1   New aspects of sulfur biogeochemistry during ore

2   deposition from δ^{34}S of elemental sulfur and organic

3   sulfur from the Here's Your Chance Pb/Zn/Ag deposit

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Abstract

22   Sulfur isotope studies of base metal sulfide deposits have mostly

23 focussed on sulfide minerals, but elemental sulfur and organic sulfur are

24 also potentially significant components of the sulfur cycle during ore

25 deposition. The δ^{34}S of elemental sulfur and organic sulfur isolated from the

26 Paleoproterozoic Here's Your Chance (HYC) Pb/Zn/Ag deposit (McArthur

27 Basin, northern Australia) were measured to be between +5 and +8 ‰,

28 approximately 6 to 7 ‰ heavier than the median values of first-generation

29 HYC sulfides. Elemental sulfur and organic sulfur are thought to have been

30 formed contemporaneously with the first generation of metal sulfides. The

31 δ^{34}S of organic sulfur showed an increasing trend along the path of the

32 mineralising fluid, as sulfate was progressively ^{34}S-enriched due to Rayleigh

33 distillation. The δ^{34}S data support a model in which bacterial sulfate

34 reduction produced dissolved sulfide with δ^{34}S of 0 to +5 ‰. The subsequent

35 oxidation of sulfide produced reactive sulfur species such as polysulfide ions,

36 which were then incorporated into organic matter.

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Keywords

39   sulfur biogeochemistry; δ34S; organic geochemistry; Lead; zinc; silver;

40 minerals

41

1. Introduction

Base metal sulfide deposits are some of the largest and most economically significant mineral accumulations in the world (Huston et al., 2006). Stable sulfur isotopic studies on these deposits have revealed important information on the transport of metal-bearing fluids and precipitation mechanisms (e.g. Broadbent et al., 1998; Ireland et al., 2004). In addition, sulfur isotopes may reflect the evolution of the sulfur cycle and ocean chemistry (Böttcher, 2011; Canfield and Teske, 1996; Farquhar et al., 2010; Nabbefeld et al., 2010a; Nabbefeld et al., 2010c). Most sulfur isotope studies have however focussed on metal sulfides, and have often neglected elemental sulfur and organic sulfur. The pool of elemental sulfur can be significant in anoxic sediments (Yücel et al., 2010; Zhang and Millero, 1993; Zopfi et al., 2008; Zopfi et al., 2004) and organic sulfur can also be a major sink of reduced sulfur in sediments (Anderson and Pratt, 1995; Brüchert and Pratt, 1996; Passier et al., 1999; Sinninghe Damsté and de Leeuw, 1990; Werne et al., 2003), yet the isotopic composition of elemental and organic sulfur in ore deposits remains largely unexplored.

Elemental sulfur is one of the products of the oxidation of dissolved sulfide. It is produced by both phototrophic and non-phototrophic sulfur bacteria (Fossing et al., 1995; Zopfi et al., 2008; Zopfi et al., 2004) as well as by non-biological oxidation processes (Fry et al., 1988; Steger and

63   Desjardins, 1980; Zhang and Millero, 1993). Elemental sulfur is considered

64   a partially oxidised intermediate product in the sulfur cycle as it can

65   undergo further oxidation, reduction and disproportionation processes in

66   sediments (Böttcher et al., 2001; Canfield and Thamdrup, 1994; Jørgensen

67   and Nelson, 2004) and can also form polysulfide ions (S_x^{-2}) through reaction

68   with dissolved sulfide (Chen and Morris, 1972; Kamyshny and Ferdelman,

69   2010).

70   Organic sulfur is considered to be formed through two main pathways.

71   Assimilatory sulfate reduction is the process by which microorganisms

72   incorporate sulfate into the cell, where it is reduced to form essential sulfur-

73   containing compounds such as amino acids (Canfield, 2001). This

74   'biosynthetic sulfur' is estimated to contribute up to 25 % of the organic

75   sulfur in marine sediments (Anderson and Pratt, 1995; Passier et al., 1999;

76   Werne et al., 2003). The second, more important pathway for the formation

77   of organic sulfur is the incorporation of reduced sulfur during diagenesis.

