Combined sulfur, carbon and redox budget constraints on genetic models for the Here's Your Chance Pb–Zn deposit, Australia

Jeffrey M. Dick [a,b,]*, Katy A. Evans [b], Alex I. Holman [a], David Leach [c], Kliti Grice [a]

[a] Department of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[c] Centre for Exploration Targeting, The University of Western Australia, 35 Stirling Highway, Crawley, Perth, WA 6009, Australia

ABSTRACT

The formation of base metal sulfide deposits requires not only a source of metals but also reduced sulfur. If incoming sulfur is present in ore fluids as sulfate, then a source of electrons is needed to drive the reduction of sulfate to sulfide. The oxidation of organic matter can release electrons that provide the reducing capacity, whether it be in low- or high-temperature settings that are conducive to biological or thermochemical sulfate reduction (BSR or TSR). The amounts of organic matter reacted and sulfide minerals formed can be estimated by mass balance calculations. In this study, an integrated mass balance expression is formulated that takes into account the sulfide mineral content and organic carbon content and H/C ratios of mineralised and non-mineralised rocks. Model calculations based on carbon, sulfur and redox budget balances suggest that the extent of oxidation of the organic matter present at the Here's Your Chance (HYC) Pb–Zn deposit is insufficient for reduction of the required quantity of sulfate. The results imply that externally derived reducing capacity and/or reduced sulfur is required to form the metal resource. Possible sources include hydrocarbon-rich fluids from deeper parts of the sedimentary sequence or formation of sulfide and organic matter as products of BSR during sedimentation/early diagenesis. However, the observed oxidation of organic matter associated with the deposit suggests that at least some reducing capacity is locally derived. Therefore, our calculations are consistent with genetic models for HYC that have multiple sources of redox budget for sulfate reduction.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/3.0/).

1. Introduction

Some aspects of the genesis of sediment-hosted Pb–Zn deposits, such as the HYC (Here's Your Chance) deposit in the McArthur Basin, remain unresolved [1]. The relative importance of synsedimentary, syndiagenetic and epigenetic ore mineral deposition, and of the involvement of hydrothermal fluids, seawater and basin brines is controversial, in spite of extensive characterisation of mineral textures [2–4], isotopic compositions [5–7] and the organic geochemistry [e.g. 8–11].

Two broad types of ore deposition process have been proposed at HYC: (1) synsedimentary, with ore precipitated on the seafloor as a result of mixing between sulfate-rich oxic, dense, hypersaline, metal-bearing hydrothermal fluids and anoxic and/or organic-rich seawater [e.g. 4,12] (2); early diagenetic with ore precipitated within the sediments from sulfate-rich oxic metal-bearing hydro-

thermal fluids [9,10]. It is generally acknowledged that some combination of these processes may have operated [e.g. 13], but few studies have quantified the relative contributions of the different processes.

Ore deposition involves reduction of sulfate in the ore fluids to produce Pb and Zn sulfides, and this reduction requires a source of electrons, which can be conveniently considered in the context of the whole-rock redox budget [14]. The required electrons may have been provided by the oxidation of organic matter within the sediments. Reduced sulfur may also have been provided by sulfidic brines or hydrothermal fluids. Ore deposition, therefore, involves a complex combination of fluxes of sulfur, carbon and electrons between geological reservoirs. The aim of this paper is to investigate whether the relative contribution of different ore-forming processes is reflected by the budgets of these components. The HYC deposit is used as a case study for the application of simultaneous mass balance expressions for sulfur, carbon, and redox budget. The results are used to constrain the combinations of genetic factors that could have contributed to deposit formation,

* Corresponding author at: Department of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia. Tel.: +61 8 9266 9792.
E-mail address: Jeffrey.Dick@curtin.edu.au (J.M. Dick).

and the implications of the results for the formation of other Pb–Zn deposits worldwide are considered.

2. Geological setting

HYC is a giant stratiform sediment-hosted base metal deposit in North East Australia [10,15]. HYC is hosted by sediments of the Middle Proterozoic McArthur Basin, an intracratonic basin containing a sediment sequence up to 12 km thick, exposed over 200,000 km^2, that was deposited between 1800–1400 Ma [16,17]. The sedimentary rocks have been described as unmetamorphosed [13], though local increases in organic maturity parameters in the vicinity of the HYC deposit have been used to suggest that rocks affected by mineralisation were heated by contact with ore-bearing solutions [18]. Mineralising fluids are thought to have flowed up the Emu fault zone prior to ore deposition (Fig. 1).

The ore occurs within the HYC Pyritic Shale Member of the Barney Creek Formation, which has been dated at 1640 Ma [20]. This member is composed of dark, carbonaceous, pyritic, dolomite-bearing laminated siltstones. Sedimentary structures within the HYC member include small scale cross lamination, scours, graded bedding, slumps [2–4] and syn-depositional faulting [20].

The HYC member is surrounded by dolomitic rocks with a Cl-rich bulk composition (in some cases over 300 ppm), which is most likely due to the presence of high-salinity fluid inclusions [2]. The high chlorine content has been interpreted as evidence for shallow evaporitic environments that could generate hypersaline fluids, facilitating transport of metals to the site of ore deposition [2]. However, later work suggests that the Barney Creek Formation formed in a deep water environment [9].

Ore horizons form layers within the host rock (Fig. 2), with ore concentrated in fine-grained silt-dominated beds. Coarser grained beds interpreted as debris flows or turbidites are less mineralised
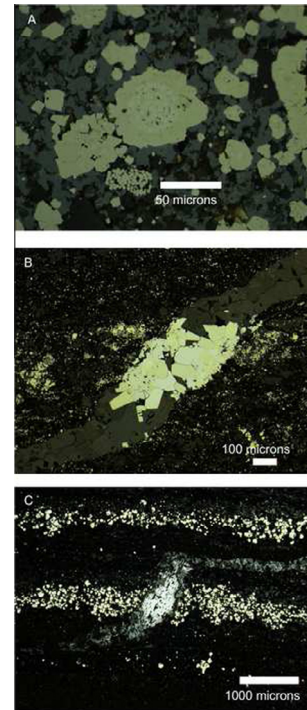

