocks. A positive

903 correlation in (a) and (b) indicates some compositional control by detrital material on the graphitic argillite. In (c), plotting in

904 zone I indicates a dominantly hydrothermal source for sediments, plotting in zone II indicates some influence of a hydrothermal

905 source mixed with detrital material, and plotting in zone III indicates a dominantly detrital source (Peciots et al., 2009).

906 **Figure 13:** Exhalite data from this study broadly follows the same negative correlation trend as observed from several iron

907 formations through time, including the Paleoproterozoic Hotazel Formation, South Africa (Tsikos et al., 2010), the Archean

908 Senqeni Formation, South Africa (Planavsky et al., 2014), and several other well-preserved Archean and Paleoproterozoic iron

909 formations compiled by Planavsky et al. (2012).

910 **Figure 14:** Cartoon cross-section showing the location of the Hart area within the basin during deposition. Iron formations were

911 deposited deeper in the basin, with heavier Fe-isotope values, and the Hart exhalite and graphitic argillite formed upslope in a

912 zone of upwelling (based on the models of Klein 2005, Beukes and Gutzmer 2008, and Bekker et al., 2010).

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914   Table 1.

Sample ID			H07-10-66.35	H07-10-73.6	H07-10-86.85	H07-56-188.9	H07-56-210.6	H08-106-98.6	Sample ID	H08-80-103.2	H08-80-107.5	H11-05-45.55	H11-05-54.25	H11-08-52.65	H11-08-52.66	Sample ID
DDH			H07-10	H07-10	H07-10	H07-56	H07-56	H08-106	DDH	H08-80	H08-80	H11-05	H11-05	H11-08	H11-08	DDH
Lithology	MDL (Geo Labs)	MDL (Acme)	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Lithology	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Lithology
SiO2	0.04	0.01	11.02	4.14	27.19	5.25	1.66	11.83	SiO2	25.43	84.35	21.56	5.01	7.19	5.73	SiO2
TiO2	0.01	0.01	0.02					0.01	TiO2	0.01	0.01	0.01		<0.01		TiO2
Al2O3	0.02	0.01	0.6	0.25	0.11	0.4	0.12	0.22	Al2O3	0.33	0.47	0.19	0.26	0.18	0.15	Al2O3
Fe2O3T	0.01	0.04	53.3	64.08	53.5	55.37	67.03	65.42	Fe2O3T	48.62	9.59	56.44	71.69	76.37	58.6	Fe2O3T
MgO	0.01	0.01	0.07	0.8	2.13	1.02	0.77	3.4	MgO	1.57	0.71	1.96	2.27	0.64	0.53	MgO
MnO	0.002	0.01	0.02	0.83	1.37	0.22	0.75	0.45	MnO	0.24	0.12	0.19	0.17	0.39	0.32	MnO
CaO	0.006	0.01	0.08	5.46	5.14	7.09	3.48	2.58	CaO	1.76	1.25	1.50	0.97	2.23	1.85	CaO
Na2O	0.02	0.01	0.01	<0.01	<0.01	0.03	<0.01	0.03	Na2O	0.03	0.08	0.07	<0.01	0.06	0.01	Na2O
K2O	0.01	0.01	0.17	0.06	<0.01	0.16	0.03	<0.01	K2O	0.03	0.06	0.03	<0.01	0.01	<0.01	K2O
P2O5	0.002	0.01	<0.01	0.03	<0.01	<0.01	0.04	<0.01	P2O5	<0.01	0.02	0.00	<0.01	0.01	<0.01	P2O5
LOI	0.05	0.01	34.6	24.3	10.5	24.9	26	16	LOI	21.5	3.2	17.7	19	13.0	32.7	LOI
CO2	0.03	0.02	0.15	1.11	1.23	1.68	0.89	0.03	CO2	0.32	0.15	0.23	0.09	3.95	0.13	CO2
S	0.01	0.02	38.48	36.99	18.58	36.03	37.66	26.34	S	27.9	6.46	32.2	28.71	10.6	40.05	S
Li	0.4								Li			0.4		0.4		Li
Be	0.04	1	<1	<1	<1	<1	<1	1	Be	3	1	0.2	<1	0.1	<1	Be
Sc	1.1	1	1	12	1	<1	12	3	Sc	<1	1	1.1	1	1.1	<1	Sc
Ti	7								Ti			53		43		Ti
V	0.8	8	<8	<8	<8	<8	10	<8	V	<8	<8	16.9	<8	1.8	<8	V