78   Reduced sulfur is produced from dissolved sulfate through dissimilatory

79   sulfate reduction, also referred to as bacterial sulfate reduction (BSR)

80   (Canfield, 2001; Jørgensen, 1982). The mechanisms by which reduced sulfur

81   is incorporated into organic matter (OM) are complex and not fully

82   understood, but the reaction of polysulfide ions with functionalised organic

83   moieties is thought to be a significant pathway in sediments (e.g. Aizenshtat

84   et al., 1995; Sinninghe Damsté and de Leeuw, 1990; Werne et al., 2008).

85   Other reduced sulfur species such as H_2S may also be incorporated into OM

86   (Asif et al., 2009; Hebting et al., 2006; Sinninghe Damsté and de Leeuw,

87   1990), and have been linked to the preservation of soft tissue associated

88   with fossilised organisms within carbonate concretions (Melendez et al.,

89   2013).

90   The isotopic composition of organic sulfur is primarily controlled by the

91   isotopic composition of the source sulfur, most commonly dissolved seawater

92   sulfate, as well as the isotopic fractionations associated with sulfate

93   reduction and incorporation into OM. Assimilatory sulfate reduction

94   produces minor fractionations of generally less than 2 ‰ (e.g. Brüchert and

95   Pratt, 1996; Kaplan and Rittenberg, 1964), hence the δ^{34}S of biosynthetic

96   sulfur will be close to that of the source sulfate. Diagenetic organic sulfur is

97   derived from isotopically light dissolved sulfide produced by dissimilatory

98   sulfate reduction, with δ^{34}S values up to 70 ‰ lower than the source sulfate

99   under open system conditions (Sim et al., 2011; Wortmann et al., 2001). The

100   magnitude of isotopic fractionation in sediments may be smaller than 70 ‰

101   due to reservoir effects (Böttcher, 2011; Brunner and Bernasconi, 2005).

102   Conditions of severe sulfate depletion (< 200 µM dissolved sulfate) can

103   reduce the isotopic fractionation to near zero, as almost all sulfate entering

104   the cell is reduced (Habicht et al., 2002). The isotopic fractionations

105   associated with the incorporation of sulfur into OM have not been

106   extensively studied, however laboratory experiments performed on pure

107   organic compounds have shown evidence of a ^{34}S enrichment in the product

108   (Amrani and Aizenshtat, 2004). In a review of marine sediments from recent

109   to Jurassic age, Anderson and Pratt (1995) found that organic sulfur and

110   elemental sulfur were enriched in ^{34}S by an average of 10 ‰ compared to co-

111   existing pyrite.

112   Here we present δ^{34}S measurements of elemental sulfur and organic

113   sulfur from a Paleoproterozoic massive sulfide deposit, to explore the

114   mechanisms of formation of these sulfur species and the biogeochemistry

115   and role of sulfur during ore deposition.

116

117   **2. Materials and methods**

118   *2.1 Geologic setting*

119   The field site of this study is the Paleoproterozoic Here's Your Chance

120   (HYC) sediment-hosted Pb/Zn/Ag deposit located in the Barney Creek

121   Formation (BCF), a 1.64 Ga black shale in the McArthur Basin, northern

122   Australia (Page and Sweet, 1998). The geologic setting of HYC has been

123   extensively described, and several models of formation have been proposed

124   (e.g. Large et al., 1998; Logan et al., 2001; Williford et al., 2011). The deposit

125   is hosted in a restricted sub-basin of the BCF (McGoldrick et al., 2010).

126   Recent evidence has suggested that ferruginous conditions were widespread

127   in the Paleoproterozoic McArthur basin (Planavsky et al., 2011), however

128   preserved *n*-alkane distributions from the deposit indicate the presence of

129   sulfate-reducing and sulfide-oxidising bacteria, implying that the deposit

130   formed under localised euxinic conditions (Holman et al., 2014). It is

131 generally agreed that the formation of the deposit involved a hydrothermal

132 fluid which leached base metals from underlying formations and

133 transported them to the BCF (Cooke et al., 1998).

134

135   *2.2 Sample storage and preparation*

136   The samples used in this study were made available from the previous

137 study of Williford et al. (2011). Samples were taken from five surface

138 exposures of ore body five, and were labelled as pits 1 to 5. The samples

139 follow the estimated flow path of the mineralising fluid from north-east to

140 south-west, with pit 1 being the first deposited. At the conclusion of the

141 Williford study the rock samples were wrapped in aluminium foil and stored

142 in the dark at room temperature (for *ca.* three years). Rock fragments were

143 ground using a RockLabs ring mill with a zirconium head, and the powdered

144 rock was stored in sealed glass jars in the dark at room temperature. Sulfide

145 minerals that are exposed to atmosphere may be oxidise to produce a range

146 of species including elemental sulfur (Chandra and Gerson, 2011). To

147 mitigate this possibility, Soxhlet extractions for the analysis of elemental

148 sulfur commenced no later than one week after the rock was powdered.