Fig. 2. Reflected light thin section photomicrographs of mineralised samples from HYC. (A) Two types of pyrite, with framboidal pyrite overgrown by coarse crystalline pyrite. Sample from pit 5 of Williford et al., 2011 [11]; (B) Coarse pyrite in a carbonate vein. Sample from pit 1 [11]; (C) Galena and sphalerite in vein that cross cuts pyrite-rich layers parallel to sedimentary layering. Sample from pit 4 [11].
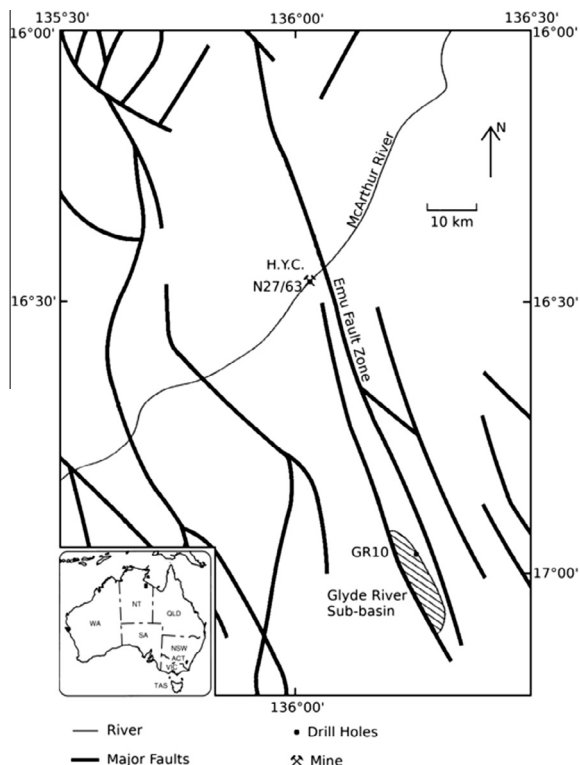
[5,21]. Pyrite and ore minerals (sphalerite and galena) form up to 60 vol% of the rock in some layers. The sulfide minerals can be separated into several generations, on the grounds of textural and isotopic evidence [e.g. 13]. Early pyrite, the stage 1 pyrite of Williams, 1978 [22], and referred to here as py1 after Ireland et al., 2004 [13], occurs as spherical and elliptical framboids, and as euhedral crystals (Fig. 2A). This pyrite is considered to have formed at the same time as the earliest sphalerite (sp1). Both py1 and sp1 represent over 80% of the total pyrite and sphalerite found at the HYC deposit [13]. However, the pyrite and sphalerite sulfur isotope signatures are decoupled, which suggests that the two phases did not form in isotopic equilibrium [5,6]. Stage 2 sphalerite, sp2, makes up 15 – 20% of the sphalerite at HYC and is often associated with carbonate (e.g. Fig. 2B). A second stage of pyrite growth formed py2, which overgrows py1 (Fig. 2A), sp1, and sp2 [13], and is associated with sulfide-carbonate veins (Fig. 2C; see also Ref. [10]).

Organic matter in the McArthur Basin is present in fine-grained clastic sedimentary rocks and comprises a combination of authigenic and migrated organic matter [18]. Biomarkers in the organic matter are consistent with the involvement of saline, sulfate-bearing waters in formation of the organic matter [23]. However, biomarkers for sulfate-reducing bacteria (SRB) and sulfur isotope systematics in pyrite have been interpreted as evidence for local ocean anoxia or sulfidic conditions [24,25].

A summary of the differences in bulk composition between mineralised and unmineralised HYC pyritic shale is provided in Table 1, based on values taken from Ref. [26]. Total organic carbon (TOC) in rocks in the mineralised zones of the HYC deposit ranges from 0.02 to 3.8 wt%, with an average of 0.36 ± 0.15 wt% (Table 1). Unmineralised HYC pyritic shale contains 0.04 to 4.9 wt % organic carbon with an average of 0.66 ± 0.80 wt% (Table 1). Mineralised units also have higher Fe and lower CO_2 than the unmineralised

Fig. 1. Location map for the HYC deposit, after Pietsch et al., 1991 [17] and Logan et al., 2001 [9]. The map shows the relationship of the HYC deposit to the major faults in the area, as well as the location of the Glyde River sub-basin, which is the source of some data for unmineralised, organic-rich shales used in this study.

Table 1

Summary of mineralised and unmineralised rock compositions from data reported by Corbett et al., 1975 [26]. Analyses for the HYC shale in a single core (Te 115) were included in the averages, and a cutoff value of 50,000 ppm Pb+Zn was used to classify rocks as mineralised. Uncertainties are 1 standard deviation.

	Unmineralised $n = 37$	Mineralised $n = 10$
CO_2 (wt%)	15.2 ± 9.6	5.7 ± 6.4
FeO (wt%)	11.1 ± 9.4	15.0 ± 4.7
S (wt%)	8.7 ± 10.6	20.0 ± 3.8
Pb (ppm)	1354 ± 2343	58900 ± 35120
Zn (ppm)	4316 ± 4929	158000 ± 61700
Organic C (wt%)	0.66 ± 0.80	0.36 ± 0.15

units, possibly due to volume loss as a consequence of dissolution of carbonate during sulfide precipitation [13].

3. Methods

3.1. Conceptual model

Mass balances for the components S, C and redox budget were calculated by consideration of fluxes of the components of interest between five different reservoirs (Fig. 3). These reservoirs are the protolith, (P), which is considered to be equivalent to unmineralised HYC shale, the ore deposit (O), oceanic water (S), hydrothermal ore-bearing fluids (H), and an external reservoir (X). In this model, reservoirs S and H provide only oxidised sulfur (sulfate), so it is also necessary to include external reservoirs (X), which provide the possibility of external sources of reduced carbon or sulfide. X could represent a reduced brine pool on the ocean floor with associated sulfidic conditions due to a high activity of sulfate-reducing bacteria, or reduced hydrocarbon-bearing fluids derived from underlying sediments.

These reservoirs have been chosen to facilitate consideration of the sources of S, C, and redox budget, and may not form physically separated volumes in time or space. For example, if mineralisation was synsedimentary, then an unmineralised protolith to an ore-bearing rock may never have existed. However, the rock that would have existed if the ore-forming process had not occurred can be considered as a source of elements to the ore-bearing rock, and thus element fluxes to the ore via non-ore-related sedimentary processes can be represented by the use of a 'protolith' reservoir. Similarly a water column containing sulfate-bearing and sulfide-bearing regions may have formed a single volume, but it is conceptually convenient to split this into sources of oceanic sulfate (the Oceans reservoir) and sulfide (the External reservoir).
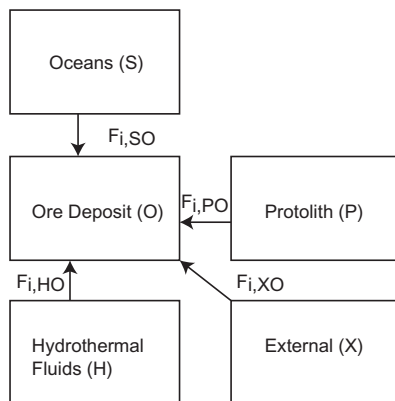

Fig. 3. Conceptual model used as the basis for mass balance calculations.

