Carbonate Replacement as the Principal Ore Formation Process in the Proterozoic McArthur River (HYC) Sediment-Hosted Zn-Pb Deposit, Australia

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Abstract

The McArthur River (HYC) Zn-Pb-Ag deposit in the Carpentaria Zn belt, northern Australia, is one of the world’s largest and most studied sediment-hosted base metal deposits, owing to its lack of deformation and preservation of sedimentary and ore textures. However, the ore formation process (syngenetic vs. epigenetic) is still a subject of controversy. In this paper we focus on key characteristics of the HYC deposit that remain unexplained: preservation of sedimentary carbonate (dolomite) and its association with Zn, and the role of thallium (Tl) and manganese (Mn) distribution in the orebody.

Our findings demonstrate a sequence of events during ore formation: Tl is hosted almost exclusively within euhedral pyritic overgrowths around early diagenetic pyrite; sphalerite mineralization occurred after Tl-bearing pyrite overgrowths, in association with acid dissolution (replacement) of laminated and nodular dolomite across the subbasin; and outer rims are enriched in Mn on preserved dolomite at the dissolution reaction front in contact with sphalerite. New thermodynamic fluid chemistry modeling demonstrates the metal distribution and paragenesis can be explained by acidic, oxidized ore fluids entering the pyrite-dolomite host lithology, allowing reduction and pH buffering by acid carbonate dissolution, resulting in stepwise metal deposition in an evolving fluid.

We argue this represents strong evidence for epigenetic ore formation at HYC. Furthermore, the primary control on ore deposition is not synsedimentary faulting in the subbasin; rather, the chemical potential of sedimentary carbonate within reduced, sulfidic lithologies appears to be of critical importance to precipitation of sphalerite.

Introduction

The super-giant McArthur River Zn-Pb-Ag deposit (commonly known as “Here’s Your Chance,” or simply “HYC,” as it is herein referred) is one of the world’s largest known sediment-hosted base metal deposits. It is hosted in the Proterozoic McArthur-Isa superbasin (Fig. 1), which forms the Carpentaria Zn belt in northern Australia, the world’s largest Zn-Pb province. The total premining resource was 227 million tonnes (Mt) and 9.2% Zn, 4.1% Pb, 41 ppm Ag, and 0.2% Cu (Porter, 2017, and references therein), and it is classified as a super giant in its class alongside neighboring deposits in the Carpentaria Zn belt such as George Fisher, Mount (Mt.) Isa, Century, and Hilton (Large et al., 2005). HYC is exceptionally well preserved with little metamorphic overprint and is regarded by some workers as one of the best examples of a sedimentary exhalative (sedex) base metal deposit (e.g., Large et al., 1998; Ireland et al., 2004b). A sedex formation process assumes that mineralization occurred following exhalation of a metalliferous brine into the water column during sedimentation and synsedimentary faulting, with resultant deposition of laminated base metal sulfide ore as a chemical sediment. This interpretation of ore formation influences exploration approaches, as it implies a direct control of the sedimentary environment and synsedimentary tectonic framework on ore deposition. As discussed by Leach et al. (2005), the term “sedex” is fundamentally misleading because it implies a specific exhalative genetic component, and most studied deposits associated with this nomenclature lack unequivocal evidence for exhalative ore. Laminated ore textures, commonly regarded as the primary evidence for exhalative processes in these deposits, have been shown to result from carbonate replacement processes in the subsurface, at some point after deposition of the host sediment, as demonstrated for deposits in the Red Dog region (e.g., Kelley et al., 2004). Likewise, the laminated ore of the Century deposit in the Isa basin has been reported to be ~28 m.y. younger than the host sediment (Broadbent et al., 1998), precluding a syngenetic ore-forming process.

The primary observation used as evidence for a syndepositional origin of the McArthur River and other deposits in the Carpentaria Zn belt is the presence of stratiform base metal sulfide textures that are interpreted as primary laminations (Large et al., 2000, 2005; Ireland et al., 2004b). However, replacement of carbonate layers by sulfides can result in similar textures (Leach et al., 2010a, b). The reality is that sulfide layering alone is not sufficient evidence for either an exhalative or replacement origin (Leach et al., 2010a, b; Sangster, 2018), and it emphasizes the circular pattern of opposing arguments that arise based on subjective, sometimes nonquantifiable, observations. Sangster (2018) further noted that even though carbonate replacement is frequently mentioned in the literature

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Fig. 1. A) Simplified regional geology map of the McArthur and Mt. Isa basins in northern Australia, showing the locations of major stratiform Zn-Pb-Ag deposits, with the McArthur River (HYC) deposit and nearby Teena deposit in the Batten fault zone highlighted. Map in upper right corner shows location of study area within Australia. B) Reduced-to-pole (RTP) magnetic survey overlaid on the tilt derivative of the Batten fault zone (dashed box in A) highlighting the current structural complexity of the basin and (modified from Kunzmann et al., 2019). Also shown are the locations of the McArthur River (HYC) and Teena deposits and an additional studied drill core (NB16DD018) from the Berjaya subbasin.
as responsible for layered sulfide textures at the HYC deposit and elsewhere, the replaced mineral phase is seldom identified. This highlights the difficulty in visually identifying residual mineral phases in altered laminated sedimentary rocks, partly as a result of the scale of analysis. Most petrographic studies are conducted on thin sections that are chosen based on visual and subjective observations. However, new technological developments such as the Maia Mapper (e.g., Ryan et al., 2014) allow quantitative mapping of trace elements that are present in low elemental abundances (e.g., Tl) at unprecedented ultrahigh definition. This permits the ability to see the spatial distribution of elements within a hand sample and allows careful data-driven selection of thin section locations.