149

150 *2.3 Quantification of elemental sulfur*

151   Elemental sulfur was quantified using a method modified from Zopfi et

152   al. (2004). 20 to 30 g of powdered rock sample was extracted with pure

153   methanol (approximately 200 mL, 48 hr) in a Soxhlet apparatus. Each

154   extract was made up to 250 mL with methanol and analysed by reverse-

155   phase chromatography using an Agilent 1200 series HPLC with an Agilent

156   pump (1260), a diode array detector and a Spherisorb S10 ODS2 column.

157   Methanol (Mallinckrodt Chemicals, UltimAR grade) was used as the mobile

158   phase at a flow rate of 1 mL/min. Elemental sulfur was detected after 5.5

159   min at a wavelength of 265 nm. Standards of elemental sulfur (Chem

160   Supply 'sulfur powder', minimum 99.6 %) were prepared at concentrations of

161   1 to 1000 µM and analysed to create an external calibration curve.

162

163   *2.4 Isolation of kerogen and elemental sulfur for isotopic measurements*

164   The isolation of kerogen from HYC samples was a modification of the

165   procedure described by Nabbefeld et al. (2010b). Briefly, removal of

166   carbonates with 1 M HCl was followed by a two-stage digestion in 24 %

167   hydrofluoric acid to remove silicate minerals. Kerogen was separated from

168   acid-insoluble sulfide minerals by heavy liquid separation using a saturated

169   zinc bromide solution.

170   Elemental sulfur for $\delta^{34}S$ analysis was obtained from Soxhlet

171   extractions following the procedure described by Williford et al. (2011) and

172   Holman et al. (2012). Powdered rock was extracted in a Soxhlet apparatus

173 using dichloromethane / methanol (9:1 v/v 96 hr). Activated copper turnings

174 (VWR Chemicals, 1 hr sonication in 4 M HCl) were added to the collection

175 flask to remove elemental sulfur from the organic extract. Dissolved

176 elemental sulfur reacts with the activated copper to form solid copper

177 sulfide, visible as a black layer on the surface of the copper. Additional

178 copper was added to the collection flask after 24 hr, and the extraction

179 continued for another 24 hr to ensure all sulfur was collected. Copper added

180 after 48 hr showed no black colouration.

181

182 *2.5 Measurement of sulfur isotopic composition*

183   Copper sulfide was scraped from the surfaces of the activated copper

184 for stable isotope measurements. Sulfur isotope measurements were carried

185 out on both copper sulfide and kerogen by combustion-isotope ratio

186 monitoring ratio mass spectrometry (C-irmMS). Samples were combusted

187 with V_2O_5 added as a catalyst in Sn cups in a Thermo Flash elemental

188 analyser coupled via a Thermo Conflo split interface to a Thermo Finnigan

189 Mat 253 gas mass spectrometer. Sulfur isotope ratios ($^{34}S/^{32}S$) are reported

190 in conventional δ-notation with a precision of approximately $\pm$ 0.3 ‰, and

191 were calibrated versus the Vienna Cañon Diablo Troilite (VCDT) scale

192 according to Mann et al. (2009), using the international reference materials

193 IAEA-S-1, -2 and -3.

194

3. Results and discussion

3.1 Distribution of sulfur species in HYC sediments

Table 1 shows the masses (µg per g sediment) of elemental sulfur and kerogen sulfur isolated from the five HYC samples. Also listed are comparative amounts of sulfur in sphalerite, galena and pyrite, separately calculated from total endowments reported by Lambert and Scott (1973) and Huston et al. (2006). Over 98 % of total sulfur at HYC exists as sulfide minerals, reflecting the rapid and efficient scavenging of dissolved sulfide by highly abundant metal species (e.g. Canfield, 1989; Druschel et al., 2002). Organic sulfur incorporated into kerogen is the next most abundant fraction, and only minor amounts of elemental sulfur are present. The amount of sulfur in HYC kerogens is higher than in previous reports of non-mineralised McArthur Basin samples (Powell et al., 1987). A noticeable increase in organic sulfur appears to have accompanied mineralisation, indicating that while the majority of reduced sulfur is consumed by metal cations, some is also incorporated into OM.