The mass balance approach considers only the start and end products of the ore-forming process, so it is unnecessary to specify the precise sequence of chemical reactions by which elements in one redox state or held in one fluid or mineral species are converted to other redox states and/or fluid/mineral species. This is fortunate, since the range of possible reactions includes kinetically controlled reactions, and is large.

The mass balance for any component i in reservoir K is specified by

$$\Delta n_{i,K} = \sum_J F_{i,JK} \tag{1}$$

where F is the time integrated flux, in moles, and the sum over J is over the reservoirs that interact with reservoir K. $\Delta n_{i,K}$ is the change in the number of moles of i in reservoir K. $n_{i,K}$ is defined by $n_{i,K} = M_i x_i / m_i$, where M_i is the total mass of the reservoir in grams, x_i is the mass fraction of element i, and m_i is the molar weight in grams per mole.

Expressions of the form of Eq. (1) were constructed for S, C and redox budget, with a focus on the ore reservoir, O. The initial value of all $n_{i,O}$ values in the ore reservoir is zero, so $\Delta n_{i,O}$ is equal to the total number of moles of component i, in the ore reservoir. Increases in $n_{i,O}$ occur via transfers from P, the protolith reservoir, and the other reservoirs. It is assumed that carbon, sulfur and redox budget in the protolith are retained in the ore deposit or transferred into fluids that, for convenience, are included in the ore deposit reservoir, i.e. $F_{i,PO} = n_{i,P}$.

The mass balance equations, and simplifying assumptions are as follows:

Carbon

The carbon mass balance is

$$n_{C,O} = n_{C,P} + F_{C,XO} \tag{2}$$

representing the sum of authigenic carbon in the protolith ($n_{C,P}$) with an externally derived carbon source ($F_{C,XO}$) to yield the total carbon in the ore ($n_{C,O}$). Organic matter is represented by the formula CH_z, where z indicates the average H:C ratio. This strategy is not intended to represent the true formulae of organic compounds in kerogen and bitumen at HYC, but to provide an indication of the average H:C ratio, and associated electron donating capacity, of the organic material. Oxidation of carbon induced by sulfate reduction is accounted for by a combination of oxidation of CH_x in the protolith to CH_y in the ore, where $y < x$, and oxidation of CH_x in the protolith to CO_2 in the ore reservoir ($n_{C,CO_2,O}$). CO_2 produced by oxidation of organic material may be retained in the rock or released in the fluid, but both are included in the ore reservoir, for convenience. The carbon balance can then be expressed in terms of the oxidised and reduced contributions to the carbon budget as

$$n_{C,O} = n_{C,CH_y,O} + n_{C,CO_2,O} = n_{C,CH_x,P} + n_{C,CO_2,P} + F_{C,XO} \tag{3}$$

The variable r is used to represent the fraction of total carbon that is preserved as organic matter in the ore, so that

$$r = \frac{n_{C,CH_y,O}}{n_{C,CH_x,P}}. \tag{4}$$

Determination of $n_{C,CO_2,O}$ by analysis of mineralised HYC shale is problematic. Abundant carbonate concretions or nodules at HYC are more common close to the ore [9], and it has also been proposed that carbonate dissolution is enhanced in the ore zones during mineralisation [20,9]. It is therefore difficult to quantify carbonate formation and dissolution given that transfer of carbonate is likely to have occurred on a range of length scales, and in a highly heterogeneous fashion. Fortunately, rearrangement of Eq. (3) allows $n_{C,CO_2,O}$ to be expressed in terms of quantities that are either known or can be specified.

$$n_{C,CO_2,O} = (1-r)n_{C,CH_x,P} + n_{C,CO_2,P} + F_{C,XO} \qquad (5)$$

Sulfur

The sulfur mass balance expression derived from Eq. (1) is

$$n_{S,O} = n_{S,pyrite,O} + n_{S,organic,O} + n_{S,Pb+Zn,O}$$
$$= n_{S,P} + F_{S,SO} + F_{S,HO} + F_{S,XO} \qquad (6)$$

where $n_{S,pyrite,O}$ and $n_{S,organic,O}$ are the number of moles of sulfur in pyrite and in organic compounds, respectively, in the ore deposit and $n_{S,Pb+Zn,O}$ is the number of moles of sulfur contained in galena and sphalerite. $n_{S,P}$ is considered to comprise a contribution from pyrite ($n_{S,pyrite,P}$) and from organic sulfur associated with kerogen ($n_{S,organic,P}$) so that

$$n_{S,P} = n_{S,organic,P} + n_{S,pyrite,P} \qquad (7)$$

$F_{S,SO}$ and $F_{S,HO}$ both involve sulfate reduction to produce H_2S that combines with Pb and Zn to form the ore sulfides. $F_{S,SO}$ can be envisaged as bacterial sulfate reduction (BSR) of seawater sulfate within the pore fluids or in the overlying water column, while $F_{S,HO}$ is the sulfur flux associated with thermochemical sulfate reduction (TSR) during ore formation. BSR and TSR occur at different temperatures but have similar products for a system of a given composition [27]. It is difficult to quantify the relative contributions of BSR and TSR because their effect on the sulfur budget and redox budget is identical, so we group both sulfate reduction processes together as $F_{S,SR}$ for these calculations:

$$F_{S,SR} = F_{S,SO} + F_{S,HO} \qquad (8)$$

The number of moles of pyrite in the ore deposit is linked to the number of moles of pyrite in the protolith via the factor q:

$$q = \frac{n_{S,pyrite,O}}{n_{S,pyrite,P}} \qquad (9)$$

If $q = 0$ then no pyrite is retained in the ore deposit, and ore deposition involves complete replacement of the pre-existing pyrite, whereas if $q = 1$ then the amount of sulfur contained in pyrite is unchanged by mineralisation. q values greater than 1 imply pyrite addition by the mineralisation process. Although pyrite replacement is not a predominant feature of HYC system, provision for destruction of pyrite as a source of sulfur for the ore minerals, or formation of pyrite, is included in the model to be able to explore the possible contributions by these processes in a more general framework (see Discussion).