Element	DL	L1	L2	L3	L4	L5	L6	L7	R1	R2	R3	R4	R5	R6
Cr	3										11		4	
Co	0.13	0.2	51.7	41.3	16	93	71.7	93.5	73.6	3.7	130.48	98.4	96.89	93.3
Ni	1.6	0.1	119.1	40.7	42.6	109.6	140.4	149.6	317.2	261.3	980.4	398 5.8	399.8	366.8
Cu	1.4	0.1	33.2	18.2	13.5	47.9	25.4	209.3	428.6	702.7	450.1	552.9	93.0	88.6
Zn	7	1	386	43	14	14	8	5	9	124	11	9	10	6
Ga	0.04	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.48	<0.5	0.35	<0.5
Rb	0.23	0.1	3.5	3.3	0.3	8.2	1.7	0.5	1.5	2.1	0.90	<0.1	0.23	<0.1
Sr	0.6	0.5	1.5	25.8	14.4	75.8	17.1	2.4	3	12.1	3.7	2.5	14.3	14.9
Y	0.05	0.1	0.2	4.9	4	2.5	2.3	7.3	5.2	2	8.31	3.5	1.92	1.7
Zr	6	0.1	106.1	33.1	44.7	63.1	44.5	32.4	66.4	3.9	6	22.4	6	2.3
Nb	0.028	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	0.037	<0.1	0.054	<0.1
Mo	0.08	0.1	1.5	2.2	0.5	2.1	0.6	6.3	0.6	0.3	0.16	0.6	0.79	0.4
Cd	0.013	0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	0.038	<0.1	0.033	<0.1
In	0.0018										0.0091		0.0040	
Sn	0.16	1	<1	<1	<1	<1	<1	<1	<1	<1	0.16	<1	0.16	<1
Sb	0.04	0.1	1.4	0.8	0.3	0.4	2.2	<0.1	0.1	<0.1	0.21	0.2	0.33	0.1
Cs	0.013	0.1	0.2	1.5	<0.1	2.2	0.9	0.3	0.5	0.2	0.316	<0.1	0.055	<0.1
Ba	0.8	1	32	6	5	20	6	3	5	14	5.3	5	30.6	36
La	0.04	0.1	0.4	2.1	0.9	2	0.8	2.8	3.1	0.7	0.51	1.1	1.04	1.5
Ce	0.12	0.1	0.5	3.4	1.4	3.3	1.1	4.3	4.8	1.6	1.25	1.2	1.62	1.7

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Table 2.

Sample							Sample							Sample							Sample						
H07-1	H07-1	H07-1	H07-5	H07-5	H08-1		H08-8	H08-8	H11-0	H11-0	H11-0	H11-0		H11-0	H11-0	H11-1	H11-1	H11-1	H11-1		H11-1	H11-1	H11-1	H11-1	H11-1	H11-1

eID	DDH	Lithology	Nd	Sm	Eu
06-663.5	H07-110	Exhalite	0.060	<0.0120	0.0031
07-63.6	H07-110	Exhalite	0.33	0.0025	0.0003
08-68.8	H07-110	Exhalite	0.34	0.0055	0.0012
6-188.8	H07-156	Exhalite	1.8	0.0353	0.0022
6-210.6	H07-156	Exhalite	1.6	0.0137	0.0004
08-106	H08-106	Exhalite	2.3	0.0164	0.0009
06-63.5	H08-80	Exhalite	0.28	0.0413	0.0030
07-63.7	H08-80	Exhalite	0.25	0.0174	0.0035
45-105.5	H11-105	Exhalite	0.70	0.37	0.15
45-105.2	H11-105	Exhalite	0.72	0.14	0.07
58-108.6	H11-108	Exhalite	0.80	0.36	0.18
58-108.6	H11-108	Exhalite	0.61	0.01	0.03
8-58.3	H11-08	Exhalite	55.4	12.40	2.69
8-63.9	H11-08	Exhalite	55.2	24.39	6.34
3C-363.5	H11-13C	Graphitic Argillite	2.02	3.49	0.44
3C-376.7	H11-13C	Graphitic Argillite	7.70	54.70	4.46
3C-378.2	H11-13C	Graphitic Argillite	14.87	57.10	6.43
3C-387	H11-13C	Graphitic Argillite	7.70	46.00	3.28
3C-389.4	H11-13C	Graphitic Argillite	1.2	0.178	0.28
6-415.4	H11-16	Exhalite	0.65	0.174	0.89
3C-357	H11-13C	Graphitic Argillite	4.14	7.186	2.87
6-399.1	H11-16	Exhalite	1.48	0.260	0.96
6-425.5	H11-16	Exhalite	1.8	12.452	0.29
6-480.6	H11-16	Graphitic Argillite	7.580	0.780	0.41

