Massive sulfide Zn deposits in the Proterozoic did not require euxinia

J.M. Magnall1*, S.A. Gleeson1,2, N. Hayward3, A. Rocholl1

Abstract

Our most important Zn resources occur within clastic-dominated (CD-type) deposits, which are located in a small number of Proterozoic and Phanerozoic sedimentary basins. The most common model for CD-type mineralisation involves sedimentary exhalative (SEDEX) processes, i.e. the venting of metal bearing fluids into a restricted, anoxic H2S-bearing (euxinic) water column. In the Carpentaria Zn Province (Australia), multiple world class deposits are hosted in Proterozoic (1.6 Ga) stratigraphy, where models of the ancient sulfur cycle have also been developed. Focusing on the most recent discovery – the Teena deposit – we report bulk rock and isotopic data (δ34S values) that provide information on the sulfur cycle during the diagenetic and hydrothermal evolution of the Teena sub-basin. In contrast to the SEDEX model, intervals containing abundant pyrite with highly positive δ34S values (>25 ‰) correspond with euxinic conditions that developed due to high organic loading (i.e. productivity) and not basin restriction. This basin wide feature, which can also be mistaken as a hydrothermal pyrite halo, is genetically unrelated to the subsequent hydrothermal mineralisation that formed beneath the palaeo-seafloor. The formation of CD-type deposits in the Proterozoic does not, therefore, require euxinic conditions.

Introduction

The Proterozoic Carpentaria Zn Province contains the largest accumulation of sediment-hosted base metals in the earth’s crust (nearly 120 Mt Zn and Pb; Huston et al., 2006). Deposits of the northern Carpentaria Province are of particularly broad interest, as they are hosted within one of the few low metamorphic grade marine sedimentary basins from the Proterozoic. Since the early 20th century, world class (upper 10th centile contained metal) clastic-dominated (CD-type) deposit discoveries in the Carpentaria Province have averaged one per 20 years (McGoldrick et al., 2010). Yet with increased urbanisation and decarbonisation the global demand for Zn will continue, and some models predict a peak in Zn production within 20 years (Mohr et al., 2018).

As the largest Zn reserves and resources occur in CD-type deposits, it is necessary to critically evaluate and improve existing genetic models to enhance the predictive capacity of exploration programmes. A restricted number of sedimentary basins in 2 broad time intervals (mid-Proterozoic and Palaeozoic) are known to host the largest CD-type deposits (Leach et al., 2010). The most widely applied genetic model involves sedimentary exhalative (SEDEX) processes, where a sulfidic (euxinic) water column provides the in situ trap for hydrothermally vented metal-bearing fluids; the stratiform textures that are characteristic of CD-type deposits are then thought to result from the direct precipitation of sulfide minerals (pyrite, sphalerite, galena) from euxinic seawater (e.g., Large et al., 1998). Although models of Proterozoic ocean chemistry have been refined over recent decades – from the Canfield Ocean of widespread euxinia (Canfield, 1998) to more recent models in which euxinia is more spatially and temporally restricted (Poulton and Canfield, 2011) – the SEDEX paradigm persists and mineralisation is frequently taken as a priori evidence that euxinic conditions were prevalent (e.g., Johnston et al., 2008).

In many cases, observations on the distribution and isotopic composition of pyrite provide the foundations for hydrothermal and palaeoenvironmental models (e.g. Lyons et al., 2000; Ireland et al., 2004). In this study, we focus on the most recent discovery in the Carpentaria Province – the Teena Zn-Pb deposit (Fig. S-1). Petrographic and geochemical data, collected through more than 600 m of stratigraphy, are presented for both mineralised and correlative un-mineralised samples. We demonstrate a high degree of variability in the overall abundance and isotopic composition (δ34S value) of non-hydrothermal pyrite and show that euxinic conditions developed in response to high productivity during periods of
high relative sea level. Contrary to the SEDEX model, hydrothermal pyrite has a much more restricted distribution and formed via sub-seafloor replacement processes. For exploration programmes, this means that the detectable footprint of CD-type deposits is more limited than predicted by the conventional SEDEX model.