Combining Eqs. (6)–(9) and solving for $n_{S,Pb+Zn,O}$ produces

$$n_{S,Pb+Zn,O} = (1-q)n_{S,pyrite,P} + n_{S,organic,P} - n_{S,organic,O} + F_{S,SR}$$
$$+ F_{S,XO} \qquad (10)$$

Redox Budget

The redox budget of a reservoir is defined as

$$RB = \sum_i n_i v_i \qquad (11)$$

where RB is the redox budget, n_i is the number of moles of redox state i present in the sample of interest, and v_i is the number of electrons required to take one mole of redox state i to the reference redox state [14]. In this study, the chosen reference state is sulfur as S(2-) and carbon as C(4-) so, for example, v_i for sulfate, to which 8 electrons must be added to reach the reference state is 8, v_i for carbon with the generalised formula CH_x is $(4-x)$, and v_i for sulfur in pyrite is 1. Fe, Pb, Zn, O and H are assumed not to change their redox states during mineralisation and therefore can be ignored in redox budget calculations. The redox budget balance is

$$n_{RB,O} = n_{RB,P} + F_{RB,HO} + F_{RB,SO} + F_{RB,XO} = n_{RB,P} + F_{RB,SR} + F_{RB,XO} \qquad (12)$$

$F_{RB,HO}$ and $F_{RB,SO}$ are grouped together as $F_{RB,SR}$, as above, assuming that sulfate is the only significant carrier of redox budget in seawater and hydrothermal fluids, and that all the sulfur in seawater and hydrothermal fluids is sulfate. In this case, $F_{RB,SR}$ is equal to $8 F_{S,SR}$. Contributions to protolith redox budget are assumed to come from pyrite ($n_{S,pyrite,P}$) and kerogen ($(4-x)n_{C,CH_x,P}$). Contributions to the ore redox budget are from pyrite ($n_{S,pyrite,O}$), organic matter ($(4-y)n_{C,CH_y,O}$), and CO_2 ($8n_{C,CO_2,O}$). Organic sulfur in the form S(2-) does not contribute to the redox budget since this sulfur is in the reference state. Eq. (12) then becomes

$$F_{RB,SR} + F_{RB,XO} + n_{S,pyrite,P} + n_{C,CH_x,P}(4-x) + 8n_{C,CO_2,P}$$
$$= n_{S,pyrite,O} + n_{C,CH_y,O}(4-y) + 8n_{C,CO_2,O} \qquad (13)$$

Carbon and sulfur in the external source (X) are assumed to be present as methane and hydrogen sulfide respectively. Both these elements are in their reference states so contributions from this reservoir do not affect redox budget, i.e. $F_{RB,XO}$ is zero.

Combination of Mass Balance Expressions

Substituting Eqs. (4) and (5) and (9) and (10) into Eq. (13) and rearranging gives

$$n_{S,Pb+Zn,O} = (7/8)n_{S,pyrite,P}(1-q)$$
$$+ (1/8)n_{C,CH_x,P}(4-4r-ry+x) + F_{S,XO} + F_{C,XO}$$
$$+ (n_{S,organic,P} - n_{S,organic,O}) \qquad (14)$$

This is the final combined equation used for subsequent calculations. Note that carbonate in the protolith ($n_{C,CO_2,P}$) does not appear in this equation. Mathematically, this occurs because, after $n_{C,CO_2,O}$ is eliminated from Eq. (13) via substitution of Eq. (5) as described above, $n_{C,CO_2,P}$ occurs on both sides of Eq. (13) and cancels during the simplification process. Thus, results based on Eq. (14) are independent of assumptions regarding the quantities of $n_{C,CO_2,O}$ and $n_{C,CO_2,P}$ because their net effects on redox budget and carbon balance are represented by the terms containing $n_{C,CH_x,P}$ and $F_{C,XO}$.

It is also useful to recognise that the coefficients for $F_{S,XO}$ and $F_{C,XO}$ are both 1, so that input of reduced carbon and sulfur both have the same effect on the ore deposit resource. $F_{C,XO}$ is envisaged to provide methane, and oxidation of CH_4 to CO_2 provides 8 electrons directly for sulfate reduction. A flux of reduced sulfur via $F_{S,XO}$ does not provide electrons directly, but, by providing reduced sulfur, reduces the need for electrons to reduce sulfate by 8 electrons per mole of sulfide. If incoming methane were not oxidised completely to CO_2 then the incoming reduced carbon flux, $F_{C,XO}$, would need to be greater to produce any given mineral resource.

Values for the input parameters, and sources for the data, are provided in Table 2. The masses of components in the ore reservoir were calculated by multiplying the concentration of the component by the total mass of the ore deposit, taken to be 227 Mt [15]. Protolith TOC concentration was taken from the TOC in unmineralised HYC pyritic shale sample, while TOC concentration in the ore was taken from analyses of mineralised HYC shale (see Table 1 for details). The concentration of pyritic sulfur in the protolith was taken from analyses of poorly mineralised samples from HYC [28]. The use of the poorly mineralised samples provides a maximum protolith S content; the implications of this decision are discussed below. The organic sulfur concentration in the protolith was calculated by combining the wt% organic carbon in the unmineralised HYC pyritic shale (Table 1) with the ratio of S:C of 0.055 in kerogen. The value of 0.055 is an average S:C ratio for samples from the Barney Creek Formation in well GR10, which is outside of the ore deposit (Fig. 1 and Ref. [29]). The total ore-sulfide hosted sulfur content was calculated on the basis of an ore deposit with 9.2 wt% Zn and 4.1 wt% Pb [15], assuming all Zn and Pb are in ZnS and PbS. The organic sulfur in the ore reservoir was calculated by combining the wt% organic carbon in the mineralised HYC pyritic

Table 2
Summary of inputs for mass balance calculations.[a]

Component	Protolith ($n_{i,P}$)	Ore ($n_{i,O}$)
Carbon	1.25×10^{11} moles[b]	0.68×10^{11} moles[c]
Sulfur	$n_{S,pyrite,P} = 3.4 \times 10^{11}$ moles[d]	$n_{S,Pb+Zn,O} = 3.64 \times 10^{11}$ moles[e]
	$n_{S,organic,P} = 4.7 \times 10^{9}$ moles[f]	$n_{S,organic,O} = 3.9 \times 10^{9}$ moles[g]
Redox budget	$x = 1.6$[h]	$y = 0.6$[i]

[a] Values of elemental abundance (wt%) were converted to moles using a total mass of the ore deposit of 227 Mt [15].
[b] Calculated from an average 0.66 wt% organic carbon in the unmineralised HYC pyritic shale (Ref. [26]; Table 1).
[c] Calculated from an average 0.36 wt% organic carbon in the mineralised HYC pyritic shale (Ref. [26]; Table 1).
[d] Calculated from a nominal value of 1.5 moles S / kg (5 wt%) for poorly mineralised samples of the HYC deposit and hanging wall [28].
[e] Calculated from 9.2 wt% Zn and 4.1 wt% Pb [15], assuming all Zn and Pb are in ZnS and PbS.
[f] Calculated by combining the wt% organic carbon in the unmineralised HYC pyritic shale (Table 1) with 0.055 S:C mass ratio in kerogen, being the average for samples from the Barney Creek Formation in well GR10 [29], which is outside of the ore deposit.
[g] Calculated by combining the wt% organic carbon in the mineralised HYC pyritic shale (Table 1) with 0.092 S:C mass ratio in kerogen, being the average for samples from the Barney Creek Formation in well N27/63 [29], which is within the ore deposit. Samples with high ash content (>30%) were excluded [29].
[h] The maximum value of H/C ratio found in immature to marginally mature samples, from Fig. 6d of Crick et al., 1988 [8].
[i] The upper limit of the H/C ratio for samples from the overmature zones of the Barney Creek Formation [8].

shale (Table 1) with an S:C mass ratio of 0.092, taken from the average for kerogen in samples from the Barney Creek Formation in well N27/63 [29], which is within the ore deposit. Samples with high ash content (>30%) were excluded [29]. Values of x and y were taken from the maximum value of H/C ratio found in immature to marginally mature samples, and the upper limit of the H/C ratio for samples from the overmature zones of the Barney Creek Formation respectively (Figure 6d of Crick et al., 1988 [8]).

