New aspects of sulfur biogeochemistry during ore deposition from $\delta^{34}$S of elemental sulfur and organic sulfur from the Here’s Your Chance Pb/Zn/Ag deposit

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Abstract

Sulfur isotope studies of base metal sulfide deposits have mostly focussed on sulfide minerals, but elemental sulfur and organic sulfur are also potentially significant components of the sulfur cycle during ore deposition. The $\delta^{34}S$ of elemental sulfur and organic sulfur isolated from the Paleoproterozoic Here’s Your Chance (HYC) Pb/Zn/Ag deposit (McArthur Basin, northern Australia) were measured to be between +5 and +8 ‰, approximately 6 to 7 ‰ heavier than the median values of first-generation HYC sulfides. Elemental sulfur and organic sulfur are thought to have been formed contemporaneously with the first generation of metal sulfides. The $\delta^{34}S$ of organic sulfur showed an increasing trend along the path of the mineralising fluid, as sulfate was progressively $^{34}S$-enriched due to Rayleigh distillation. The $\delta^{34}S$ data support a model in which bacterial sulfate reduction produced dissolved sulfide with $\delta^{34}S$ of 0 to +5 ‰. The subsequent oxidation of sulfide produced reactive sulfur species such as polysulfide ions, which were then incorporated into organic matter.

Keywords

sulfur biogeochemistry; $\delta^{34}S$; organic geochemistry; Lead; zinc; silver; minerals
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
Desjardins, 1980; Zhang and Millero, 1993). Elemental sulfur is considered a partially oxidised intermediate product in the sulfur cycle as it can undergo further oxidation, reduction and disproportionation processes in sediments (Böttcher et al., 2001; Canfield and Thamdrup, 1994; Jørgensen and Nelson, 2004) and can also form polysulfide ions (S_{x}^{2-}) through reaction with dissolved sulfide (Chen and Morris, 1972; Kamyszny and Ferdelman, 2010).

Organic sulfur is considered to be formed through two main pathways. Assimilatory sulfate reduction is the process by which microorganisms incorporate sulfate into the cell, where it is reduced to form essential sulfur-containing compounds such as amino acids (Canfield, 2001). This ‘biosynthetic sulfur’ is estimated to contribute up to 25 % of the organic sulfur in marine sediments (Anderson and Pratt, 1995; Passier et al., 1999; Werne et al., 2003). The second, more important pathway for the formation of organic sulfur is the incorporation of reduced sulfur during diagenesis. Reduced sulfur is produced from dissolved sulfate through dissimilatory sulfate reduction, also referred to as bacterial sulfate reduction (BSR) (Canfield, 2001; Jørgensen, 1982). The mechanisms by which reduced sulfur is incorporated into organic matter (OM) are complex and not fully understood, but the reaction of polysulfide ions with functionalised organic moieties is thought to be a significant pathway in sediments (e.g. Aizenshtat et al., 1995; Sinninghe Damsté and de Leeuw, 1990; Werne et al., 2008).

Other reduced sulfur species such as H_{2}S may also be incorporated into OM
(Asif et al., 2009; Hebting et al., 2006; Sinninghe Damsté and de Leeuw, 1990), and have been linked to the preservation of soft tissue associated with fossilised organisms within carbonate concretions (Melendez et al., 2013).

The isotopic composition of organic sulfur is primarily controlled by the isotopic composition of the source sulfur, most commonly dissolved seawater sulfate, as well as the isotopic fractionations associated with sulfate reduction and incorporation into OM. Assimilatory sulfate reduction produces minor fractionations of generally less than 2 ‰ (e.g. Brüchert and Pratt, 1996; Kaplan and Rittenberg, 1964), hence the $\delta^{34}$S of biosynthetic sulfur will be close to that of the source sulfate. Diagenetic organic sulfur is derived from isotopically light dissolved sulfide produced by dissimilatory sulfate reduction, with $\delta^{34}$S values up to 70 ‰ lower than the source sulfate under open system conditions (Sim et al., 2011; Wortmann et al., 2001). The magnitude of isotopic fractionation in sediments may be smaller than 70 ‰ due to reservoir effects (Böttcher, 2011; Brunner and Bernasconi, 2005).