Quantification of elemental sulfur has not been reported for non-mineralised sediments from the McArthur Basin, but the amounts at HYC (2.5 to 11.8 µg/g) appear comparable to modern euxinic sediments (Henneke et al., 1997; Yücel et al., 2010). Elemental sulfur is known to be produced by phototrophic sulfur bacteria (Zerkle et al., 2009), which have been identified in the mineralised zones of HYC (Holman et al., 2014) and also in

217 unmineralised sections of the BCF (Brocks et al., 2005). These bacteria

218 produce elemental sulfur through the oxidation of dissolved sulfide, but also

219 consume elemental sulfur when the supply of sulfide is limited (Zerkle et al.,

220 2009). During mineralisation the rapid reaction of sulfide with metal ions

221 would have greatly reduced the availability of sulfide for phototrophic

222 oxidation and may have forced the bacteria to consume elemental sulfur.

223 Elemental sulfur may also be consumed by bacterial disproportionation

224 reactions (Böttcher et al., 2001; Canfield and Thamdrup, 1994) or mobilised

225 by reaction with dissolved sulfide to form polysulfide ions (Aizenshtat et al.,

226 1995).

227   Extractable organic sulfur compounds such as dibenzothiophenes

228 (DBTs) have been detected in only trace amounts in HYC sediments (Chen

229 et al., 2003), hence are not considered significant to the sulfur cycle of the

230 HYC mineral system (Section 3.3). DBTs may form through either the

231 breakdown of sulfur-containing kerogen during thermal maturation

232 (Aizenshtat et al., 1995) or the incorporation of sulfur into existing aromatic

233 compounds (Asif et al., 2009; Fenton et al., 2007). The low abundance of

234 DBTs in HYC bitumen suggests that these processes did not occur to a

235 significant extent during mineralisation. It may also reflect the thermal

236 cracking of DBTs to H_2, H_2S and biphenyls, as has been demonstrated in

237 pyrolysis experiments (Dartiguelongue et al., 2006).

238

3.2 δ^{34}S of kerogen and elemental sulfur

240   The δ^{34}S values of kerogen and elemental sulfur from the five HYC

241   sample pits are shown in Table 1. These were consistently between +6 and

242   +8 ‰ except for pit 1 kerogen (+4.9 ‰). The δ^{34}S of kerogen and elemental

243   sulfur from each sample pit were within 1 ‰ apart from pit 1, where the

244   kerogen was 2.4 ‰ lighter. This close equivalence matches previous

245   observations of co-existing kerogen and elemental sulfur (summarised by

246   Anderson and Pratt, 1995) and has been attributed to a common sulfur

247   source for the two species.

248   The δ^{34}S values of all kerogen samples, with the exception of pit 2,

249   show a steady increase from +5 ‰ to +8 ‰ along the path of hydrothermal

250   fluid flow (Fig. 1). Such an increase is consistent with a genetic model in

251   which base metal sulfides and organic sulfur are formed from sulfate carried

252   by the mineralising fluid, likely sourced from evaporitic units that are

253   present throughout the McArthur Basin (e.g. Cooke et al., 2000). Sulfate

254   reduction (bacterial or thermochemical) produces sulfide with a significant

255   depletion in ^{34}S, hence the residual sulfate is progressively enriched through

256   Rayleigh distillation (e.g. Hartmann and Nielsen, 2012; Seal, 2006). The pit

257   2 kerogen value of +8.5 ‰ is an exception to this otherwise consistent trend.

258   This sample also exhibits an anomalously low weight percentage of sulfur (8

259   wt. % of kerogen, compared to > 23 wt. % for the other samples), suggesting

260   that it may have been affected by localised processes that have removed a

261   large fraction of organic sulfur, with the remained being enriched in ^{34}S.

262   The large input of sulfate with the mineralising fluid also fits with the

263   recent evidence for euxinic conditions during the formation of HYC while

264   the wider McArthur basin was predominantly ferruginous (Holman et al.,

265   2014). Such an influx of sulfate into the restricted HYC sub-basin could

266   have caused the development of euxinic conditions via the increased

267   production of sulfide by sulfate-reducing bacteria (Poulton et al., 2010).