The following is a dense data matrix in which each numeric value is typeset vertically (one character per line). The grid is divided into four horizontal panels, each repeating the row labels Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf. The visible characters are reproduced below as a stacked-digit grid.

```
           Panel 1                     Panel 2                 Panel 3                     Panel 4
        0                                      0      0            0 0     0 2 1              0 0 1      2
Gd  0 . 0 0 0   0     0          Gd    . . 5 0 1 .    Gd  . . 0 . . .      Gd  0 . . . . 0 .
    0 0 . . .   0 . 0 .                . 5 2 9 . 8 1      1 2 . 4 5 3          . 1 6 6 . 7
    0 0 0 4 . 3 . 5              d     5 2 1 4 2 9 7  d   2 7 7 6 7 0     d    3 6 8 2 4 8
    9 5 8 5 3 5 2 5                                       5 2 5 6 3 1          5 6 8 1 6 7
    0 <
          <
Tb  0 0 0 0 0 0 0 0              Tb  0 0 1 0 0 0    Tb  0 0 0 0 4 1      Tb  0 0 1 2 0 4
    0 . . . . . . .                  . . 0 . 2 .        1 3 . 6 2 8          . 1 0 6 . 3
    2 0 0 0 0 0 0 0              b    0 0 1 0 9 0   b    6 8 0 7 8 5     b    0 9 9 3 0 8
    3 1 1 5 3 6 1 8                   7 2 6 2 7 2        2 1 9 7 7 7          6 2 2 1 6 9
    0
Dy  0 0 0 0 0 0 0 0              Dy  0 0 . 0 . 0    Dy  . . 0 . . .      Dy  0 . . . 0 .
    0 . . . . . . .                  . . 7 . 1 .        1 2 . 4 8 1          . 1 6 6 . 7
    0 0 0 4 2 3 2 6              y    4 1 1 2 9 1   y    1 7 7 8 8 8     y    3 1 7 7 4 3
    9 5 7 2 9 3 2 8                   2 9 9 4 0 8        9 9 5 1 6 9          8 3 0 7 1 3
    0 <
Ho  0 0 0 0 0 0 0 0              Ho    0 1 0 0 0    Ho  0 0 0 1 5 2      Ho  0 0 1 3 0 5
    0 . . . . . . .             o   0 . 8 . 4 .    o    2 6 . 1 9 5     o    . 2 4 6 . 5
    2 0 0 0 0 0 0 1                   . 0 1 0 4 0        7 2 1 2 3 0          1 7 0 5 1 6
    5 2 2 9 8 7 4 5                   1 5 6 5 7 3        0 9 8 5 9 0          1 8 1 9 1 5
    0
Er  0 0 0 0 0 0 0 0              Er  0 0 . . 0      Er  . . . . . .      Er  0 . . . 0 .
    0 . . . . . . .             r    . . 5 0 1 .   r    0 2 0 3 7 7     r    . 0 4 0 . 6
    7 0 0 3 2 2 1 4                   3 1 8 . 5 1        8 1 . 7 2 9          3 8 0 9 3 4
    0 3 4 9 6 1 4 7                   7 7 7 2 0 2        3 3 6 7 1 4          9 3 1 2 8 9
      <       <
Tm  0 0 0 0 0 0 0 0              Tm  0 0 0 0 0 0    Tm  0 0 0 0 2 1      Tm  0 0 0 1 0 2
    0 . . . . . . .             m    . . 8 . 2 .   m    1 3 . 5 4 1     m    . 1 5 6 . 4
    1 0 0 0 0 0 0 0                   0 0 7 0 2 0        5 1 0 4 2 5          0 3 8 0 0 2
    9 1 1 3 4 2 1 6                   4 2 2 3 0 1        1 1 8 5 9 1          5 4 5 5 5 3
    0
Yb  0 0   0 0 0 0                Yb  0 0 . . 0      Yb  . . 0 . . .      Yb  0 . . . 0 .
    0 . . . . . .               b    . . 5 0 1 .   b    0 1 . 3 5 7     b    . 0 3 0 . 6
    0 0 0 . 2 1 1 4                   3 2 7 . 4 1        9 9 5 5 5 3          3 8 8 7 3 2
    9 5 5 3 4 2 1 6                   4 5 5 2 0 3        2 8 9 5 3 8          2 5 2 2 1 8
    0
      <       <                                         . . . . <
Lu  0 0 0 0 0 0 0                Lu  0 0 0 0 0 0    Lu  0 0 0 0 2 1      Lu  0 0 0 1 0 2
    0 . . . . . . .             u    . . 9 . 2 .   u    1 3 . 6 4 1     u    . 1 5 7 . 4
    0 0 0 0 0 0 0 0                   0 0 3 0 4 0        5 5 0 0 3 9          0 6 3 1 0 7
    2 1 1 3 3 2 1 7                   4 2 1 3 7 1        2 2 8 4 7 6          6 1 7 3 5 4
    0
                                     < <    < <         < < < < 3 1          < 0 1      2
Hf  . 0 2 0 0 1     0            Hf  1 0 0 0 0 0    Hf  0 0 0 0 . .      Hf  0 0 . . 0 .
    1 . . . . .     .            f    . . . . . .   f    . . . . 6 2     f    . . 6 1 . 9
    4 1 3 8 9 4 1 7                   5 1 1 5 1 1        1 1 1 1 6 6          4 1 6 1 1 0
```