Values for the parameters q, r, $F_{S,XO}$ and $F_{C,XO}$ are either poorly constrained or unavailable in the literature so these parameters were treated as variables for the purposes of the calculations. Ranges of q and r can be proposed that are consistent with observations of the rocks. Comparison of the organic carbon content in mineralised and unmineralised rocks (Table 1) suggests that r (Eq. 4) should be around 0.5, or a little higher, to account for some decrease in the value of TOC caused by the increase in rock density associated with mineralisation. r may have been lower if decreases in H:C ratio associated with mineralisation were localised rather than distributed throughout the whole deposit. In this case, the average extent of organic carbon oxidation may, in fact, be less than estimated from bulk rock analyses [20]. Conversely, r may be higher if the actual organic carbon content of the sediments was higher than TOC recorded in the unmineralised rocks (Table 1). Therefore, r is considered to have been between 0.35 and 0.75.

With respect to q (Eq. 9), some pyrite growth accompanies mineralisation (Fig. 2B). However it is unclear if growth of py2 is due to local remobilisation or net addition of pyrite. The differences in isotope systematics of pyrite and ore minerals [5,6] suggests that the formation of much of the pyrite and sphalerite are decoupled, so values of q are most likely close to 1, or greater if there is significant pyrite addition. A nominal upper limit of q of 1.35 is consistent with the increase in the FeO content (Table 1) in mineralised rocks and with the observation that up to ~20% of pyrite in the mineralised rocks is stage 2 pyrite (py2) that overprints earlier sulfides [7,13]. Values of q between 0.8 and 1.35 were considered reasonable.

$F_{S,XO}$ and $F_{C,XO}$ are unknowns with true values that shed light on the nature of ore formation processes at HYC. Initially, the total

mineral resource, represented by sulfide in Pb and Zn minerals ($n_{S,Pb+Zn,O}$), was calculated from Eq. (14) as a function of q and r for zero contribution from external reservoirs (i.e. $F_{S,XO} = F_{C,XO} = 0$). Subsequent calculations investigated the values of $F_{S,XO}$, $F_{C,XO}$ and $n_{S,organic,P}$ that would be required to produce the observed mineral resource. A final set of calculations was made for a protolith with the same high pyrite content as the most pyritic hanging wall samples (25 wt% S), with the same organic carbon content as the previous runs.

Uncertainties of 20% relative were assumed for $n_{C,CH_x,P}$ and $n_{S,pyrite,P}$ and of 0.2 absolute on y and x. These assumed uncertainties are, to some extent, arbitrary, but are based on variation in measured values for these parameters. The estimated uncertainties on these input parameters form the basis for uncertainties on calculated parameters, which are derived by application of standard analytical error propagation techniques, assuming that the uncertainties are uncorrelated.

4. Results

Preliminary calculations were carried out by assigning values to all variables in Eq. (14) except q and r, using data from Table 2 and zero $F_{S,XO}$ and $F_{C,XO}$. Fig. 4A depicts the calculated quantity of sulfur in ore minerals (y-axis) as a function of q (x-axis) and r (contour lines). If values of q and r were in the range we speculate to be reasonable (shaded diagonal area in Fig. 4A), then less than 30 % of the observed mineral resource at HYC (horizontal bar in Fig. 4A) could be produced by reduction of sulfate in the ore-forming fluids driven by oxidation of organic matter in the protolith. Uncertainties are less than 10% of the actual total $n_{S,Pb+Zn,O}$ (1sigma, Fig. 4A), so this result is robust even with the relatively large uncertainties on the input parameters.

The results of calculations that investigated the size of external fluxes of reduced carbon and sulfur required to produce the known mineral resource (Figs. 4B, C) indicate that substantial external fluxes are required if the known mineral resource is to be reconciled with the proposed q and r values. The contours in Figs. 4B-D represent the necessary additional contributions of externally derived reduced sulfur (Fig. 4B) or reduced carbon (Fig. 4C), or organic sulfur in the protolith (Fig. 4D) if the known mineral resource is to be produced for the values of q and r found on the x and y axes of the figures.

Reduced S fluxes from an external reservoir ($F_{S,XO}$) of 2 to 3.64×10^{11} moles (i.e. all of the sulfur in the Pb–Zn sulfides in the deposit) are required for the specified range of q and r values if external reduced carbon was not available (Fig. 4B). This quantity is equivalent to a flux of sulfur of the same order as that present in the protolith pyrite. Similarly, additional reduced C fluxes ($F_{C,XO}$) of 2 to 3.64×10^{11} moles are required to produce the observed resource (Fig. 4C). This range is greater than the quantity of carbon in the protolith. The sulfide (Fig. 4B) and reduced carbon (Fig. 4C) figures are identical, as implied by the stoichiometry of Eq. (14), and discussed above.

The required quantity of additional organic sulfur in the protolith to produce the mineralised resource with positive q and r values without external reduced carbon and sulfur fluxes was calculated to be a factor of 20 to 60 times higher than the weight of organic sulfur in the unmineralised protolith (Fig. 4D). Therefore, sulfide from organic sulfur does not make a major contribution to the formation of the ore minerals in the deposit.