McArthur basin regional geology

The ca. 1815 to 1450 Ma McArthur basin (Fig. 1A) preserves a 5- to 15-km-thick succession of mixed carbonate and siliciclastic rocks with intercalated bimodal volcanic rocks near the base (Plumb, 1979a, b; Jackson et al., 1987; Ahmad and Munson, 2013). The McArthur basin is exposed in northeast Northern Territory and western Queensland, where it forms part of a series of linked, intracratonic basins that extended across the North and South Australian cratons and into the interior of Laurentia during the Proterozoic (Rawlings, 1999; Betts et al., 2008; Allen et al., 2015). These basins had a long-lived evolution and experienced transient episodes of extension and basin inversion driven by far-field plate boundary processes (Betts and Lister, 2001; Betts and Giles, 2006; Betts et al., 2008). In the McArthur basin, this resulted in large basin-scale normal and strike-slip faults that changed orientation as the basins evolved (O’Dea et al., 1997) and were periodically reactivated during different phases of the basin’s development (e.g., Scott et al., 2000; Southgate et al., 2000; Betts and Lister, 2001). A complex depositional architecture developed, with shifting depocenters and growth faults that changed orientation depending on the regional stress field (Fig. 1B). The structural subdivision of the McArthur basin encompasses the northern and southern McArthur basin, separated by the Urupanga fault zone (Fig. 1A). The southern McArthur basin is stratigraphically divided into the Tawallah, McArthur, Nathan, and Roper groups (Rawlings, 1999; Ahmad and Munson, 2013: App. 1, Fig. A1).

The HYC deposit is hosted in the 1640 ± 3 Ma Barney Creek Formation (Page et al., 2000), within the middle McArthur Group. The Barney Creek Formation is up to 900 m thick and is subdivided into the basal W-Fold Shale Member, the overlying HYC Pyritic Shale member (informal), the Cooley Dolostone Member and an upper undifferentiated unit. The W-Fold Shale Member comprises red-green dolomitic siltstone and dolostone. The HYC Pyritic Shale member comprises pyritic, laminated, and nodular dolomitic siltstones and organic silty mudstones (Kunzmann et al., 2019). The Cooley Dolostone Member, which represents a fault-associated mass-flow breccia that is composed of carbonate clasts derived from the underlying Emerunga dolostone and Teena dolostone units, is interbedded with other Barney Creek Formation units (Ahmad and Munson, 2013: App. 1, Fig. A1). The upper undifferentiated part of the Barney Creek Formation comprises dolomitic siltstones, carbonate mass-flow deposits, and dolarenite (Kunzmann et al., 2019). The Barney Creek Formation was deposited in a highly compartmentalized basin (Fig. 1B), characterized by kilometer-scale subbasins and paleohighs (McGoldrick et al., 2010; Kunzmann et al., 2019). Deposition of dolomitic siltstone and dolostone of the W-Fold Shale member of the lower Barney Creek Formation was accompanied by subbasin opening and followed deposition of peritidal carbonate rocks of the Teena and Emerunga dolostone units, which were deposited on a shallow marine environment. The HYC Pyritic Shale member, which hosts the mineralization in subbasin depocenters, was deposited in deep subtidal to slope environments below storm wave base (Bull, 1998; Kunzmann et al., 2019). A detailed facies analysis, sequence stratigraphic, and chemostratigraphic interpretation was provided by Kunzmann et al. (2019).

HYC ore deposit geology

The Barney Creek Formation is subdivided into informally named subunits at the HYC deposit, which are as follows. The gray-green dolomitic siltstone of the W-Fold Shale Member occurs at the base of the succession, named after the synform fold on the western side of the deposit. This unit transitions into the unmineralized lower dolomitic silt of the HYC Pyritic Shale member. The Zn-Pb mineralization occurs within the HYC Pyritic Shale member, which is up to ~80 m in thickness and is subdivided into 8 distinct high-grade ore lenses, each 1 to 5 m thick. The ore lenses are interbedded with sedimentary mass flow talus breccia deposits that comprise angular dolomite clasts, centimeters to several meters in diameter, along with nonmineralized (or pyritic) siltstones, and minor tuff beds. The mineralized lenses are overlain by weakly mineralized pyritic siltstones interbedded with talus mass flow breccia units (Fig. 2; App. 1, Fig. A2). These mass flow breccias thicken in the HYC subbasin to the northeast of the deposit (Ireland et al., 2004a), where some individual clasts reach many meters in diameter. The top of the succession is marked by a parallel bedded pyritic bituminous mudstone unit, which is in fault contact with older upthrust carbonate units east of the Basal Cooley fault. A summary of the Barney Creek Formation stratigraphy, HCY mine stratigraphy, and a simplified cross section of the McArthur Group geology in the HCY area is shown in Figure 2.

The ore lens facies and textures vary laterally within the deposit. Mineralized laminated pyritic and poorly dolomitic siltstone occur in the central zone of the deposit, and mineralization in nodular-laminated dolomite interbedded with laminated pyrite and siltstone occurs in the outer margins (Fig. 3). These lateral facies variations likely reflect the geometry of the subbasin, with laminated sulfide and carbonate deposition in the depocenter and nodular carbonate on the slopes (Ireland et al., 2004b).

The central zone of the deposit is comprised of planar or wavy rippled carbonaceous siltstone and sulfide laminae, typically submillimeter in thickness but with local centimeter-scale beds (Fig. 3B). Thicker siltstone layers commonly fine upward and may be devoid of pyrite or other sulfides. Thinner siltstone laminae may contain abundant pyrite, and in many cases these laminae are better described as pyrite laminae with minor siltstone. The siltstone-pyrite laminae are interbedded with dolomite laminae comparable in thickness, or they locally form thicker crust-like layers a few millimeters
thick. The dolomite laminae locally contain Zn-Pb sulfides (sphalerite > galena). Dolomite nodules several centimeters in diameter are common within finely laminated facies and are observed to displace laminae at the edges. The laminations have been disrupted by post depositional processes, including soft-sediment slumping of multiple combined layers or thicker beds and recumbent folds, centimeter-scale normal synsedimentary microfaults in intrabeds, and centimeter-scale microthrusts (Fig. 3B).