Note: values are correlation/probability figures rendered one digit per line; "<" marks indicate "less than" entries.

Block 1

	LOD							
Ta	0.0230	<0.151	<0.151	<0.152	<0.151	<0.151	<0.151	<0.151
W	0.0050	0.055	0.055	0.055	0.055	0.055	0.055	0.055
Tl	0.0005	<0.051	2.056	<0.052	0.051	<0.051	<0.053	0.051
Pb	0.60	0.1	7.9	3.3	1.3	0.9	3.6	4.2
Bi	0.150	0.01	0.08	<1.04	0.01	0.07	0.07	0.01
Th	0.0180	<0.022	<0.022	<0.022	<0.022	<0.022	<0.022	<0.022
U	0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011

Block 2

Ta	<0.011	<0.011	40.232	<0.131	40.232	<0.131
W	0.055	0.055	0.060	0.077	0.070	0.055
Tl	<0.011	<0.011	0.038	<0.051	0.045	<0.051
Pb	3.7	4.6	60.0	7.8	41.1	3.8
Bi	0.03	0.01	<0.420	0.02	<0.240	0.11
Th	<0.022	<0.022	0.049	<0.022	0.043	<0.022
U	<0.011	<0.011	0.025	<0.051	0.058	<0.051

Block 3

Ta	0.023	0.023	<0.011	0.039	5.096	1.565
W	<0.120	<0.130	1.090	<0.180	0.050	0.050
Tl	0.099	0.032	<0.011	1.070	2.064	2.095
Pb	4.3	4.0	0.7	5.8	0.8	1.9
Bi	<0.160	<0.170	0.010	<0.150	0.052	0.051
Th	0.063	0.073	<0.022	0.083	5.018	0.088
U	0.184	1.011	<0.011	1.033	7.371	4.300

Block 4

Ta	0.01	0.02	0.05	1.93	<0.031	3.82
W	<0.052	1.045	5.057	7.077	<0.073	0.631
Tl	<0.012	0.026	7.066	0.047	0.017	6.177
Pb	4.4	0.6	8.3	47.7	2.9	67.7
Bi	<0.011	0.018	0.016	4.621	<0.011	3.392
Th	<0.012	0.044	6.447	3.778	<0.022	0.830
U	0.011	1.010	3.158	4.384	0.022	5.829