268   Temperature estimates for the mineralising fluids at HYC, which generally

269   range between 150 to 200 °C (e.g. Large et al., 1998; Williford et al., 2011),

270   are above the range at which microbes can survive. When the fluid reached

271   the HYC sub-basin dissolved sulfate in the fluid would have been consumed

272   by sulfate-reducing bacteria existing within the water column and

273   sediments. The mixing of the hot mineralising fluid with the basin water

274   would likely have lowered the temperature to within the viable range of

275   sulfate reducing bacteria, which have been shown to be active at

276   temperatures up to 85 °C (Canfield et al., 2000).

277   The increase in kerogen δ^{34}S along the path of fluid flow is further

278   illustrated in Fig. 2, in which δ^{34}S of kerogen is plotted against the average

279   δ^{13}C of PAHs from the same sample pits reported by Williford et al. (2011).

280   The δ^{13}C of PAHs decreases from pits 1 to 5 along the flow path of the

281   mineralising fluid, due to the decreasing input of migrated PAHs that are

282   relatively enriched in ^{13}C (Williford et al., 2011). The concurrent increase of

283   kerogen δ^{34}S may be explained by a Rayleigh distillation process as

284   discussed above. The δ^{34}S of elemental sulfur does not reflect a similar trend

13

285 and shows no clear pattern along the flow path of the hydrothermal fluid.

286 Elemental sulfur is a highly reactive species which be consumed by

287 oxidation and/or disproportionation reactions (Section 3.1) and can also be

288 generated after deposition by the oxidation of sulfide minerals or aqueous

289 sulfide (Steger and Desjardins, 1980; Zhang and Millero, 1993). Any trend

290 in the $\delta^{34}S$ of elemental sulfur along the fluid flow path is likely to have

291 been overprinted by such local effects.

292   A possible alternative explanation for the increase in kerogen $\delta^{34}S$

293 along the flow path of the mineralising fluid is a temperature control effect.

294 The flow of the mineralising fluid is believed to have produced a gradient of

295 decreasing temperature from pits 1 to 5 as the fluid cooled during deposition

296 (Williford et al., 2011). The isotopic fractionation associated with BSR has

297 been shown to be influenced by temperature, with increased temperatures

298 generally producing higher rates of sulfate reduction and reduced

299 fractionation (Kaplan and Rittenberg, 1964). If temperature was an

300 important control, the highest temperature pit (pit 1) would have

301 experienced the least fractionation during sulfate reduction and would thus

302 be the most enriched in ^{34}S. This is the opposite of the observed trend, as

303 seen in Fig. 1, hence the temperature of the mineralising fluid does not

304 appear to have significantly affected the $\delta^{34}S$ of organic sulfur at HYC. This

305 finding fits with previous observations that the isotopic fractionation of BSR

306 remains relatively constant at temperatures of 60 °C and above (Böttcher et

307 al., 1999; Canfield et al., 2000).

14

308   Fig. 3 shows a comparison of the measured $\delta^{34}S$ of kerogen and

309   elemental sulfur with previous sulfur isotopic studies of sulfide minerals

310   from HYC and other McArthur Basin sediments. Detailed isotopic

311   measurements have revealed two main phases of sulfide precipitation at

312   HYC. Eldridge et al. (1993) proposed that first-generation pyrite (with $\delta^{34}S$ -

313   13 to +15 ‰) was formed during early diagenesis from sulfide produced by

314   BSR, while a later second-generation pyrite (-5 to +45 ‰) was formed in a

315   closed system from residual sulfide that was relatively more enriched in ^{34}S.

316   A subsequent investigation by Ireland et al. (2004) identified two phases of

317   sphalerite: an early sphalerite with $\delta^{34}S$ of 0 to +12 ‰ which precipitated

318   prior to first-generation pyrite, and a later, heavier phase (+3 to +19 ‰).

319   First-generation mineralisation comprises over 80 % of all pyrite and

320   sphalerite at HYC (Ireland et al., 2004).

321   Kerogen and elemental sulfur measured in this study are 3 to 7 ‰

322   heavier than the average $\delta^{34}S$ of first-generation HYC sulfides. This broadly

323   fits with the findings of Anderson and Pratt (1995), who showed that

324   kerogen and elemental sulfur are ^{34}S-enriched from co-existing pyrite in

325   marine sediments by an average of 10 ‰. Elemental sulfur and organic

326   sulfur at HYC likely formed contemporaneously with the first-generation

327   sulfides. The second generation of sulfides at HYC are relatively enriched in

328   ^{34}S, which was attributed to the formation from ^{34}S-heavy pore-water sulfate

329   in a closed system (Eldridge et al., 1993). This limited supply of sulfur would

330   have been efficiently scavenged by metal cations. The lower $\delta^{34}S$ of

15

331   elemental sulfur and organic sulfur indicates that these species were formed

332   from the more freely available and relatively lighter sulfide responsible for

333   the first-generation metal sulfides.