**Samples and Methods**

The Teena deposit is hosted within the 1.64 Ga Barney Creek Formation (BCF) and is located approximately 8 km from the super giant McArthur River Zn-Pb deposit in correlative stratigraphy. Samples were taken from 3 drill cores that intersect the two main mineralisation lenses and the hanging wall sequence of the Teena deposit (Figs. 1 and S-2). Each sample was examined under binocular microscope, and representative sub-samples were prepared as polished thin sections for petrographic analysis. Sub-samples for isotopic microanalysis were extracted from thin section blocks using a 4 mm diameter micro-drill, and then cast into an epoxy mount for imaging and SIMS analysis. See Supplementary Information for further details.

**Results**

**Spatial and temporal pyrite distribution.** There are two main generations of pyrite, each with two sub-types: (1a) micro-crystalline (<5 μm) and occasionally frambooidal pyrite, which defines discontinuous laminations (Figs. 2a and S-3a), and (1b) slightly larger (>5 μm), idiomorphic euhedral pyrite, typically formed on the margins of nodular carbonate (Fig. 2b); (2a) spherical, concentrically zoned crystals with abundant host rock inclusions (Fig. 2c), and (2b) more irregular, anhedral overgrowths, which contain interstitial sphalerite and galena mineralisation (Fig. 2d). Both sub-types of py-2 preserve As and Pb enrichments (Fig. S-4). Volumetrically minor generations of coarse grained euhedral pyrite are associated with late stage sulfide-carbonate-quartz veins (py-3).

Pyrite-1a pre-dates dolomite nodule formation (Fig. 3b inset), whereas py-1b occurs on the margins of dolomite nodules (Fig. 2b), consistent with formation during later stages of nodule growth. The pyrite associated with the sphalerite and galena is more massive, and forms anhedral overgrowths of earlier py-1 (Fig. 2d). Sphalerite does not occur within nodular dolomite, but commonly replaces nodule margins, attesting to a strictly post-nodule timing for mineralisation.

The only pyrite present throughout the stratigraphic interval is py-1a, which is highly abundant within correlating carbonaceous intervals in all 3 drill holes (Figs. 1 and S-5). All other types of pyrite are restricted either to samples containing nodular carbonate (py-1b; Fig. 2b), or to within the mineralised interval (py-2; Fig. 2c,d). In terms of a lateral pyrite halo, the overall abundance of pyrite clearly decreases within the mineralised interval (across 1.5 km from 019 > 012 > 015; Figs. 1 and S-5).

δ³⁴Spyrite values. The δ³⁴S values for pyrite are shown in Figure 4. There is a strong stratigraphic control on the isotopic composition of py-1a, and highly positive δ³⁴S values are preserved in all 3 drill holes within the high pyrite abundance interval (Figs. 1 and 4). Within the mineralised intervals there is a high degree of isotopic heterogeneity within individual crystals, i.e. on the micro-scale. The zoned aggregates of py-2 preserve δ³⁴S values that are intermediate between the end members of py-1a, but there are no systematic trends within individual samples.
Figure 2  (a) Aggregates of py-1a within organic rich mudstone matrix. (b) Euhedral py-1b crystals within and around carbonate nodule. (c) Zoned aggregates of py-2a. (d) Aggregate of py-1a overgrown by py-2b.

Figure 3  (a) Thin section block of sample selected for SIMS analysis (mineralised interval @ 925 m in 019; see Fig. 1). (b) Binocular photomicrograph of area selected for micro-drilling and inset showing a backscatter electron (BSE) image of the sample. Notice py-1a contained within dolomite nodule, indicating a pre-nodule origin. (c,d) BSE images of pyrite from the inset in (b). (e) Electron dispersive X-ray (EDX) false colour image, showing Pb enrichment (warm colours) in the fuzzy py-2b overgrowth.
Discussion