Conditions of severe sulfate depletion (< 200 μM dissolved sulfate) can reduce the isotopic fractionation to near zero, as almost all sulfate entering the cell is reduced (Habicht et al., 2002). The isotopic fractionations associated with the incorporation of sulfur into OM have not been extensively studied, however laboratory experiments performed on pure organic compounds have shown evidence of a $^{34}$S enrichment in the product (Amrani and Aizenshtat, 2004). In a review of marine sediments from recent
to Jurassic age, Anderson and Pratt (1995) found that organic sulfur and elemental sulfur were enriched in $^{34}$S by an average of 10‰ compared to co-existing pyrite.

Here we present $\delta^{34}$S measurements of elemental sulfur and organic sulfur from a Paleoproterozoic massive sulfide deposit, to explore the mechanisms of formation of these sulfur species and the biogeochemistry and role of sulfur during ore deposition.

2. Materials and methods

2.1 Geologic setting

The field site of this study is the Paleoproterozoic Here’s Your Chance (HYC) sediment-hosted Pb/Zn/Ag deposit located in the Barney Creek Formation (BCF), a 1.64 Ga black shale in the McArthur Basin, northern Australia (Page and Sweet, 1998). The geologic setting of HYC has been extensively described, and several models of formation have been proposed (e.g. Large et al., 1998; Logan et al., 2001; Williford et al., 2011). The deposit is hosted in a restricted sub-basin of the BCF (McGoldrick et al., 2010). Recent evidence has suggested that ferruginous conditions were widespread in the Paleoproterozoic McArthur basin (Planavsky et al., 2011), however preserved $n$-alkane distributions from the deposit indicate the presence of sulfate-reducing and sulfide-oxidising bacteria, implying that the deposit formed under localised euxinic conditions (Holman et al., 2014). It is
generally agreed that the formation of the deposit involved a hydrothermal fluid which leached base metals from underlying formations and transported them to the BCF (Cooke et al., 1998).

2.2 Sample storage and preparation

The samples used in this study were made available from the previous study of Williford et al. (2011). Samples were taken from five surface exposures of ore body five, and were labelled as pits 1 to 5. The samples follow the estimated flow path of the mineralising fluid from north-east to south-west, with pit 1 being the first deposited. At the conclusion of the Williford study the rock samples were wrapped in aluminium foil and stored in the dark at room temperature (for ca. three years). Rock fragments were ground using a RockLabs ring mill with a zirconium head, and the powdered rock was stored in sealed glass jars in the dark at room temperature. Sulfide minerals that are exposed to atmosphere may be oxidise to produce a range of species including elemental sulfur (Chandra and Gerson, 2011). To mitigate this possibility, Soxhlet extractions for the analysis of elemental sulfur commenced no later than one week after the rock was powdered.

2.3 Quantification of elemental sulfur
Elemental sulfur was quantified using a method modified from Zopfi et al. (2004). 20 to 30 g of powdered rock sample was extracted with pure methanol (approximately 200 mL, 48 hr) in a Soxhlet apparatus. Each extract was made up to 250 mL with methanol and analysed by reverse-phase chromatography using an Agilent 1200 series HPLC with an Agilent pump (1260), a diode array detector and a Spherisorb S10 ODS2 column. Methanol (Mallinckrodt Chemicals, UltimAR grade) was used as the mobile phase at a flow rate of 1 mL/min. Elemental sulfur was detected after 5.5 min at a wavelength of 265 nm. Standards of elemental sulfur (Chem Supply ‘sulfur powder’, minimum 99.6 %) were prepared at concentrations of 1 to 1000 μM and analysed to create an external calibration curve.