The nodular carbonate-dominated facies surrounding the central zone of the deposit is composed of millimeter- to centimeter-thick beds of dolomitic carbonate (Fig. 3C). These beds may be laterally continuous for tens of centimeters but are commonly brecciated, folded, or slumped, and some dis-

### Table 1. Correlation Matrix Between Major Metals and Trace Elements from the HYC Orebody

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Zn</th>
<th>Pb</th>
<th>Fe</th>
<th>Cu</th>
<th>Cd</th>
<th>As</th>
<th>Ag</th>
<th>Ge</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1</td>
<td>0.3548</td>
<td>–0.1378</td>
<td>0.7665</td>
<td>0.9197</td>
<td>0.6774</td>
<td>0.7823</td>
<td>0.7152</td>
<td>–0.03563</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3548</td>
<td>1</td>
<td>–0.1578</td>
<td>0.5904</td>
<td>0.5102</td>
<td>0.2187</td>
<td>0.7184</td>
<td>0.7986</td>
<td>0.01579</td>
</tr>
<tr>
<td>Fe</td>
<td>–0.1378</td>
<td>–0.1578</td>
<td>1</td>
<td>–0.1656</td>
<td>–0.1745</td>
<td>0.3017</td>
<td>–0.1895</td>
<td>–0.00683</td>
<td>0.787</td>
</tr>
<tr>
<td>Cu</td>
<td>0.7665</td>
<td>0.5904</td>
<td>–0.1656</td>
<td>1</td>
<td>0.8613</td>
<td>0.6054</td>
<td>0.9019</td>
<td>0.6711</td>
<td>–0.06647</td>
</tr>
<tr>
<td>Cd</td>
<td>0.9197</td>
<td>0.5102</td>
<td>–0.1745</td>
<td>0.8613</td>
<td>1</td>
<td>0.7268</td>
<td>0.9274</td>
<td>0.7981</td>
<td>–0.04497</td>
</tr>
<tr>
<td>As</td>
<td>0.6774</td>
<td>0.2187</td>
<td>0.3017</td>
<td>0.6054</td>
<td>0.7268</td>
<td>1</td>
<td>0.6148</td>
<td>0.5118</td>
<td>0.3848</td>
</tr>
<tr>
<td>Ag</td>
<td>0.7823</td>
<td>0.7184</td>
<td>–0.1805</td>
<td>0.9019</td>
<td>0.9274</td>
<td>0.6148</td>
<td>1</td>
<td>0.8354</td>
<td>–0.02265</td>
</tr>
<tr>
<td>Ge</td>
<td>0.7152</td>
<td>0.7986</td>
<td>–0.09808</td>
<td>0.7981</td>
<td>0.5118</td>
<td>0.8354</td>
<td>1</td>
<td>0.05946</td>
<td>1</td>
</tr>
<tr>
<td>Tl</td>
<td>–0.03563</td>
<td>0.01579</td>
<td>0.787</td>
<td>–0.06647</td>
<td>–0.04497</td>
<td>0.3848</td>
<td>–0.02265</td>
<td>0.05946</td>
<td>1</td>
</tr>
</tbody>
</table>
play imbricated breccia-like structures. Where brecciated, the crust-like nodular dolomite displays centimeter-thick elongate blebs. Locally, upper surfaces of the dolomite display domal structures a few millimeters thick, and carbonaceous or pyritic siltstone laminae form blankets over these topographic highs. The thicker dolomite beds are typically composed of numerous individual beds or thinner laminae and may be interbedded with minor carbonaceous and/or pyritic laminae (Fig. 3C). Carbonaceous siltstone beds, locally >5 cm thick, may be entirely devoid of visible pyrite or Zn-Pb sulfides. Beds of submillimeter pyrite laminae, which cumulatively measure several centimeters in thickness, are common and may be mixed with carbonaceous laminae in soft-sediment deformation zones.

Pyrite: Two distinct textures of pyrite have been recognized in HCY ores. The most volumetrically abundant is stage 1 pyrite (py1; Williams, 1978; Eldridge et al., 1993), which is present in dolomitic siltstone facies as both laminated subhedral crystals 5 to 10 µm in diameter and spheroidal and ellipsoidal aggregates of (possible) frambooids up to hundreds of microns in diameter. The timing of formation of py1 is considered syngenetic with deposition of the Barney Creek Formation or early diagenetic (Croxford, 1968; Croxford and Jephcott, 1972; Williams, 1978; Eldridge et al., 1993; Large et al., 1998; Ireland et al., 2004b). Stage 2 pyrite (py2; Williams, 1978; Eldridge et al., 1993) is a distinctive phase of concentric euhedral overgrowths on and around py1. These overgrowths are up to ~20 µm thick and can add significant volume to earlier
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**Table 2. Correlation Matrix Between Zn and Other Trace Elements from the Center and Northern and Southern Margins of the HYC Deposit**

<table>
<thead>
<tr>
<th>Center of deposit</th>
<th>Correlation (n = 22)</th>
<th>Zn</th>
<th>Ag</th>
<th>Cd</th>
<th>Cu</th>
<th>Ge</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1</td>
<td>0.43</td>
<td>0.78</td>
<td>0.53</td>
<td>0.39</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.43</td>
<td>1</td>
<td>0.86</td>
<td>0.85</td>
<td>0.69</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.78</td>
<td>0.86</td>
<td>1</td>
<td>0.84</td>
<td>0.67</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.53</td>
<td>0.85</td>
<td>0.84</td>
<td>1</td>
<td>0.4</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>0.39</td>
<td>0.69</td>
<td>0.67</td>
<td>0.4</td>
<td>1</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.63</td>
<td>0.49</td>
<td>0.7</td>
<td>0.64</td>
<td>0.28</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

**North margin**

| Zn                | 1                    | 0.97| 0.98| 0.88| 0.96| 0.52|
| Ag                | 0.97                 | 1   | 0.99| 0.95| 0.97| 0.59|
| Cd                | 0.98                 | 0.99| 1   | 0.93| 0.97| 0.55|
| Cu                | 0.88                 | 0.95| 0.93| 1   | 0.91| 0.64|
| Ge                | 0.96                 | 0.97| 0.97| 0.91| 1   | 0.62|
| As                | 0.52                 | 0.59| 0.55| 0.64| 0.62| 1   |

**South margin**

| Zn                | 1                    | 0.84| 0.95| 0.77| 0.67| 0.72|
| Ag                | 0.84                 | 1   | 0.93| 0.95| 0.96| 0.66|
| Cd                | 0.95                 | 0.93| 1   | 0.87| 0.68| 0.73|
| Cu                | 0.77                 | 0.95| 0.87| 1   | 0.47| 0.56|
| Ge                | 0.67                 | 0.63| 0.68| 0.47| 1   | 0.58|
| As                | 0.72                 | 0.66| 0.73| 0.56| 0.58| 1   |

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py1. The overgrowths also locally cement aggregates of individual crystals within frambois. Most workers suggest that base metal sulfide precipitation postdated formation of py2 overgrowths (Eldridge et al., 1993; Broadbent et al., 1998; Huston et al., 2006; Polito et al., 2006; Leach et al., 2010a). Both py1 and py2 textures are described in detail by Eldridge et al. (1993) and Ireland et al. (2004b), and therefore detailed descriptions are not given here.