334   It is notable that the $\delta^{34}S$ of elemental sulfur and kerogen show a

335   greatly reduced range of values compared to base metal sulfides at HYC

336   (Fig. 3). Elemental sulfur and kerogen were analysed by bulk techniques

337   using > 20 g of rock from each sample pit (section 2.4). Conversely, the ion

338   probe and laser ablation measurements of Eldridge et al. (1993) and Ireland

339   et al. (2004) measured $\delta^{34}S$ of base metal sulfides at high resolution,

340   revealing extreme isotopic heterogeneity on a fine scale. Microscale *in situ*

341   measurements of organic $\delta^{34}S$, such as demonstrated by Bontognali et al.

342   (2012), may reveal similar heterogeneity of organic sulfur isotopes.

343

344   *3.3 Model of sulfur transformations at HYC*

345   The measured $\delta^{34}S$ of elemental sulfur and organic sulfur fit well with

346   the simplified model of sulfur transformations during the deposition of HYC

347   presented in Fig. 4. The model is based on a middle Proterozoic seawater

348   sulfate isotopic composition of +20 to +25 ‰ (Strauss, 1993). Sulfate

349   reduction was assumed to be accompanied by an estimated ^{34}S-depletion of

350   20 ‰, which was proposed by Shen et al. (2002) as being typical for BSR in

351   euxinic sections of the McArthur Basin with limited supply of sulfate. The

352   HYC deposit was formed in a tectonically-controlled sub-basin in which local

353 conditions were conducive to BSR and exchange with the main basin was

354 partially restricted (McGoldrick et al., 2010).

355   This degree of fractionation is also within the range reported for

356 thermochemical sulfate reduction (TSR; Machel et al., 1995). The respective

357 contributions of BSR and TSR during the deposition of HYC have been

358 difficult to resolve (Logan et al., 2001). Ireland et al. (2004) concluded that

359 while both BSR and TSR likely contributed to the formation of the deposit,

360 BSR was the dominant process. *n*-Alkane distributions indicative of sulfate-

361 reducing bacteria have recently been detected in highly-mineralised regions

362 of HYC (Holman et al., 2014). The ^{34}S-enrichment of benzothiophenes

363 compared to dibenzothiophenes has been proposed as a proxy for TSR

364 (Amrani et al., 2012), however dibenzothiophenes have been detected only in

365 trace amounts at HYC (Section 3.1) while benzothiophenes have not been

366 reported. For the purposes of this simplified model it was considered that

367 the sulfide was formed solely by BSR.

368   The assumed fractionation of 20 ‰ during BSR would produce sulfide

369 with δ^{34}S of 0 to +5 ‰. Only minor fractionation occurs during the

370 precipitation of sulfide minerals from dissolved sulfide (Böttcher et al., 1998;

371 Butler et al., 2004; Price and Shieh, 1979), therefore the δ^{34}S of sulfide

372 minerals is also expected to be close to 0 to +5 ‰. This is consistent with the

373 sulfur isotopic composition of first-generation HYC sulfides measured by

374 Eldridge et al. (1993) and Ireland et al. (2004), and also with the δ^{34}S of

375 pyrite from the Wollogorang Formation (-2 to +6 ‰), which underlies the

376 BCF and through which the mineralising fluid is believed to have flowed

377 (Donnelly and Jackson, 1988; Shen et al., 2002).

378   Dissolved sulfide that does not react to form sulfide minerals may be

379 oxidised by a range of microorganisms and also by abiotic reactions

380 (Canfield, 2001). The $\delta^{34}S$ of elemental sulfur at HYC (+6 to +8 ‰) is

381 slightly higher than the sulfide minerals (Fig. 3) consistent with production

382 by phototrophic sulfur bacteria. Biomarker evidence for the presence of

383 phototrophic sulfur bacteria has been detected at HYC (Holman et al.,

384 2014), as well as non-mineralised sections of the BCF (Brocks et al., 2005).