The final calculation, which investigated the mineralised resource produced by a protolith with 25 wt% sulfur, instead of the ~5 wt% used in the calculations, found that replacement of less than 20% of the pyrite ($q \approx 0.8$) would be sufficient to form the ore minerals in the deposit (not shown).
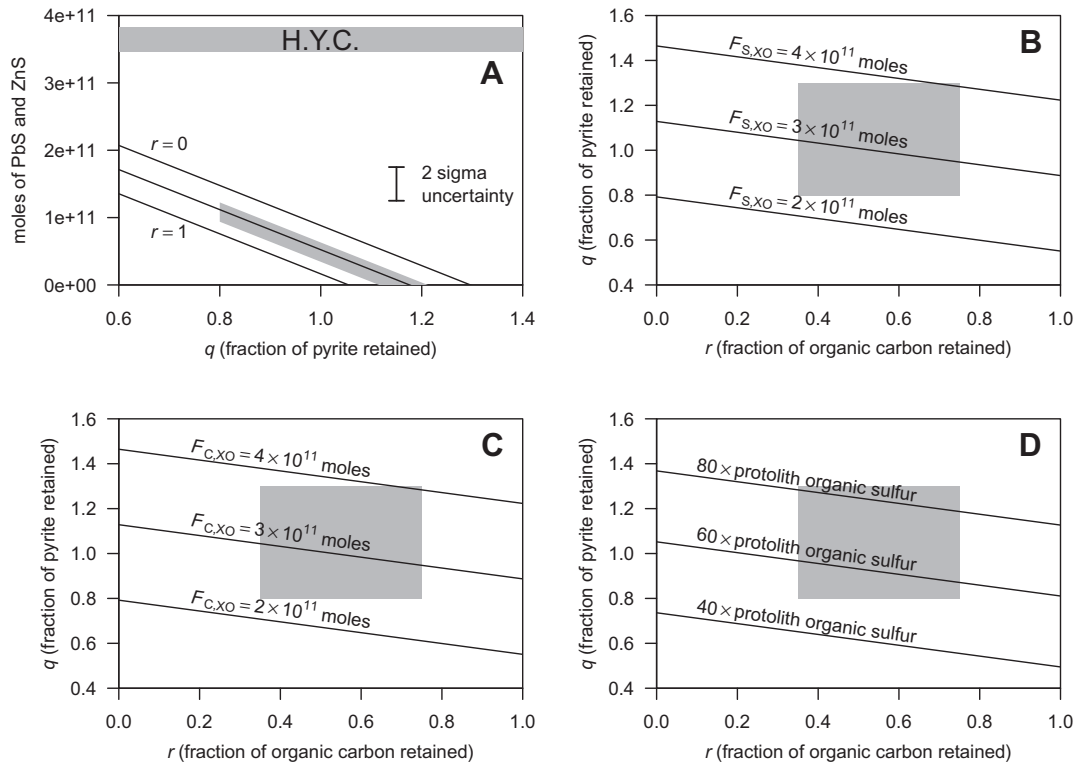
Fig. 4. Results of mass balance calculations. (A) calculated ore reserve as sulfur in ore minerals as a function of q, the proportion of pyrite retained during mineralisation, contoured for r, the proportion of carbon retained in CH_y compounds; (B) contribution of sulfur from an external reservoir needed to make the known ore reserve as a function of r and q; (C) contribution of carbon from an external reservoir needed to make the known ore reserve as a function of r and q; (D) contribution of reduced sulfur in organic compounds needed to make the known ore reserve as a function of r and q. The horizontal band in (A) represents the known ore reserve. The other shaded areas (diagonal area in A; boxes in B–D) indicate the probable limits of values for r and q (see text).

5. Discussion

The major quantitative result of our model is that oxidation of in-situ organic carbon provides at most 1/3 of the redox budget needed to reduce sulfate to form the known quantity of ore minerals at HYC (shaded areas in Fig. 4A), so long as the protolith was not excessively pyrite-rich. However, if substantial pyrite is also formed during the mineralisation process ($q > 1$ in Fig. 4A), then there is less reducing capacity available for the formation of the ore minerals.

The calculated deficiency of reducing capacity supports a contribution in the form of reduced sulfur and/or carbon (Figs. 4B, C) in externally derived fluids, although the sources of the fluids are not well constrained by the calculations. Recent evidence suggests that the Early Proterozoic oceans were anoxic and largely ferruginous, with euxinic (sulfidic) waters restricted to the continental margins [30,31]. Deep seawater is likely to have become progressively more sulfidic after 1.8 Ga [32]. Therefore, one possible source of reducing capacity is a sulfidic pool near the ocean bottom, formed through BSR acting on a localised source of sulfate, which could have been the ore fluid. BSR could produce sulfide in the water, near the sediment-water interface, that is incorporated into the formation of sulfide minerals. A more detailed conceptualisation of this process is inherent in the deep brine/anoxic pool models that have been proposed to drive the formation of synsedimentary pyrite and sphalerite at HYC [e.g. 4,33,13,34].

Mineralogical and textural analyses were used by Ireland et al., 2004 to suggest that most of the sphalerite (sp1) at HYC was formed by synsedimentary deposition, with reduced sulfur provided in a manner similar to the process described above [13]. The remainder of the sphalerite (sp2), ca. 15-20% of the total at

HYC, was proposed to have formed during early diagenesis, in burial conditions that would be conducive to TSR [13]. The results of the calculations presented here are broadly consistent with these proportions of sp1 and sp2. Sulfur or reducing capacity for formation of early sp1 could be supplied by an external reservoir (e.g. a localised sulfidic brine pool), and formation of sp2 supported by diagenetic processes, such as reduction of sulfate in ore-bearing fluids by in-situ organic carbon, i.e. by a combination of carbon from the protolith (P) reservoir with sulfate from the hydrothermal (H) reservoir in the model.

While the textural interpretations of [13] call for a reduced sulfur source in the form of a dense sulfide-bearing brine pool, alternate external inputs of reducing fluids can also be considered. One such alternative is provided by migrating hydrocarbons or a sour-gas or hydrocarbon reservoir in the subsurface. Analysis of bituminous material from the HYC deposit revealed the presence of aromatic hydrocarbons (Chen et al. [10] and Williford et al. [11]) that are thought to have formed at temperatures greater than 200 °C, which suggests migration from a deeper source. These migrated hydrocarbons could have acted as reduced carbon from an external reservoir, although their contribution cannot yet be quantified.

The need for an external reservoir is reduced or removed if the protolith is taken to have extremely high S contents, of around 25 wt% S. However, this scenario requires a high pyrite content in a protolith that extends over the same volume as the deposit. Pyritic sulfur contents as high as 25 wt% have been documented, but are restricted to discrete pyrite-flooded bands [13] or samples from the hanging wall [28]. It therefore seems unlikely that sufficient pyrite is present to supply the sulfur necessary to form the mineral resource, especially given the lack of evidence for extensive pyrite replacement.

5.1. Comparison to previous work

Dixon and Davidson [35] considered redox-linked mass balance constraints for another deposit in the Mt. Isa Inlier. These workers calculated that a volume consistent with alteration haloes observed in the McArthur River deposits [3] would be sufficient to host the organic carbon necessary to produce the Dugald River Pb–Zn deposit in the Mt. Isa Inlier. However, Dixon and Davidson [35] require metals to be borne by reduced H_2S-bearing fluids, rather than by sulfate-bearing fluids, as is assumed here. The solubility of Pb and Zn in H_2S-bearing fluids is low, unless the fluids are quite acidic [36]. Acidic fluids are incompatible with the observed carbonate-bearing stratigraphic sequence.