**Sphalerite**: Sphalerite is the most abundant base metal sulfide phase in the HYC deposit. Sphalerite textures vary across the deposit, with laminated and finely disseminated textures in laminar siltstones and aggregates associated with nodular and crustiform dolomite. The laminated sphalerite has been interpreted that early while pyrite (py1) likely formed during early episodes of hydrocarbons in both ore and mudstone from ore lens 2 were similar to other hydrothermally generated examples under high temperatures of around 250° to 400°C and that mineralization likely occurred by lateral migration of hot metalliferous brines.

**Contrasting interpretations for ore genesis**

Currently, despite having been well studied for more than 50 years, controversy remains over the formation process of the HYC mineral system. This is largely due to technological limitations on the analysis of key geochemical characteristics from the deposit scale to nanoscale that have thus far prevented significant advances in the understanding of ore-forming processes.

**Syngenetic exhalative (sedex) interpretation**: The evidence for a synsedimentary-exhalative origin of HYC (and other similar deposits in the region) is primarily built on the interpretation that ores with fine-grained laminated textures and sedimentary structures such as load casts and flames within sphalerite-bearing (sp1) carbonaceous beds are sedimentary in origin (Croxford, 1968; Croxford and Jephcott, 1972; Large et al., 1998), and clasts with laminated ore textures within intraformational talus breccias indicate mineralization occurred before individual fault movements (Ireland et al., 2004b). Lithogeochemical halos of anomalous trace element contents—for example, manganese (Mn) and thallium (Tl)—in the ore zone and surrounding and overlying lithologies are also reported to reflect synsedimentary origin, derived from lateral movement of exhaled metalliferous plumes (Large et al., 2000). Relatively high Mn concentrations in the underlying W-Fold Shale compared to the ore zone were also interpreted by Large et al. (2000) to have formed by exhalation of an early connate brine into the water column prior to Zn-Pb–bearing fluid exhalation. Sulfur isotope (δ34S) compositions of pyrite, sphalerite, and galena, which increase between the footwall and hanging wall, were ascribed as further evidence of a dual source of sulfur and thereby a syngenetic origin (Smith and Croxford, 1973). Large et al. (1998) argued the position of the deposit within the deepest part of the basin and corresponding euxinic (anoxic, sulfidic) conditions at the sediment-water interface were stated as necessary conditions for exhalative ore formation.

In summary, the exhalative formation process interpretation involved multiple exhalations from multiple fluid venting episodes within a tectonically active and euxinic subbasin.

**Subsurface replacement interpretation**: Williams and Rye (1974) disputed the syngenetic interpretation based on sulfur isotope data presented by Smith and Croxford (1973), arguing that this simply indicates deposition of the host sediments in an euxinic restricted basin, and the stratigraphic upward increases in δ34S values reflect progressive depletion of isotopically light sulfur as sedimentary pyrite was deposited. Croxford and Jephcott (1972) and Williams (1978) demonstrated that early while pyrite (py1) likely formed during early diagenesis, followed by later overgrowths (py2), both pyrite phases preceded sphalerite and galena precipitation, which supports an epigenetic origin of the HYC ores. Eldridge et al. (1993) and Logan et al. (2001) interpreted variable δ34S values in the base metal sulfides to reflect sulfur derivation by thermochemical sulfate reduction, thus differing from the earlier biogenic py1 and possibly py2.

An organic geochemistry study by Chen et al. (2003) demonstrated that hydrocarbons in both ore and mudstone from ore lens 2 were similar to other hydrothermally generated examples under high temperatures of around 250° to 400°C and that mineralization likely occurred by lateral migration of hot metalliferous brines.

Direct replacement of preexisting sedimentary laminae as a deposition mechanism for base metal sulfides was proposed by Perkins and Bell (1998), who argued the laminated base metals were the result of replacement of bituminous laminae. Carbonate-specific replacement was argued by Himan (1996), who suggested laminated sulfide textures represent stylolaminar replacement and later demonstrated that comparisons between the mineralized and unmineralized Barney Creek Formation strata indicated significant carbonate disso-
olution at HYC (Hinman, 2001). These replacement processes were discussed in a review on the Australian sediment-hosted Zn-Pb deposits by Huston et al. (2006) as a counterargument for the interpretation that the laminated sulfide textures represent a syngenetic origin for ore deposition.

**Approach taken in this study**

In this study we present evidence for a subsurface carbonate dissolution-style process for the HYC deposit by employing new state-of-the-art analytical techniques and, critically, by quantitatively examining mineralized samples from different portions of the deposit through a range of scales from the sub- to the nanometer scale. We focus on aspects that have been previously inadequately explored, such as the distribution of sphalerite in relationship to sedimentary carbonate, preservation of original carbonate in the sphalerite zones, the distribution of trace Mn and Tl and their occurrence in the ore paragenetic sequence, and thermodynamic modeling of the hydrothermal ore fluid.

**Methods and Materials**

**Sampling**

Seventy-four samples for multielement geochemistry and microstructural and petrographic analysis were collected from two diamond drill cores, BS024_1 and MRM_2012_03, which intersected the ore lenses in the center and southern margins of the deposit, respectively (Fig. 3A). Large (>30 × 30 cm) samples were also collected from transects in the open pit from exposures at the northern and southern margins of the pit and from an exposure of the upper ore lens stratigraphy in the central zone (Fig. 3A). The ore lens numbers for samples from the drill core, northern margin, and central zones were recorded, but most samples from the southern margin were loose and were collected close to the logged ore lens horizons; thus, the ore lens from which they are derived is uncertain, and they are regarded as “unassigned.” The samples were prepared by cutting with a slab saw, and samples for Maia Mapper analysis were polished to a mirror finish with a diamond lap and finally with a cloth lap. Thin sections were prepared for transmitted and reflective light and scanning electron microscopy (SEM).