Timing and distribution of mineralisation in the Teena sub-basin. The Teena deposit shares many features (e.g., stratiform sulphide textures; Fig. S-3) with the McArthur River (HVC) deposit, which is used as the type example of SEDEX mineralisation in the Carpentaria Province (Large et al., 1998). In the SEDEX model, coeval formation of py-1 and sphalerite occurs within an anoxic brine pool (e.g., Ireland et al., 2004) and py-2 post-dates hydrothermal mineralisation (e.g., Large et al., 1998). These relationships are not observed in the Teena deposit as macro-scale observations show that sphalerite clearly post-dates formation of early diagenetic py-1 (e.g., Fig. 2) and is interstitial to py-2 (which is also hydrothermally enriched in As and Pb; Fig. S-4).

A minimum depth constraint for the timing of mineralisation in the subsurface can be inferred from the paragenetic relationship between py-2 and nodular dolomite within the hanging wall sequence. At the top of the Lower HYC Member (925 m, TNDD019; pink star in Fig. 1), the py-1a that is overgrown by nodular dolomite has been protected from hydrothermal overgrowth (py-2b), unlike the pyrite that formed within the mudstone matrix (Fig. 3). The weak mineralisation at this stratigraphic level postdates the formation of nodular dolomite and represents the uppermost expression of the high grade mineralisation 200 m lower in the stratigraphy.

There is also a marked decrease in the lateral distribution of pyrite within the mineralised interval, which in TNDD015 is at levels overlapping with the un-mineralised Middle to Upper HYC Members (<0.5 mol/kg FeS2; Fig. 1). As a result, the lateral extent of hydrothermal pyrite in the Teena sub-basin (<1.5 km; Fig. S-5) is far more restricted than the 10s of km suggested by the SEDEX model (e.g., Mukherjee and Large, 2017).

Stratigraphic variability of δ34S_pyr in the Teena sub-basin. The interpretation of δ34S_pyr values forms a common framework for both the SEDEX model and studies that focus on broader aspects of Proterozoic seawater chemistry. In either case, the development of highly positive δ34S values has been linked to water mass restriction, during which microbial sulfate reduction (MSR) produced basin scale closed system Rayleigh fractionation effects (e.g., Lyons et al., 2000, 2006).

There is general agreement that the δ34S value of 1.64 Ga seawater sulfate was >25‰ (Li et al., 2015). Following on, the lowest δ34S_py-1a values in the Teena sub-basin represent a large offset from seawater sulfate (Δ34S ≤ 35‰), typical of sulfide generated during MSR in relatively open system conditions. Pyrite associated with nodular carbonate (py-1b) is characterised by δ34S values that are higher than the majority of py-1a (e.g., Fig. 4; high pyrite abundance interval excluded). The development of more positive δ34S values is characteristic of sulfide generated within pore fluids during later diagenesis, either via MSR or sulfide reduction coupled with anaerobic oxidation of methane at the sulfate methane transition zone (e.g., Borowski et al., 2013; Lin et al., 2016; Magnall et al., 2016). In either case, the development of more positive δ34S values is restricted to pore fluids and cannot be linked to water mass restriction. In contrast, the interval of high pyrite abundance preserves particularly positive δ34S_py-1b values, which are clearly different from all other sub-types of pyrite (Fig. 4). Moreover, correlation of this interval between the 3 drill holes indicates it is not a localised effect, but a larger scale feature of the sulfur cycle in the Teena sub-basin. The development of positive δ34S values on a basin scale typically occurs during pyrite formation under sulfate limited, euxinic conditions (Gomes and Hurtgen, 2015).

Water mass restriction is commonly cited as a driving mechanism for sulfate limitation in Proterozoic basins (e.g., Lyons et al., 2000). Nevertheless, the high pyrite abundance intervals within the BCF correspond with a marine transgression and a period of high relative sea level (Fig. 1; Kunzmann et al., 2019), meaning basin restriction is unlikely to have been the primary control on sulfate limitation. Instead, we propose that sulfate limited conditions developed in a euxinic water column when a high organic carbon flux promoted MSR (Johnston et al., 2010). For individual sub-basins within the McArthur Basin, rising sea level would have resulted in enhanced circulation and nutrient replenishment, following which sulfate limitation developed as a symptom of high productivity (and organic flux) rather than water mass restriction (e.g., Cox et al., 2016).