Mass balance for single components, such as sulfur, or electron budgets have been tried at other Pb–Zn deposits [e.g. 37,38,35,39], with strikingly varied results. In one case, Powell and Macqueen [39] suggested that ore formation at the Mississippi-Valley Type (MVT) Pine Point deposit in Canada does not require external reducing capacity beyond that provided by oxidation of the organic matter within the deposit. Their stoichiometric analysis is based on a reaction that starts with elemental sulfur as the source for sulfide in the ore deposit, requiring only 2 electrons per S(2-) formed. However, thermochemical sulfate reduction, which is the relevant chemical process identified [39], requires a redox budget that provides 8 electrons per sulfur. In a model consistent with this stoichiometry, the quantity of reduced carbon needed at Pine Point is ca. 4x greater than that proposed by Powell and Macqueen [39]. By comparison, Anderson [38] used an electron balance scheme (requiring the expected 8 electrons per sulfate reduced) to show that reducing capacity from local organic carbon within the ore deposit would be insufficient to form the known quantity of metal sulfides in the MVT deposits of the Bonneterre Formation of South Eastern Missouri. To satisfy the redox balance constraints, Anderson [38] invoked external methane fluxes from a calculated volume that arguably coincides with the alteration zone surrounding the deposit. Cathles et al. [37] undertook an electron balance calculation for the giant Kupferschiefer Cu deposit. These workers calculated that sulfate requirements for the Kupferschiefer Cu deposits are larger than those available from the Lubin basin, which was previously proposed to provide sulfate involved in ore deposition.

The range of results obtained by previous work reflects, to some extent, the range of different starting assumptions and the consideration of only one or two of the three critical and potentially limiting components, carbon, sulfur, and redox budget, which control the supply of electrons for sulfate reduction. The combined approach described here has the potential to provide better constraints on the processes that lead to ore deposition.

6. Conclusions

The calculations presented above suggest that in-situ sulfate reduction is insufficient to produce the HYC deposit if the organic carbon abundance and composition in the modeled protolith and mineralised rocks are representative of the carbon that is available during ore formation. Additional reducing capacity and/or reduced sulfur is required from external reservoirs, such as localised sulfidic ocean water or infiltrating organic-rich fluids. The combined framework outlined here also has the potential to allow recognition of global patterns in the relative contributions of internally and externally derived redox budget in the formation of other Pb–Zn deposits.

Acknowledgments

References

[1] Leach DL, Bradley DC, Huston D, Pisarevsky SA, Taylor RD, Gardoll SJ. Sediment-hosted lead-zinc deposits in Earth history. Econ Geol 2010;105(3):593–625. http://dx.doi.org/10.2113/gsecongeo.105.3.593.

[2] N.J.W. Croxford, S. Jephcott, The McArthur lead-zinc-silver deposit, Northern Territory, Australia, in: Proceedings: Australasian Institute of Mining and Metallurgy, Vol. 243, 1972, pp. 1–26.

[3] Lambert IB, Features The McArthur zinc-lead-silver deposit:. Metallogenesis and comparisons with some other stratiform ores. In: Wolf KH, editor. Handbook of Strata-Bound and Stratiform Ore Deposits. II. Regional Studies and Specific Deposits. Cu, Zn, Pb, and Ag deposits, Vol. 6. Elsevier; 1976. p. 545–85.

[4] Large RR, Bull SW, Cooke DR, McGoldrick PJ. A genetic model for the HYC deposit, Australia: based on regional sedimentology, geochemistry, and sulfide-sediment relationships. Econ Geol 1998;93(8):1345–68. http://dx.doi.org/10.2113/gsecongeo.93.8.1345.

[5] Smith JW, Croxford NJ. Sulphur isotope ratios in the McArthur lead-zinc-silver deposit. Nat Phys Sci 1973;245(140):10–2. http://dx.doi.org/10.1038/physci245010a0.

[6] Rye DM, Williams N. Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: III. The stable isotope geochemistry of the H.Y.C., Ridge, and Cooley deposits. Econ Geol 1981;76(1):1–26. http://dx.doi.org/10.2113/gsecongeo.76.1.1.

[7] Eldridge CS, Williams N, Walshe JL. Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion microprobe SHRIMP: II. A study of the H.Y.C. deposit at McArthur River, Northern Territory, Australia. Econ Geol 1993;88(1):1–26. http://dx.doi.org/10.2113/gsecongeo.88.1.1.

[8] Crick IH, Boreham CJ, Cook AC, Powell TG. Petroleum geology and geochemistry of middle Proterozoic McArthur Basin, northern Australia; II, Assessment of source rock potential. AAPG Bull 1988;72(12):1495–514. URL:http://aapgbull.geoscienceworld.org/content/72/12/1495.short.

[9] Logan GA, Hinman MC, Walter MR, Summons RE. Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments, Northern Territory, Australia. Geochim Cosmochim Acta 2001;65(14):2317–36. http://dx.doi.org/10.1016/S0016-7037(01)00599-3.

[10] Chen J, Walter MR, Logan GA, Hinman MC, Summons RE. The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern Australia: organic geochemistry and ore genesis. Earth Planet Sci Lett 2003;210(3-4):467–79. http://dx.doi.org/10.1016/S0012-821X(03)00171-7.

[11] Williford KH, Grice K, Logan GA, Chen J, Huston D. The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. Earth Planet Sci Lett 2011;301(1-2):382–92. http://dx.doi.org/10.1016/j.epsl.2010.11.029.

[12] Lambert IB, Scott KM. Implications of geochemical investigations of sedimentary rocks within and around the McArthur zinc-lead-silver deposit, Northern Territory. J Geochem Explor 1973;2(4):307–30. http://dx.doi.org/10.1016/0375-6742(73)90016-2.

[13] Ireland T, Large RR, McGoldrick P, Blake M. Spatial distribution patterns of sulfur isotopes, nodular carbonate, and ore textures in the McArthur River (HYC) Zn–Pb–Ag deposit, Northern Territory, Australia. Econ Geol 2004;99(8):1687–709. http://dx.doi.org/10.2113/99.8.1687.

[14] Evans KA. Redox decoupling and redox budgets: conceptual tools for the study of earth systems. Geology 2006;34(6):489–92. http://dx.doi.org/10.1130/G22390.1.

[15] Huston DL, Stevens B, Southgate PN, Muhling P, Wyborn L. Australian Zn–Pb–Ag ore-forming systems: a review and analysis. Econ Geol 2006;101(6):1117–57. http://dx.doi.org/10.2113/gsecongeo.101.6.1117.