**Maia micro-X-ray fluorescence (µXRF) mapping**

The Maia Mapper is a new laboratory µXRF mapping system for efficient elemental imaging of drill core sections for use in minerals research and industrial applications. It targets intermediate spatial scales, with imaging of up to ~80 M pixels, each 30 µm, over a 500- × 150-mm sample area, as part of the analytical workflow of the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Advanced Resource Characterisation Facility. The Maia Mapper brings together (1) the Maia detector and imaging system (Siddons et al., 2014), with its capabilities for high-efficiency detection (1.3 sr solid-angle), event-mode operation, millisecond pixel transit times in fly scan mode, and real-time spectral deconvolution and imaging (Ryan et al., 2014), (2) the high brightness MetalJet D2 liquid metal microfocus X-ray source from Excillum (www.excillum.com) with high indium alloy anode and 200-W power at 70 kV into an effective 20-µm source size, filtered using a 1.0-mm aluminum window, and (3) an efficient XOS polycapillary lens with a flux gain of 15,900 at 21 keV into a ~32-µm focus, all integrated with stage raster scanning for automated imaging and analysis of drill core sections (Ryan et al., 2018).

Polished slab samples 300 to 400 mm in length from the central, southern, and northern zones of the pit were analyzed on the Maia Mapper. Particular focus was paid to the distribution of Tl, which is otherwise difficult, if not impossible, to detect as a trace element within major minerals using standard laboratory XRF techniques because of X-ray peak overlaps with Pb and S. Therefore, validation of Tl distribution requires interrogation of some spatial regions to explore and extract the Tl signal. The close proximity of Tl and Pb X-ray peaks may lead to some Tl artifact when Pb is high. Hence, we use associations to select high-Tl but low-Pb pixels, to separate each element in geochemical maps.

For the presentation of Maia Mapper data in this paper, some of the full scans have been cropped to only show part of the sample, but full size and resolution (1 pixel = 30 µm) versions of all of the maps in this paper are available in Appendix 1. Full methodology for the Maia Mapper µXRF analysis is also available in Appendix 2.

**Petrographic analysis**

**SEM and electron backscatter diffraction (EBSD):** Polished thin sections were coated with 5 nm of carbon to prevent charging. Sulfide microstructures were imaged using a Tescan Mira field emission gun-scanning electron microscope (FEG-SEM) at 15 keV and beam current of 1.9 nA. To examine the carbonate and sulfide grain structures, samples were polished with a 20-nm, colloidal silica suspension in dilute NaOH to remove crystal lattice damage from thin section preparation. The surface was coated with an ~5-nm carbon coat to prevent charging in the SEM. EBSD mapping was performed using a Zeiss UltraPlus FEG-SEM fitted with an Oxford Instruments Symmetry EBSD detector and XMaxN-80 energy-dispersive X-ray spectroscopy (EDS) detector. During mapping, both EBSD patterns and EDS spectra were collected from each point simultaneously to allow examination of the relationships between crystallographic (grain) boundaries and chemical variations. Data were acquired using an incident electron beam with a beam current of 15 nA and accelerating voltage of 20 keV. The sample was tilted so that the sample normal was inclined at 70° to the incident electron beam to increase diffraction electron yield. Maps were collected with a step size between measurements of 250 nm to ensure that submicron grains were captured and at an acquisition rate of 490 Hz. EBSD patterns were indexed against orientation databases selected by the user for the following phases: calcite (Laue class m; a = 4.99 Å, c = 17.06 Å), pyrite (Laue class m; a = 5.417 Å), quartz (Laue class m; a = 4.913 Å, c = 5.405 Å), and sphalerite (Laue class mm; a = 5.409 Å). Calcite was used instead of dolomite because the lack of mirror symmetry perpendicular to the c-axis in dolomite leads to systematic misindexing that does not occur when using the calcite crystal lattice. Galena (Laue class mm; a = 5.93) was indexed as sphalerite (the similarity in the following phases: calcite (Laue class m; a = 4.99 Å, c = 17.06 Å), pyrite (Laue class m; a = 5.417 Å), quartz (Laue class m; a = 4.913 Å, c = 5.405 Å), and sphalerite (Laue class mm; a = 5.409 Å). Calcite was used instead of dolomite because the lack of mirror symmetry perpendicular to the c-axis in dolomite leads to systematic misindexing that does not occur when using the calcite crystal lattice. Galena (Laue class mm; a = 5.93) was indexed as sphalerite (the similarity in the crystallographic structures).
tent from the EDS mapping. Data were postprocessed by removing single pixel measurements (either isolated measurements or misindexed/misidentified single pixels within other correct measurements) and grains with fewer than four pixels, as these are deemed unreliable. Missing data were then interpolated using the surrounding measurements following the BC constrained method outlined in Prior et al. (2009) to prevent postprocessing artifacts.

Electron backscatter diffraction and EDS data are displayed in a number of formats. The band contrast is a measure of the EBSD diffraction pattern quality, which is high within grains and lower at grain boundaries. Therefore, the band contrast highlights the grain structure of the EBSD map. Orientations are displayed using an inverse pole figure (IPF) coloring. This shows which crystallographic axis is parallel to a given direction relative to the sample coordinates (in this case, z, the sample normal). Misorientations are displayed relative to arbitrarily chosen reference points within grains. Each pixel is colored by the angular rotation required to rotate the crystal in that pixel’s orientation into the same orientation as the reference orientation.

Focused ion beam-time of flight-secondary ionization mass spectrometry (FIB-TOF-SIMS): The trace element content of pyrite was mapped at high spatial resolution (nanometer scale) using FIB-TOF-SIMS. A focused Ga ion beam is used to sputter material from the surface of the sample, and that material is accelerated into a TOF mass spectrometer attached to the microscope. The resulting spectrum consists of peaks at different mass to charge ratios, which can be interpreted in terms of isotopes present in the sample. Plotting spatial variations in peak intensity gives a map of the relative abundance of the isotope in question. Since material is removed from the sample into the mass spectrometer, the data volume can be used to show variations in 3-D. However, the maps displayed in this contribution are the signal intensity integrated over the entire depth analyzed. Data were collected using a Tescan LYRA3GM FIB-SEM with a Tofwerk TOF-SIMS. All elements are presented at parts per million concentration, apart from Re, which was measured at parts per billion level.

A 0.1-g sample was digested in a mixture of hydrofluoric, nitric, phosphoric, and hydrochloric acids in sealed digestion vessels for 60 min, using an Anton-Paar MW3000 microwave digestion system. The digestion took place at a temperature of approximately 160°C and a 16-bar pressure. After the addition of boric acid to neutralize remaining hydrofluoric acid, the solutions were made to volume with deionized water. Internal standards are added to the solutions at the digestion stage. The solutions were then presented to inductively coupled plasma-mass spectrometry (ICP-MS; Perkin-Elmer Nexion 3000) and ICP-optical emission spectrometry (ICP-OES; Perkin-Elmer Optima 7300DV) for determination of the desired analytes.