2.4 Isolation of kerogen and elemental sulfur for isotopic measurements

The isolation of kerogen from HYC samples was a modification of the procedure described by Nabbefeld et al. (2010b). Briefly, removal of carbonates with 1 M HCl was followed by a two-stage digestion in 24 % hydrofluoric acid to remove silicate minerals. Kerogen was separated from acid-insoluble sulfide minerals by heavy liquid separation using a saturated zinc bromide solution.

Elemental sulfur for δ34S analysis was obtained from Soxhlet extractions following the procedure described by Williford et al. (2011) and Holman et al. (2012). Powdered rock was extracted in a Soxhlet apparatus.
using dichloromethane / methanol (9:1 v/v 96 hr). Activated copper turnings (VWR Chemicals, 1 hr sonication in 4 M HCl) were added to the collection flask to remove elemental sulfur from the organic extract. Dissolved elemental sulfur reacts with the activated copper to form solid copper sulfide, visible as a black layer on the surface of the copper. Additional copper was added to the collection flask after 24 hr, and the extraction continued for another 24 hr to ensure all sulfur was collected. Copper added after 48 hr showed no black colouration.

2.5 Measurement of sulfur isotopic composition

Copper sulfide was scraped from the surfaces of the activated copper for stable isotope measurements. Sulfur isotope measurements were carried out on both copper sulfide and kerogen by combustion-isotope ratio monitoring ratio mass spectrometry (C-irmMS). Samples were combusted with V$_2$O$_5$ added as a catalyst in Sn cups in a Thermo Flash elemental analyser coupled via a Thermo Conflo split interface to a Thermo Finnigan Mat 253 gas mass spectrometer. Sulfur isotope ratios ($^{34}$S/$^{32}$S) are reported in conventional δ-notation with a precision of approximately ± 0.3 ‰, and were calibrated versus the Vienna Cañon Diablo Troilite (VCDT) scale according to Mann et al. (2009), using the international reference materials IAEA-S-1, -2 and -3.
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
unmineralised sections of the BCF (Brocks et al., 2005). These bacteria produce elemental sulfur through the oxidation of dissolved sulfide, but also consume elemental sulfur when the supply of sulfide is limited (Zerkle et al., 2009). During mineralisation the rapid reaction of sulfide with metal ions would have greatly reduced the availability of sulfide for phototrophic oxidation and may have forced the bacteria to consume elemental sulfur. Elemental sulfur may also be consumed by bacterial disproportionation reactions (Böttcher et al., 2001; Canfield and Thamdrup, 1994) or mobilised by reaction with dissolved sulfide to form polysulfide ions (Aizenshtat et al., 1995).

Extractable organic sulfur compounds such as dibenzothiophenes (DBTs) have been detected in only trace amounts in HYC sediments (Chen et al., 2003), hence are not considered significant to the sulfur cycle of the HYC mineral system (Section 3.3). DBTs may form through either the breakdown of sulfur-containing kerogen during thermal maturation (Aizenshtat et al., 1995) or the incorporation of sulfur into existing aromatic compounds (Asif et al., 2009; Fenton et al., 2007). The low abundance of DBTs in HYC bitumen suggests that these processes did not occur to a significant extent during mineralisation. It may also reflect the thermal cracking of DBTs to H₂, H₂S and biphenyls, as has been demonstrated in pyrolysis experiments (Dartiguelongue et al., 2006).
3.2 $\delta^{34}$S of kerogen and elemental sulfur

The $\delta^{34}$S values of kerogen and elemental sulfur from the five HYC sample pits are shown in Table 1. These were consistently between +6 and +8 ‰ except for pit 1 kerogen (+4.9 ‰). The $\delta^{34}$S of kerogen and elemental sulfur from each sample pit were within 1 ‰ apart from pit 1, where the kerogen was 2.4 ‰ lighter. This close equivalence matches previous observations of co-existing kerogen and elemental sulfur (summarised by Anderson and Pratt, 1995) and has been attributed to a common sulfur source for the two species.