[16] Plumb KA, Derrick GM, Needham RS, Shaw RD. The Proterozoic of Northern Australia. In: Hunter DR, editor. Precambrian of the Southern Hemisphere. Elsevier; 1981. p. 205–307.

[17] Pietsch BA, Rawlings DJ, Creaser PM, Kruse PD, Ahmad M, Ferenczi PA, et al. Bauhinia downs SE53-3, 1:250,000 geological map series explanatory notes. Northern Territ Geol Surv 1991.

[18] Crick IH. Petrological and maturation characteristics of organic matter from the Middle Proterozoic McArthur Basin, Australia. Aust J Earth Sci 1992;39(4):501–19. http://dx.doi.org/10.1080/08120099208728042.

[19] Large RR, Bull SW, McGoldrick PJ, Walters S, Derrick G, Carr GR. Stratiform and strata-bound Zn–Pb–Ag deposits in Proterozoic sedimentary basins, Northern Australia. In: Economic geology 100th anniversary volume, Society of economic geologists; 2005.

[20] Hinman M. Constraints, timing and processes of stratiform base metal mineralization at the HYC Ag–Pb–Zn deposit, McArthur River. In: Baker T, Rotherham JF, Richmond JM, Mark G, Williams PJ, editors. MIC '96: new developments in metallogenic research: the McArthur, Mt. Isa, Cloncurry Minerals Province, vol. 55. James Cook University of North Queensland, Economic Geology Research Unit; 1996. p. 56–9.

[21] Large R, McGoldrick P, Bull S, Cooke D. Proterozoic stratiform sediment-hosted zinc-lead-silver deposits of Northern Australia. In: Deb M, Goodfellow WD, editors. Sediment-hosted lead–zinc sulphide deposits. attributes and models

of some major deposits in India, Australia and Canada. New Delhi: Narosa Publishing House. p. 1–23.

[22] Williams N. Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: II. The sulfide-S and organic-C relationships of the concordant deposits and their significance. Econ Geol 1978;73(6):1036–56. http://dx.doi.org/10.2113/gsecongeo.73.6.1036.

[23] Summons RE, Powell TG, Boreham CJ. Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia: III. Composition of extractable hydrocarbons. Geochim Cosmochim Acta 1988;52(7):1747–63. http://dx.doi.org/10.1016/0016-7037(88)90001-4.

[24] Shen Y, Canfield DE, Knoll AH. Middle Proterozoic ocean chemistry: Evidence from the McArthur Basin, Northern Australia. Am J Sci 2002;302(2):81–109. http://dx.doi.org/10.2475/ajs.302.2.81.

[25] Johnston DT, Farquhar J, Summons RE, Shen Y, Kaufman AJ, Masterson AL, et al. Sulfur isotope biogeochemistry of the Proterozoic McArthur Basin. Geochim Cosmochim Acta 2008;72(17):4278–90. http://dx.doi.org/10.1016/j.gca.2008.06.004.

[26] Corbett JA, Lambert IB, Scott KM, Results of analyses of rocks from the McArthur River, Northern Territory, Technical Communication 57, CSIRO Minerals Research Laboratories, Division of Mineralogy; August 1975.

[27] Machel HG. Bacterial and thermochemical sulfate reduction in diagenetic settings – old and new insights. Sediment Geol 2001;140(1-2):143–75. http://dx.doi.org/10.1016/S0037-0738(00)00176-7.

[28] Scott KM, Lambert IB. Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: II. Sulfide-S and organic-C relationships of the concordant deposits and their significance – A discussion. Econ Geol 1979;74(7):1693–4. http://dx.doi.org/10.2113/gsecongeo.74.7.1693.

[29] Powell TG, Jackson MJ, Sweet IP, Crick IH, Boreham CJ, Summons RE. Petroleum geology and geochemistry, Middle Proterozoic McArthur Basin, Record 48, Bureau of Mineral Resources, Geology and Geophysics; 1987.

[30] Planavsky NJ, McGoldrick P, Scott CT, Li C, Reinhard CT, Kelly AE, et al. Widespread iron-rich conditions in the mid-Proterozoic ocean. Nature 2011;477(7365). http://dx.doi.org/10.1038/nature10327. 448-U95.

[31] Poulton SW, Canfield DE. Ferruginous conditions: a dominant feature of the ocean through Earth's history. Elements 2011;7(2):107–12. http://dx.doi.org/10.2113/gselements.7.2.107.

[32] Farquhar J, Wu N, Canfield DE, Oduro H. Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal sulfide deposits. Econ Geol 2010;105(3):509–33. http://dx.doi.org/10.2113/gsecongeo.105.3.509.

[33] Large RR, Bull SW, Winefield PR. Carbon and oxygen isotope halo in carbonates related to the McArthur River (HYC) Zn–Pb–Ag deposit, North Australia: implications for sedimentation, ore genesis, and mineral exploration. Econ Geol 2001;96(7):1567–93. http://dx.doi.org/10.2113/96.7.1567.

[34] Holman AI, Grice K, Greenwood PF, Böttcher ME, Walshe JL, Evans KA. New aspects of sulfur biogeochemistry during ore deposition from δ^{34}S of elemental sulfur and organic sulfur from the Here's Your Chance Pb/Zn/Ag deposit. Chem Geol 2014;387:126–32. http://dx.doi.org/10.1016/j.chemgeo.2014.08.025.

[35] Dixon G, Davidson GJ. Stable isotope evidence for thermochemical sulfate reduction in the Dugald River (Australia) strata-bound shale-hosted zinc-lead deposit. Chem Geol 1996;129(3-4):227–46. http://dx.doi.org/10.1016/0009-2541(95)00177-8.

[36] Cooke DR, Bull SW, Large RR, McGoldrick PJ. The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment-hosted Pb–Zn (Sedex) deposits. Econ Geol 2000;95(1):1–17. http://dx.doi.org/10.2113/gsecongeo.95.1.1.

[37] Cathles LM, Oszczepalski S, Jowett EC. Mass balance evaluation of the late diagenetic hypothesis for Kupferschiefer Cu mineralization in the Lubin basin of southwestern Poland. Econ Geol 1993;88(4):948–56. http://dx.doi.org/10.2113/gsecongeo.88.4.948. III.

[38] Anderson GM. Organic maturation and ore precipitation in southeast Missouri. Econ Geol 1991;86(5):909–26. http://dx.doi.org/10.2113/gsecongeo.86.5.909.

[39] Powell TG, Macqueen RW. Precipitation of sulfide ores and organic matter: sulfate reactions at Pine Point, Canada. Science 1984;224(4644):63–6. http://dx.doi.org/10.1126/science.224.4644.63.