Alkaline fusion major element analysis: Analysis for major elements (oxides) Al₂O₃, CaO, Fe₂O₃, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂, and loss on ignition (LOI) was performed by LabWest Minerals Analysis using their in-house method AF-03.

This method gives total recovery of major rock-forming metals. A 0.1-g portion of the sample was fused with a lithium metaborate/tetraborate flux at 1,000°C. The resulting bead was dissolved in dilute (2%) nitric acid. Solutions were then presented to ICP-OES (Perkin-Elmer Optima 7300DV) for determination of the desired analytes. LOI was performed gravimetrically, with ignition of a separate 1-g sample portion at 1,000°C for 30 min. Elements are reported as oxides at percent level concentrations.

Thermodynamic modeling

The thermodynamic modeling of predominant Tl, Fe, Zn, and Mn minerals and aqueous species as a function of log fO₂ and pH was conducted using The Geochemist’s Workbench (Bethke, 2007). The thermodynamic properties for Tl minerals and aqueous species are from Xiong (2007), for Zn-Cl species from Mei et al. (2015), for Mn-Cl species from Sulimenov and Seward (2000), and for Fe-Cl species from Testemate et al. (2009). The thermodynamic data for other aqueous species and minerals are from the Lawrence Livermore National Laboratory thermodynamic database version R9 (Wolery, 1992).

Results

Geochemistry

All geochemical results are available in Appendix 3, including the QA/QC results from analytical standards and duplicate analysis.

Ore grade and distribution: New geochemical analyses from 74 samples show that ore lens 2 has the highest mean and maximum Zn concentrations (Fig. 4A), consistent with the observations of Lambert (1976). The trend of decreasing grade upsection, as suggested by Lambert (1976), is generally

\[ \text{HRD} (%) = \left( \frac{\text{assay}_1 - \text{assay}_2}{\text{assay}_1 + \text{assay}_2} \right) \cdot 100. \]
also observed in our mean values from ore lenses 2 through 8, with some notable high exceptions in ore lens 6 and 8 (Fig. 4A). Samples from the central zone have lowest mean and maximum Zn concentrations, and the laminated-nodular dolomite facies in the southern margin has the greatest mean values, whereas the northern margin has the highest maximum Zn concentrations from ore lens 2 (Fig. 4B). The maximum concentrations of Zn from each location in the deposit, however, all cluster ~20 to 26%. A similar distribution is observed for Tl with a larger mean and higher maximum concentrations in the northern and southern margins of the deposit (Fig. 4C).

The Pb concentration shows a distinctive decrease from the northern margin to the south (Fig. 4D). The other minor metals (Ag, Cu) are present in the highest concentrations in the highest-grade Zn samples in the northern margin, but the highest mean concentrations are present in the central zone of the deposit (Fig. 4E, F).

**Zinc and associated trace elements:** The samples with the highest grade of Zn have a negative correlation with CaO concentrations ($R^2 = 0.336$), which represent dolomitic dolomite in these samples (Fig. 5A).

Samples with high carbonate contents (up to ~33% CaO) have the lowest Zn in sphalerite, and vice versa. There is no correlation between Zn grade and organic carbon content.
(additional methodology and data in Apps. 2, 3) or any other major element oxide.

The association between Zn and other key elements that are anomalous in this deposit or are known from other similar sediment-hosted Zn deposits (Pb, Fe, Cu, Cd, As, Ag, Ge, and Tl) are shown in the correlation (R^2) matrix in Table 1. This shows a positive correlation between Zn and Ag, Cd, Cu, Ge, and As in the HYC deposit, also shown in Figure 5, and negative correlation between Tl with all elements other than Fe. There is also a strong correlation between the secondary base metal Pb and Ag and Ge.

Elements such as Ag, Cd, Cu, Ge, and As show strong correlation with Zn dependent on location within the deposit (Table 2; Fig. 5). In the northern margin, all elements except As have strongly positive correlation coefficients (R^2 > 0.88) with Zn, whereas the correlation between Zn and these elements is weaker in samples from the central and southern parts of the deposit.

Thallium and Fe are strongly correlated in all parts of the deposit (Fig. 5B; Tables 1, 2), with Tl concentrations ranging up to 444 ppm in a sample from the south margin. However, there is no apparent relationship between Zn and Tl, which...
have negative correlation, although it is noted that the samples with the highest-grade Zn have the lowest concentrations of Tl.

Petrography

Large-scale ore sulfide and carbonate textures: The Maia Mapper µXRF analysis of large samples shows that medium-grade samples have easily observable dolomite, whereas some high-grade samples have little or no visible dolomite. For example, a medium- to low-grade ore sample (~15% Zn; Fig. 6A) of laminated pyrite and sphalerite contains thin laminae of pyrite, sphalerite, and dolomite (i.e., high Fe in red, Zn in green, and Ca in blue on Fig. 6B). Sphalerite in these laminae is present within and around dolomite grains. Higher-magnification images (Fig. 6C) highlight in more detail the presence of Zn within dolomite laminae. Sphalerite is observed to occur in higher concentrations in laminae with minor dolomite than in laminae with abundant dolomite. However, in the highest-grade ore samples (up to 26.4% Zn in our data) with planar and wavy sedimentary textures and syndepositional soft-sediment slumps and normal microfaults (Fig. 7A) typical of the Barney Creek Formation dolomitic siltstones, little or no dolomite is present, as shown in the Maia Map (Fig. 7B). The only Ca is present in late calcite-filled fractures and Ca-bearing siliciclastic grains in coarser fining-up silt laminae. Sphalerite in these ore samples is present predominantly as millimeter-scale laminae that contain only minimal pyrite with some larger centimeter-scale pyrite aggregates. Sphalerite-rich layers are interlaminated with carbonaceous mud and siltstone-sandstone laminae that are locally moderately pyritic (Fig. 7C).