The $\delta^{34}$S values of all kerogen samples, with the exception of pit 2, show a steady increase from +5 ‰ to +8 ‰ along the path of hydrothermal fluid flow (Fig. 1). Such an increase is consistent with a genetic model in which base metal sulfides and organic sulfur are formed from sulfate carried by the mineralising fluid, likely sourced from evaporitic units that are present throughout the McArthur Basin (e.g. Cooke et al., 2000). Sulfate reduction (bacterial or thermochemical) produces sulfide with a significant depletion in $^{34}$S, hence the residual sulfate is progressively enriched through Rayleigh distillation (e.g. Hartmann and Nielsen, 2012; Seal, 2006). The pit 2 kerogen value of +8.5 ‰ is an exception to this otherwise consistent trend. This sample also exhibits an anomalously low weight percentage of sulfur (8 wt. % of kerogen, compared to > 23 wt. % for the other samples), suggesting that it may have been affected by localised processes that have removed a large fraction of organic sulfur, with the remained being enriched in $^{34}$S.
The large input of sulfate with the mineralising fluid also fits with the recent evidence for euxinic conditions during the formation of HYC while the wider McArthur basin was predominantly ferruginous (Holman et al., 2014). Such an influx of sulfate into the restricted HYC sub-basin could have caused the development of euxinic conditions via the increased production of sulfide by sulfate-reducing bacteria (Poulton et al., 2010).

Temperature estimates for the mineralising fluids at HYC, which generally range between 150 to 200 °C (e.g. Large et al., 1998; Williford et al., 2011), are above the range at which microbes can survive. When the fluid reached the HYC sub-basin dissolved sulfate in the fluid would have been consumed by sulfate-reducing bacteria existing within the water column and sediments. The mixing of the hot mineralising fluid with the basin water would likely have lowered the temperature to within the viable range of sulfate reducing bacteria, which have been shown to be active at temperatures up to 85 °C (Canfield et al., 2000).

The increase in kerogen $\delta^{34}S$ along the path of fluid flow is further illustrated in Fig. 2, in which $\delta^{34}S$ of kerogen is plotted against the average $\delta^{13}C$ of PAHs from the same sample pits reported by Williford et al. (2011). The $\delta^{13}C$ of PAHs decreases from pits 1 to 5 along the flow path of the mineralising fluid, due to the decreasing input of migrated PAHs that are relatively enriched in $^{13}C$ (Williford et al., 2011). The concurrent increase of kerogen $\delta^{34}S$ may be explained by a Rayleigh distillation process as discussed above. The $\delta^{34}S$ of elemental sulfur does not reflect a similar trend
and shows no clear pattern along the flow path of the hydrothermal fluid. Elemental sulfur is a highly reactive species which be consumed by oxidation and/or disproportionation reactions (Section 3.1) and can also be generated after deposition by the oxidation of sulfide minerals or aqueous sulfide (Steger and Desjardins, 1980; Zhang and Millero, 1993). Any trend in the $\delta^{34}\text{S}$ of elemental sulfur along the fluid flow path is likely to have been overprinted by such local effects.

A possible alternative explanation for the increase in kerogen $\delta^{34}\text{S}$ along the flow path of the mineralising fluid is a temperature control effect. The flow of the mineralising fluid is believed to have produced a gradient of decreasing temperature from pits 1 to 5 as the fluid cooled during deposition (Williford et al., 2011). The isotopic fractionation associated with BSR has been shown to be influenced by temperature, with increased temperatures generally producing higher rates of sulfate reduction and reduced fractionation (Kaplan and Rittenberg, 1964). If temperature was an important control, the highest temperature pit (pit 1) would have experienced the least fractionation during sulfate reduction and would thus be the most enriched in $^{34}\text{S}$. This is the opposite of the observed trend, as seen in Fig. 1, hence the temperature of the mineralising fluid does not appear to have significantly affected the $\delta^{34}\text{S}$ of organic sulfur at HYC. This finding fits with previous observations that the isotopic fractionation of BSR remains relatively constant at temperatures of 60 °C and above (Böttcher et al., 1999; Canfield et al., 2000).
Fig. 3 shows a comparison of the measured $\delta^{34}S$ of kerogen and elemental sulfur with previous sulfur isotopic studies of sulfide minerals from HYC and other McArthur Basin sediments. Detailed isotopic measurements have revealed two main phases of sulfide precipitation at HYC. Eldridge et al. (1993) proposed that first-generation pyrite (with $\delta^{34}S$ -13 to +15 ‰) was formed during early diagenesis from sulfide produced by BSR, while a later second-generation pyrite (-5 to +45 ‰) was formed in a closed system from residual sulfide that was relatively more enriched in $^{34}S$. A subsequent investigation by Ireland et al. (2004) identified two phases of sphalerite: an early sphalerite with $\delta^{34}S$ of 0 to +12 ‰ which precipitated prior to first-generation pyrite, and a later, heavier phase (+3 to +19 ‰).