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Sample ID	DDH/Trench	Lithology/Comment	$\delta^{33}S_{\text{V-CDT}}$ ±0.3 (2σ)	$\delta^{34}S_{\text{V-CDT}}$ ±0.3 (2σ)	$\Delta^{33}S$ ±0.02 (2σ)	$\delta^{56/54}Fe_{\text{IRMM-14}}$ ±0.06 (2σ)
H07-10-66.35	H07-10	Exhalite	0.1	3.0	-1.37	-2.04
H07-10-73.6	H07-10	Exhalite	-3.4	-5.6	-0.55	-1.80
H07-10-86.85	H07-10	Exhalite	-3.1	-4.9	-0.54	-1.91
H07-56-188.9	H07-56	Exhalite	-0.6	0.7	-0.95	-1.63
H07-56-210.6	H07-56	Exhalite	0.5	2.4	-0.70	-2.13
H08-106-98.6	H08-106	Exhalite	0.6	2.4	-0.69	
H08-80-103.2	H08-80	Exhalite	-2.5	-4.1	-0.42	-1.60
H08-80-107.5	H08-80	Exhalite	-4.4	-7.6	-0.54	-1.60
H11-05-45.55	H11-05	Exhalite	-5.2	-9.0	-0.58	-1.22
H11-05-54.25	H11-05	Exhalite	2.1	5.5	-0.74	-1.40
H11-08-52.65	H11-08	Exhalite	-6.3	-11.4	-0.46	-2.04
H11-08-58.3	H11-08	Exhalite	-5.3	-9.3	-0.45	-1.75
H11-08-63.9	H11-08	Exhalite	3.2	7.6	-0.66	
H11-13C-363	H11-13C	Exhalite	0.6	2.1	-0.46	-1.36
H11-13C-376.5	H11-13C	Exhalite	-3.4	-5.2	-0.75	-1.90
H11-13C-378.7	H11-13C	Exhalite	0.6	2.6	-0.79	-1.73
H11-13C-387.2	H11-13C	Exhalite	-0.5	-0.3	-0.34	-1.96
H11-13C-389.45	H11-13C	Exhalite	-0.4	0.2	-0.43	-2.08
H11-16-411.4	H11-16	Exhalite	-0.1	0.7	-0.44	-0.85
H11-16-425.5	H11-16	Exhalite	-1.4	-1.7	-0.49	-1.45
MGH502	MGH502	Exhalite	-6.2	-11.0	-0.53	
MGH600A	MGH600	Exhalite	-2.1	-2.8	-0.66	
MGH600B	MGH600	Exhalite	2.1	5.5	-0.73	
MGH601B	MGH601	Exhalite	-5.8	-10.0	-0.61	
H11-13C-357.1	H11-13C	Graphitic Argillite	0.9	3.5	-0.94	-1.86
H11-16-399.1	H11-16	Graphitic Argillite	0.6	1.6	-0.19	-1.96
H11-16-480.6	H11-16	Graphitic Argillite	2.3	5.0	-0.28	-1.66

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923   Table 3.

Anomaly	Formula used to Calculate Anomaly	H11-05-45.55	H11-08-52.66	H11-08-58.3	H11-08-63.9	H11-13C-376.5	H11-13C-378.7	H11-13C-387.2	H11-16-411.4	H07-10-66.35	H07-10-73.6	H07-10-86.85	H07-56-188.9	H07-56-210.6
		Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite	Exhalite
La	La/(3Pr-2Nd)*	-5.566	1.272	2.476	1.656	1.565	0.980	1.070	1.362	0.610	1.028	0.884	1.672	1.104
Ce	Ce/(2Pr-Nd)*	1.469	0.954	1.264	1.011	1.054	0.910	0.953	1.024	0.408	0.801	0.713	1.132	0.745
Pr	Pr/(1/2Ce+1/2Nd)*	0.905	1.024	0.913	0.994	0.976	1.050	1.023	0.989	1.503	1.111	1.185	0.945	1.150
Eu	Eu/(2/3Sm+1/3Tb)*	1.205	4.546	3.856	5.335	4.171	3.214	2.406	2.817		3.634	3.891	1.636	8.047
Gd	Gd/(2Tb-Dy)*	1.171	1.122	1.632	1.503	1.386	1.124	1.237	1.399		2.447	4.139	0.889	-2.027
Y/Ho		45.760	42.953	40.000	58.347	42.933	32.598	33.720	43.885		54.444	50.000	35.714	57.500
Gd/Yb*		0.625	0.817	0.822	0.831	0.794	1.003	1.067	1.182	0.968	0.908	0.756	1.765	1.100
Pr/Yb*		0.117	0.429	0.389	0.668	0.364	0.838	0.849	0.954	0.766	0.500	0.266	0.985	0.465

*Calculated using PAAS-normalized values

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