Breciated (imbricate) crustiform nodular dolomite ore samples consist of beds of elongate ~2-cm-long dolomite breccia clasts with interstitial pyritic muds overlying undisturbed planar interbedded dolomite, carbonaceous siltstone, and pyritic laminae (Fig. 8A). Sphalerite in all nodular dolomite samples analyzed in this study is present in the outer margins and interiors of dolomite nodules and crusts (Fig. 8B). Sphalerite is present throughout elongate dolomite clasts and crusts, mimicking dissolution breccia textures on the microscale within the dolomite. Sphalerite is absent in pyritic and carbonaceous siltstone laminae. At higher magnification (Fig. 8C), the association of sphalerite and dolomite clasts is particularly obvious, as is the presence of pyrite inclusions.
within dolomite clasts. Pyrite inclusions here are surrounded by sphalerite within the dolomite. Uniquely, within dolomite breccia samples such as that shown in Figure 8, pyrite forms the matrix between sphalerite-bearing breccia clasts. This is spatially limited to the upper part of the brecciated bed (in this sample), and the pyrite matrix is not present throughout the entire unit (Fig. 8B, C). The textures in these facies are extremely complex, however, and in places sphalerite associated with the outer margins of dolomite clasts is apparently enveloped by this pyrite matrix.

In ore samples that exhibit soft-sediment deformation textures such as slumping and folding of laminated pyrite-siltstone beds and crustiform nodular dolomite (Fig. 9A), sphalerite is associated with nodular dolomite clasts, similar to those in brecciated dolomite facies (Fig. 8). Additionally, minor finely disseminated laminated sphalerite also occurs in nonpyritic siltstone layers that are devoid of any detectable carbonate (Fig. 9B, D). Zones of pyrite occur between and closely associated with sphalerite-bearing nodular dolomite clasts (within dolomite zone in incumbent fold in Fig. 9B). Thick interbeds of pyritic and carbonate siltstone in the middle section of this sample are draped over nodular dolomite; these interbeds are almost entirely void of sphalerite, other than a few ~<100-µm inclusions, and carbonate is not detectable.

In samples of laterally extensive crustiform nodular dolomite, sphalerite occurs within dissolution replacement textures and is absent in pyritic and siltstone laminae (Fig. 10A, B). These facies also display sphalerite that forms subvertical veinlets that crosscut the crustiform dolomite. Detailed examination of these shows that the fractures persist over several layers of dolomite but have not affected the pyritic interbeds. Sphalerite in these fractures does not extend into the pyritic bed, but it does extend into the broader dolomite nodules (Fig. 10C).

We encourage readers to refer to the full-resolution and extended versions of the Maia Map figures in Appendix 1.

**Manganese dolomite and manganese enrichment**

In order to understand the significance of Mn enrichments in the HYC deposit, we must first consider the distribution and behavior of Mn in the Barney Creek Formation and other basins of similar age. Manganese enrichments in the dolomitic W-Fold Shale underlying the HYC orebody (up to ~1.7% MnO) have previously been interpreted to represent early connate brine exhalation prior to base metal brine exhalation and, thus, a synsedimentary ore formation process for the HYC deposit (Large et al., 1998). While it is beyond the scope of this study to look at the systematics of the Mn enrichment specifically in the W-Fold Shale in detail, it is im-

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**Fig. 7.** A) Reflected-light photograph of polished slab of very high grade laminated Zn ore from the central zone of the deposit showing soft-sediment deformation slump and microfault textures. B) Maia Map of the sample showing distributions of iron (red), zinc (green), and calcium (blue), which indicate pyrite, sphalerite, and multiple Ca-bearing phases, respectively. No dolomite was identified in this sample. C) Detailed view of area indicated in white box in B showing the spatial distribution of laminated sphalerite (sp) within laminae that display textures typical of laminated carbonate in lithofacies 16. Minor laminated and nodular pyrite (py) are present, and late calcite (ca) locally fills microfaults. We interpret this laminated sphalerite texture to reflect precipitation of sphalerite at the site of total dissolution replacement of carbonate. The “ca” label in the figure indicates the calcite mineral phase. Full resolution and expanded version of this Maia Map is available in Appendix 1, Figure A7.
important to consider this in the broad sense. Concentrations of Mn in contemporaneous (~1.6 Ga) dolomitic marine shelf facies underlying deep marine black shales in the Edmund basin of Western Australia are similar to that of the W-Fold Shale and range up to 1.43% (Spinks et al., 2018). That study showed that Mn was uniformly distributed throughout dolomite facies because of consistent enhanced uptake of Mn$^{2+}$ from Mn-rich anoxic Proterozoic bottom waters, rather than through exhalation of brines. If this comparison is valid, the Mn concentrations in the dolomitic W-Fold Shale are not anomalous for late Paleoproterozoic to early Mesoproterozoic marine shelf dolomite facies. This also suggests that it may not be valid to compare the Mn systematics in the Barney Creek Formation facies to those in recent marine environments (Large et al., 1998). Thus, we argue the high Mn concentration in the W-Fold Shale most likely reflects uptake of marine Mn$^{2+}$ (which substitutes for Ca/Mg) in stratiform dolomite and does not indicate any localized early brine exhalation processes.

There are pronounced Mn enrichments in the HYC ore zone compared to the lateral equivalent nonmineralized stratigraphy. Large et al. (2000) reported up to ~0.7% MnO contents in the orebody, compared to ~<0.25% in lateral equivalent stratigraphy, while our data show MnO concentrations up to 1.56%, (see App. 3). This demonstrates the HYC Pyritic Shale member in the HYC subbasin is unique in terms of its Mn content, which implies the ore fluid provided an additional source of Mn and thus may provide clues to the ore-forming process. Previous to this study, the specific systematics of Mn enrichment in the HYC orebody were not studied in detail, but it was interpreted represent Mn dolomite and ankerite that extends into the hanging-wall pyritic shales (Large et al., 2000). Our study highlights the distribution of Mn and shows that Mn is present throughout the nodular dolomite (Fig. 9C, F). The presence of Mn throughout the unaltered nodular dolomite may represent Mn$^{2+}$ uptake from anoxic marine water during formation (Spinks et al., 2018). However, we interpret the enhanced concentrations in outer rims of dolomite nodules that are adjacent to sphalerite mineralization and around micrometer-scale sphalerite inliers in the nodules (Figs. 9C, F, 11C) to represent Fe-Mn alteration during the dissolution front during carbonate dissolution and simultaneous sphalerite precipitation. This local Fe-Mn enrichment in dolomite adjacent to the sphalerite in the HYC ore zone (HYC Pyritic Shale member) would explain why the ore zone has higher Mn concentrations than nonmineralized stratigraphy elsewhere in the basin (Large et al., 2000).