First-generation mineralisation comprises over 80 % of all pyrite and sphalerite at HYC (Ireland et al., 2004).

Kerogen and elemental sulfur measured in this study are 3 to 7 ‰ heavier than the average $\delta^{34}S$ of first-generation HYC sulfides. This broadly fits with the findings of Anderson and Pratt (1995), who showed that kerogen and elemental sulfur are $^{34}S$-enriched from co-existing pyrite in marine sediments by an average of 10 ‰. Elemental sulfur and organic sulfur at HYC likely formed contemporaneously with the first-generation sulfides. The second generation of sulfides at HYC are relatively enriched in $^{34}S$, which was attributed to the formation from $^{34}S$-heavy pore-water sulfate in a closed system (Eldridge et al., 1993). This limited supply of sulfur would have been efficiently scavenged by metal cations. The lower $\delta^{34}S$ of
elemental sulfur and organic sulfur indicates that these species were formed from the more freely available and relatively lighter sulfide responsible for the first-generation metal sulfides.

It is notable that the $\delta^{34}S$ of elemental sulfur and kerogen show a greatly reduced range of values compared to base metal sulfides at HYC (Fig. 3). Elemental sulfur and kerogen were analysed by bulk techniques using $> 20$ g of rock from each sample pit (section 2.4). Conversely, the ion probe and laser ablation measurements of Eldridge et al. (1993) and Ireland et al. (2004) measured $\delta^{34}S$ of base metal sulfides at high resolution, revealing extreme isotopic heterogeneity on a fine scale. Microscale in situ measurements of organic $\delta^{34}S$, such as demonstrated by Bontognali et al. (2012), may reveal similar heterogeneity of organic sulfur isotopes.

### 3.3 Model of sulfur transformations at HYC

The measured $\delta^{34}S$ of elemental sulfur and organic sulfur fit well with the simplified model of sulfur transformations during the deposition of HYC presented in Fig. 4. The model is based on a middle Proterozoic seawater sulfate isotopic composition of $+20$ to $+25$ ‰ (Strauss, 1993). Sulfate reduction was assumed to be accompanied by an estimated $^{34}S$-depletion of $20 \%$, which was proposed by Shen et al. (2002) as being typical for BSR in euxinic sections of the McArthur Basin with limited supply of sulfate. The HYC deposit was formed in a tectonically-controlled sub-basin in which local
conditions were conducive to BSR and exchange with the main basin was partially restricted (McGoldrick et al., 2010).

This degree of fractionation is also within the range reported for thermochemical sulfate reduction (TSR; Machel et al., 1995). The respective contributions of BSR and TSR during the deposition of HYC have been difficult to resolve (Logan et al., 2001). Ireland et al. (2004) concluded that while both BSR and TSR likely contributed to the formation of the deposit, BSR was the dominant process. n-Alkane distributions indicative of sulfate-reducing bacteria have recently been detected in highly-mineralised regions of HYC (Holman et al., 2014). The $^{34}$S-enrichment of benzothiophenes compared to dibenzothiophenes has been proposed as a proxy for TSR (Amrani et al., 2012), however dibenzothiophenes have been detected only in trace amounts at HYC (Section 3.1) while benzothiophenes have not been reported. For the purposes of this simplified model it was considered that the sulfide was formed solely by BSR.