385 Elemental sulfur produced by phototrophic sulfur bacteria in bacterial

386 culture experiments was reported to be 1 to 3 ‰ enriched in ^{34}S compared

387 to the source sulfide (Zerkle et al., 2009). Conversely, a depletion of 4 to 5 ‰

388 is typical for the abiotic oxidation of sulfide to elemental sulfur (Fry et al.,

389 1988) which does not fit the available data. The $\delta^{34}S$ of elemental sulfur at

390 HYC must be interpreted with caution as a significant proportion has likely

391 been consumed by oxidation and/or disproportionation reactions, and some

392 may also have been generated by non-biological oxidation reactions after

393 deposition (sections 3.1 and 3.2). The isotopic composition of the remaining

394 elemental sulfur will have been modified by these post-depositional

395 processes, so firm conclusions on its formation cannot be drawn based on

396 this data. Nevertheless, the available isotopic and biomarker evidence

397 supports the oxidation of sulfide by phototrophic sulfur bacteria.

398   Polysulfide ions exist in isotopic equilibrium with elemental sulfur and

399   dissolved sulfide, and have been shown in laboratory experiments to be 2 to

400   4 ‰ enriched in [34]S compared to sulfide (Amrani et al., 2006). The

401   incorporation of polysulfides into OM may result in further [34]S-enrichment.

402   This process has not been widely studied, but Amrani and Aizenshtat (2004)

403   reported that the reaction of model polysulfide solutions with pure carbonyl

404   compounds produced organic sulfur compounds (primarily alkyl chains

405   connected by polysulfide bridges) that were [34]S-enriched by 4 to 5 ‰.

406   Sedimentary organic sulfur is thought to derive from a combination of

407   diagenetic and biosynthetic pathways, with biosynthetic sulfur being

408   relatively enriched in [34]S as it is formed with similar δ^{34}S to the seawater

409   sulfate source (Brüchert and Pratt, 1996; Kaplan and Rittenberg, 1964).

410   Biosynthetic sulfur has been estimated to contribute up to 25 % of organic

411   sulfur in marine sediments (Anderson and Pratt, 1995; Brüchert and Pratt,

412   1996; Passier et al., 1999), although this proportion may be reduced with

413   thermal maturation as the highly labile biosynthetic sulfur compounds are

414   expected to be rapidly remineralised (Werne et al., 2003). Assuming a

415   contribution from biosynthetic sulfur of 10 %, the model predicts organic

416   sulfur with δ^{34}S between +7 and +15 ‰. The measured δ^{34}S of HYC kerogen

417   (+5 to + 8 ‰) is at the lower end of this range. This may suggest a lower

418   degree of [34]S-enrichment during incorporation of sulfur into OM than was

419   reported from the laboratory experiments of Amrani and Aizenshtat (2004).

420   Recently reported compound-specific δ^{34}S measurements of diagenetic

421 organic sulfur compounds from the Cariaco Basin showed that some

422 compounds were significantly [34]S-depleted compared to co-existing sulfide

423 (Raven et al., 2013), suggesting that diagenetic sulfurisation may result in a

424 wider range of fractionations than previously reported. Alternatively the

425 contribution from biosynthetic sulfur at HYC may have been lower than the

426 assumed 10 %.

427   The model shown in Fig. 4 presents only a simplified view of the

428 chemical transformations of sulfur during the deposition of HYC, but

429 matches well with the measured δ^{34}S of elemental sulfur and kerogen. It

430 should be noted that the simplified model presented here is based on a

431 system that is open for all relevant processes. A natural environment with

432 closed or semi-closed precipitation conditions, and the potential for changes

433 in conditions during the evolution of the system, may alter the predicted

434 trends and further complicate interpretations of the genetic relationships of

435 the different sulfur-bearing phases.

436

437 **4. Conclusions**

438   The sulfur isotopic composition of elemental sulfur and organic sulfur

439 at HYC reveal information on sulfur cycling during the formation of the

440 base metal sulfide deposit. These species are 3 to 7 ‰ enriched in [34]S

441 compared to first-generation sulfide minerals. The measured δ^{34}S values

442 strongly support a genetic model in which elemental sulfur and organic

443   sulfur were formed simultaneously with base metal sulfides from dissolved

444   sulfide that was produced by BSR. Organic sulfur is believed to have been

445   formed through the incorporation of polysulfide ions into OM. While the

446   five pit samples represent a modest sample set, the organic sulfur displayed

447   a trend of increasing $\delta^{34}S$ along the path of the mineralising fluid which may

448   result from Rayleigh distillation, suggesting that $\delta^{34}S$ of organic sulfur may

449   be useful for the targeted exploration of minerals. The enrichment in ^{34}S of

450   elemental sulfur compared to HYC sulfide minerals suggests that

451   phototrophic sulfur oxidation may have been an important process, but the

452   likely alteration of the isotopic signal by post-depositional processes renders

453   this conclusion uncertain.