Figure 4 A cumulative frequency diagram of δ34S values of all stages of the pyrite paragenesis. The sub-group of highly positive δ34S_py values is from samples from the high abundance interval. Mixed analyses where the analysis was of adjoining py-1 and 2 grains = py (mixed). The blue dashed line represents a minimum value for 1.64 Ga seawater sulfate (Li et al., 2015).
The evidence of sulfate limitation also poses a mass balance problem for models in which mineralisation forms from reduced sulfur derived in situ and entirely from seawater sulfate. For example, the maximum sulfide abundance within the MFS intervals (<1.5 mol/kg), which represents an upper limit to the reduced sulfur available under steady state conditions, is much lower than in the mineralised interval (>4 mol/kg). To satisfy the hydrothermal mass balance, therefore, requires an additional source of reduced sulfur to the system, e.g., sulfur supplied by the hydrothermal fluid (Cooke et al., 2000) or sour gas (Cai et al., 2003).

**Implications.** In the Teena sub-basin, the laterally extensive high abundance pyrite intervals within the hanging wall stratigraphy are unrelated to hydrothermal processes, meaning exploration strategies that focus on pyrite detection alone as an indication of prospectivity may be ineffective. Instead, pyrite formation was enhanced during periods of high biological activity that was stimulated by nutrient supply under conditions of high relative sea level. In Proterozoic basins, future researchers should avoid invoking basin wide euxinia on account of the preservation of CD-type deposits and instead focus efforts towards understanding feedbacks between sea level, nutrient supply and biological productivity (e.g., Cox et al., 2019).

In terms of the mineral system, there is growing consensus that euxinic conditions are not a pre-requisite for the formation of CD-type deposits, either in the Proterozoic (this study) or Phanerozoic (e.g., Johnson et al., 2018; Magnall et al., 2018). As a result, mineralisation may not necessarily occur within the most reducing lithologies and the in situ metal trap that is invoked by the SEDEX model should be reconsidered. Similar to hydrocarbon studies, new genetic models should be derived from more basin scale approaches that can describe subsurface hydrothermal mass transfer and metal trap dynamics. Ultimately, this will lead to a greater understanding of what restricts the distribution of CD-type deposits to a few specific basins in the geologic record and facilitate a more predictive approach to exploration.

**Conclusions**

The distribution of fine grained pyrite around the mid-Proterozoic Teena CD-type deposit has no relationship with hydrothermal mineralisation. Moreover, intervals of high pyrite abundance and highly positive $\delta^{34}S_{pyrite}$ values correspond with periods of high relative sea level and have no relationship with basin restriction. Mineralisation formed later and during burial diagenesis. Altogether, this means that:

1. Evidence of sulfate limitation in Proterozoic basins is not necessarily indicative of basin restriction.
2. Mineralisation at the Teena deposit formed during burial diagenesis, meaning CD-type deposits should not be used *a priori* as evidence of a sulfidic (euxinic) water column.
3. Formation of the sulfide mineralisation at Teena requires an additional source of reduced sulfur, either from basinal (e.g., sour gas) or hydrothermal fluids.

**Acknowledgements**

We acknowledge funding from the Helmholtz-Rekrutierungssinn, thank Frederic Coufignal (GFZ) for assistance with SIMS analyses, Franz Wilke (GFZ) for help with EPMA mapping, and Richard Stern for supplying the S0302A pyrite standard. The logistical support and permission to publish from Teck is gratefully acknowledged. Finally, we would like to thank 2 reviewers (Sam Spinks and anonymous) for their constructive comments.

**Editor: Ariel Anbar**

**Additional Information**

**Supplementary Information** accompanies this letter at http://www.geochemicalperspectivesletters.org/article2008.

This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at http://www.geochemicalperspectivesletters.org/copyright-and-permissions.


**References**