The assumed fractionation of 20 ‰ during BSR would produce sulfide with $\delta^{34}$S of 0 to +5 ‰. Only minor fractionation occurs during the precipitation of sulfide minerals from dissolved sulfide (Böttcher et al., 1998; Butler et al., 2004; Price and Shieh, 1979), therefore the $\delta^{34}$S of sulfide minerals is also expected to be close to 0 to +5 ‰. This is consistent with the sulfur isotopic composition of first-generation HYC sulfides measured by Eldridge et al. (1993) and Ireland et al. (2004), and also with the $\delta^{34}$S of pyrite from the Wollogorang Formation (-2 to +6 ‰), which underlies the
BCF and through which the mineralising fluid is believed to have flowed (Donnelly and Jackson, 1988; Shen et al., 2002).

Dissolved sulfide that does not react to form sulfide minerals may be oxidised by a range of microorganisms and also by abiotic reactions (Canfield, 2001). The $\delta^{34}S$ of elemental sulfur at HYC (+6 to +8 ‰) is slightly higher than the sulfide minerals (Fig. 3) consistent with production by phototrophic sulfur bacteria. Biomarker evidence for the presence of phototrophic sulfur bacteria has been detected at HYC (Holman et al., 2014), as well as non-mineralised sections of the BCF (Brocks et al., 2005).

Elemental sulfur produced by phototrophic sulfur bacteria in bacterial culture experiments was reported to be 1 to 3 ‰ enriched in $^{34}S$ compared to the source sulfide (Zerkle et al., 2009). Conversely, a depletion of 4 to 5 ‰ is typical for the abiotic oxidation of sulfide to elemental sulfur (Fry et al., 1988) which does not fit the available data. The $\delta^{34}S$ of elemental sulfur at HYC must be interpreted with caution as a significant proportion has likely been consumed by oxidation and/or disproportionation reactions, and some may also have been generated by non-biological oxidation reactions after deposition (sections 3.1 and 3.2). The isotopic composition of the remaining elemental sulfur will have been modified by these post-depositional processes, so firm conclusions on its formation cannot be drawn based on this data. Nevertheless, the available isotopic and biomarker evidence supports the oxidation of sulfide by phototrophic sulfur bacteria.
Polysulfide ions exist in isotopic equilibrium with elemental sulfur and dissolved sulfide, and have been shown in laboratory experiments to be 2 to 4 ‰ enriched in $^{34}$S compared to sulfide (Amrani et al., 2006). The incorporation of polysulfides into OM may result in further $^{34}$S-enrichment. This process has not been widely studied, but Amrani and Aizenshtat (2004) reported that the reaction of model polysulfide solutions with pure carbonyl compounds produced organic sulfur compounds (primarily alkyl chains connected by polysulfide bridges) that were $^{34}$S-enriched by 4 to 5 ‰.

Sedimentary organic sulfur is thought to derive from a combination of diagenetic and biosynthetic pathways, with biosynthetic sulfur being relatively enriched in $^{34}$S as it is formed with similar $\delta^{34}$S to the seawater sulfate source (Brüchert and Pratt, 1996; Kaplan and Rittenberg, 1964). Biosynthetic sulfur has been estimated to contribute up to 25 % of organic sulfur in marine sediments (Anderson and Pratt, 1995; Brüchert and Pratt, 1996; Passier et al., 1999), although this proportion may be reduced with thermal maturation as the highly labile biosynthetic sulfur compounds are expected to be rapidly remineralised (Werne et al., 2003). Assuming a contribution from biosynthetic sulfur of 10 %, the model predicts organic sulfur with $\delta^{34}$S between +7 and +15 ‰. The measured $\delta^{34}$S of HYC kerogen (+5 to + 8 ‰) is at the lower end of this range. This may suggest a lower degree of $^{34}$S-enrichment during incorporation of sulfur into OM than was reported from the laboratory experiments of Amrani and Aizenshtat (2004). Recently reported compound-specific $\delta^{34}$S measurements of diagenetic
organic sulfur compounds from the Cariaco Basin showed that some compounds were significantly $^{34}$S-depleted compared to co-existing sulfide (Raven et al., 2013), suggesting that diagenetic sulfurisation may result in a wider range of fractionations than previously reported. Alternatively the contribution from biosynthetic sulfur at HYC may have been lower than the assumed 10%.