454   Although organic and elemental sulfur are quantitatively minor

455   components of the total sulfur inventory at HYC, this study has shown that

456   they reveal important aspects of the sulfur cycle during the formation of the

457   deposit, complementing and extending the more traditional studies of

458   mineral sulfides. These species should not be neglected in isotopic

459   investigations of base metal deposits, or of any sedimentary system in which

460   the sulfur cycle plays an important role.

461

462   **Acknowledgements**

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743

744

745 **Captions of tables and figures**

746

747 *Table 1*

748 δ^{34}S of kerogen and elemental sulfur for the five HYC sample pits

749 (error is ± 0.3 ‰), plus masses of sulfur contained in kerogen and elemental

750 sulfur in the five HYC sample pits, reported in µg of sulfur per g of rock.

751 Average masses of sulfur in sulfide minerals were calculated from data

752 reported by Huston et al. (2006) for ZnS and PbS, and Lambert and Scott

753 (1973) for FeS_2.

754

755 *Figure 1*

756 δ^{34}S of kerogen and elemental sulfur from the five HYC sample pits.

757 Error bars indicate uncertainty of 0.3 ‰.

758

759 *Figure 2*

760 δ^{34}S of kerogen from the five HYC sample pits (error bars indicate

761 uncertainty of 0.3 ‰), plotted against average δ^{13}C of PAHs (reported by

762 Williford et al., 2011). The input of ^{13}C-enriched, non-indigenous PAHs

763 decreases from pits 1 to 5 (section 3.2).

764

765   *Figure 3*

766   Box-and-whisker plots of $\delta^{34}S$ data for kerogen and elemental sulfur

767   from HYC (this study) and reported $\delta^{34}S$ of sulfide minerals from HYC and

768   the McArthur Basin. Whiskers show the full range of reported $\delta^{34}S$, boxes

769   represent the middle 50 % of the data (first to third quartiles). Estimated

770   isotopic composition of Paleoproterozoic seawater sulfate (+20 to +25 ‰:

771   Strauss, 1993) is indicated by the lightly shaded area. 1 Eldridge et al.

772   (1993), 2 Ireland et al. (2004), 3 Johnston et al. (2008), 4 Shen et al. (2002).

773

774   *Figure 4*

775   Proposed scheme for the formation of organic sulfur, elemental sulfur

776   and sulfide minerals at HYC. Details of the scheme are discussed in Section

777   3.3. Boxes represent the $\delta^{34}S$ of the various sulfur species (vertical axis is

778   not to scale), and arrows represent predicted fractionations during

779   transformation processes. $\delta^{34}S$ values in bold were measured either in this

780   study (elemental sulfur and organic sulfur) or by previous researchers. $\delta^{34}S$

781   values in italics are predictions calculated from the measured values and

782   fractionations reported in previous studies. 1 Strauss (1993), 2 Canfield

783   (2001), 3 Shen et al. (2002), 4 Machel et al. (1995), 5 Eldridge et al. (1993), 6

784   Ireland et al. (2004), 7 Zerkle et al. (2009), 8 Amrani et al. (2006), 9 Amrani

785   and Aizenshtat (2004), 10 Anderson and Pratt (1995).

Table 1

	Pit 1	Pit 2	Pit 3	Pit 4	Pit 5
Distance from pit 1	0	104	372	553	710
$\delta^{34}S$ (‰)					
Kerogen	4.9	8.5	6.2	6.5	8.0
Elemental sulfur	7.3	7.9	6.0	7.1	7.0
Kerogen sulfur (% dry wt.)	26	8	23	28	25
Mass (µg S / g rock)					
Kerogen S	2054	384	1104	1344	1400
Elemental S	2.9	8.4	2.5	11.8	10.7

	PbS	ZnS	FeS_2
Average mass (µg S / g rock)	6345.9	45127.6	80390.3

δ³⁴S (‰)