The model shown in Fig. 4 presents only a simplified view of the chemical transformations of sulfur during the deposition of HYC, but matches well with the measured $\delta^{34}$S of elemental sulfur and kerogen. It should be noted that the simplified model presented here is based on a system that is open for all relevant processes. A natural environment with closed or semi-closed precipitation conditions, and the potential for changes in conditions during the evolution of the system, may alter the predicted trends and further complicate interpretations of the genetic relationships of the different sulfur-bearing phases.

4. Conclusions

The sulfur isotopic composition of elemental sulfur and organic sulfur at HYC reveal information on sulfur cycling during the formation of the base metal sulfide deposit. These species are 3 to 7‰ enriched in $^{34}$S compared to first-generation sulfide minerals. The measured $\delta^{34}$S values strongly support a genetic model in which elemental sulfur and organic
sulfur were formed simultaneously with base metal sulfides from dissolved sulfide that was produced by BSR. Organic sulfur is believed to have been formed through the incorporation of polysulfide ions into OM. While the five pit samples represent a modest sample set, the organic sulfur displayed a trend of increasing $\delta^{34}S$ along the path of the mineralising fluid which may result from Rayleigh distillation, suggesting that $\delta^{34}S$ of organic sulfur may be useful for the targeted exploration of minerals. The enrichment in $^{34}S$ of elemental sulfur compared to HYC sulfide minerals suggests that phototrophic sulfur oxidation may have been an important process, but the likely alteration of the isotopic signal by post-depositional processes renders this conclusion uncertain.

Although organic and elemental sulfur are quantitatively minor components of the total sulfur inventory at HYC, this study has shown that they reveal important aspects of the sulfur cycle during the formation of the deposit, complementing and extending the more traditional studies of mineral sulfides. These species should not be neglected in isotopic investigations of base metal deposits, or of any sedimentary system in which the sulfur cycle plays an important role.

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Captions of tables and figures

Table 1

$\delta^{34}$S of kerogen and elemental sulfur for the five HYC sample pits (error is ± 0.3 ‰), plus masses of sulfur contained in kerogen and elemental sulfur in the five HYC sample pits, reported in μg of sulfur per g of rock. Average masses of sulfur in sulfide minerals were calculated from data reported by Huston et al. (2006) for ZnS and PbS, and Lambert and Scott (1973) for FeS$_2$.

Figure 1

$\delta^{34}$S of kerogen and elemental sulfur from the five HYC sample pits. Error bars indicate uncertainty of 0.3 ‰.

Figure 2

$\delta^{34}$S of kerogen from the five HYC sample pits (error bars indicate uncertainty of 0.3 ‰), plotted against average $\delta^{13}$C of PAHs (reported by Williford et al., 2011). The input of $^{13}$C-enriched, non-indigenous PAHs decreases from pits 1 to 5 (section 3.2).
Figure 3

Box-and-whisker plots of δ³⁴S data for kerogen and elemental sulfur from HYC (this study) and reported δ³⁴S of sulfide minerals from HYC and the McArthur Basin. Whiskers show the full range of reported δ³⁴S, boxes represent the middle 50% of the data (first to third quartiles). Estimated isotopic composition of Paleoproterozoic seawater sulfate (+20 to +25 ‰: Strauss, 1993) is indicated by the lightly shaded area. 1 Eldridge et al. (1993), 2 Ireland et al. (2004), 3 Johnston et al. (2008), 4 Shen et al. (2002).

Figure 4

Proposed scheme for the formation of organic sulfur, elemental sulfur and sulfide minerals at HYC. Details of the scheme are discussed in Section 3.3. Boxes represent the δ³⁴S of the various sulfur species (vertical axis is not to scale), and arrows represent predicted fractionations during transformation processes. δ³⁴S values in bold were measured either in this study (elemental sulfur and organic sulfur) or by previous researchers. δ³⁴S values in italics are predictions calculated from the measured values and fractionations reported in previous studies. 1 Strauss (1993), 2 Canfield (2001), 3 Shen et al. (2002), 4 Machel et al. (1995), 5 Eldridge et al. (1993), 6 Ireland et al. (2004), 7 Zerkle et al. (2009), 8 Amrani et al. (2006), 9 Amrani and Aizenshtat (2004), 10 Anderson and Pratt (1995).
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<tr>
<td><strong>Distance from pit 1</strong></td>
<td>0</td>
<td>104</td>
<td>372</td>
<td>553</td>
<td>710</td>
</tr>
<tr>
<td><strong>δ$^{34}$S (‰)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kerogen</td>
<td>4.9</td>
<td>8.5</td>
<td>6.2</td>
<td>6.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Elemental sulfur</td>
<td>7.3</td>
<td>7.9</td>
<td>6.0</td>
<td>7.1</td>
<td>7.0</td>
</tr>
<tr>
<td><strong>Kerogen sulfur (% dry wt.)</strong></td>
<td>26</td>
<td>8</td>
<td>23</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td><strong>Mass (µg S / g rock)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kerogen S</td>
<td>2054</td>
<td>384</td>
<td>1104</td>
<td>1344</td>
<td>1400</td>
</tr>
<tr>
<td>Elemental S</td>
<td>2.9</td>
<td>8.4</td>
<td>2.5</td>
<td>11.8</td>
<td>10.7</td>
</tr>
<tr>
<td><strong>PbS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ZnS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>FeS$_2$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average mass (µg S / g rock)</td>
<td>6345.9</td>
<td>45127.6</td>
<td>80390.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Kerogen $\delta^{34}S$ (‰)

PAH $\delta^{13}C$ (‰)

Pit 1

Pit 2

Pit 3

Pit 4

Pit 5

-31

-30.5

-30

-29.5

-29

-28.5

4 5 6 7 8 9

Kerogen $\delta^{34}S$ (‰)
HYC kerogen

HYC $S^0$

HYC pyrite 1 (1)

HYC pyrite 2 (1)

HYC galena (1)

HYC sphalerite 1 (2)

HYC sphalerite 2 (2)

BCF pyrite (3)

Wollogorang pyrite (4)
Seawater sulfate +20 to +25 ‰ (1)

Biosynthetic sulfur +18 to +23 ‰

Contribution from biosynthetic S 10 % (10)

Dissolved sulfide 0 to +5 ‰

Sulfate reduction -20 ‰ (3,4)

Elemental sulfur +1 to +8 ‰

HYC elemental sulfur +6 to +8 ‰

Sulfide oxidation +1 to +3 ‰ (7)

Polysulfides +2 to +9 ‰

Equilibrium enrichment +2 to +4 ‰ (8)

Sulfide precipitation < 1 ‰ (2)

Assimilatory sulfate reduction -2 ‰ (2)

Sulfate reduction -20 ‰ (3,4)

Sulfide oxidation +1 to +3 ‰ (7)

Equilibrium enrichment +2 to +4 ‰ (8)

Incorporation into OM +4 to +5 ‰ (9)

Digenetic organic S +6 to +14 ‰

Total organic sulfur +7 to +15 ‰

HYC organic sulfur +5 to +8 ‰

Sulfide minerals 0 to +5 ‰

HYC early sulfides -5 to +6 ‰ (5,6)

Sulfide oxidation +1 to +3 ‰ (7)