Nonmineralized Barney Creek Formation: The µXRF analysis of nonmineralized laminated dolomitic siltstone from the lithofacies equivalent to the HYC ore zone (lithofacies 16, silty dolarenite/dolomitic siltstone) from a drill hole (NB16DD018) from the nearby Berjaya subbasin (Fig. 1B) is shown in Appendix 1, Figure A3. This facies of dolomitic and carbonaceous-silty laminae with some laminated and nodular pyrite contains only minor traces of submillimeter sphalerite (Zn, green) within the dolomitic laminae (App. 1, Fig. A3B).

Microanalysis of pyrite: Pyrite aggregates near the dolomite-associated sphalerite (Fig. 11A) are composed of interlocking pyrite grains, each of which is a single crystal with no internal orientation variation (Fig. 11B). Nodular pyrite aggregates are composed predominantly of grains with 1-
to 2-µm diameter with a few larger (~10 µm) grains. The grains are neither equant nor uniform in size and therefore inconsistent with the morphologies documented by EBSD by Ohfuji et al. (2005). Therefore, we suggest that the pyrite aggregates in these rocks are modified from their original (possible) framboidal microstructures. Pyrite aggregates not immediately (sub-mm) proximal to dolomite-associated sphalerite within the carbonaceous silt matrix are composed of less coarse elongate aggregates of noninterlocked crystals and disseminated individual crystals (Fig. 11A).

Manganese-iron alteration of dolomite: Based on whole-rock geochemical analysis, the highest manganese concentrations (up to 1.56%) are associated with high CaO (see full data table in App. 3), suggesting that Mn resides in carbonate (dolomite) minerals. Maia Mapper µXRF analysis shows high Mn concentrations, particularly around the outer margins of dolomite clasts that are in contact with sphalerite and in the interiors of dolomite clasts that display sphalerite replacement textures (Fig. 9C). Closer, detailed views of this map highlight the differences in dolomite composition proximal to sphalerite mineralization. Higher concentrations of Mn are observed in dolomite clasts that contain sphalerite (sp) mineralization. The white box indicates the detailed field of view shown in E. D) Detailed Maia Map of area in white box in B, showing sphalerite mineralization within modular dolomite (dol) but absent in pyrite (py) and carbonaceous silt (OM) laminae. E) Detailed Maia Map of area in white box in C showing Mn-altered dolomite (Mn-dol) proximal to and hosting sphalerite mineralization. Full resolution and expanded version of these Maia Maps are available in Appendix 1, Figure A9.
Fig. 10. A) Maia Map of crustiform nodular carbonate Zn-Pb ore interbedded with pyritic-carbonaceous siltstone laminae from the northern margin of the deposit showing distributions of iron (red), zinc (green), and calcium (blue), which indicate pyrite, sphalerite, and dolomite, respectively. Sphalerite mineralization occurs around partial-dissolution rims around carbonate and as subvertical veinlets that crosscut carbonate. White boxes indicate detailed fields of view shown in B and C. B) Detailed view of sphalerite (sp) mineralization within and around nodular and crustiform dolomite (dol) at the site of dissolution. No sphalerite is observed in the pyritic (py) and carbonaceous siltstone (OM) laminae. C) Detailed view of sphalerite mineralization in subvertical fractures that crosscut crustiform dolomite but not pyritic laminae. Fractures are observed to continue across several layers of dolomite, with sphalerite mineralization extending into the surrounding dolomite (replacively), suggesting carbonate was brittle during ore formation but the pyritic interlayers were not. Full resolution and expanded version of this Maia Map is available in Appendix 1, Figure A10.
band contrast to highlight the relationship between chemical alteration (Fe and Mn enrichment) in dolomite and sphalerite distribution. Fe is used because it has a higher concentration than Mn, but Fe is correlated with Mn, both of which substitute for Mg in the dolomite structure. Manganese-rich dolomite occurs as a rim around the outer margins of the dolomite nodule with faceted embayments formed by sphalerite growth. Sub-10-µm sphalerite inliers within the outer part of
the dolomite nodule are similarly surrounded by Fe-Mn enrichment in the dolomite. The Mn dolomite rim does not have a unique crystal orientation to the wider nodule.

Numerous micron-scale dolomite outliers within the crystalline sphalerite mass (Fig. 11D) share the same (or within 20°) crystal orientation as the closest crystal on the right of the nodule (grain 3), suggesting they belong to the same formerly larger parent grain. These are highlighted in the detailed field of view in Figure 11E, which is indicated by the white box in Figure 11D.

Thallium distribution: Based on strong correlations between Fe and Tl in the whole-rock geochemical data (Fig. 5B), study of the distribution of Tl in pyrite was undertaken on large samples. Zones of high Tl and low Pb in some areas are spatially distinct. For example, Figure 12A shows high Tl within the pyritic (py1 and py2) band within the folded dolomite spatially proximal to the sphalerite, in the same sample as shown in Figure 9. Selecting this band of pixels with high Tl, allowed the high-Tl and low-Pb pixel associations to be highlighted, effectively filtering artifacts (X-ray peak overlaps). This is shown in Appendix 1, Figure A4. The region spectrum fit shows very clear Tl lines. The Tl L\(_{\alpha}\) is less clear on the side of the Pb L\(_{\alpha}\) peak, but the Tl L\(_{\beta}\) makes a good shoulder on the Pb L\(_{\beta}\) peak, at an energy where we do not see many lines, around 12.2 keV. Therefore, Tl appears genuine. Filtering high-Tl and low-Pb pixel associations allowed separation of Tl from Pb and mapping of their spatial occurrence.

In the ore sample shown in Figure 12A (same sample as Figs. 9, 11) the central pyritic band within the dolomite has higher Tl than the laminated pyritic band in the pyrite. This appears as brighter red in the pXRF red-green-blue map shown in Figure 12A. The filtered Tl concentration heat map shown in Figure 12B demonstrates that there is higher Tl in this zone (up to 811 ppm in the brightest pixels) than in the laminated pyrite. The pattern of high-Tl zones of pyrite proximal to dolomite-associated sphalerite and Mn-rich dolomite (Fig. 9) is observed throughout our suite of nodular dolomite ore facies.

Detailed SEM analysis of the Tl-rich pyrite zone shows that it is composed of cores of early py1 overgrown by numerous concentric euhedral zoned overgrowths of later py2 (Fig. 13A, B). The latest py2 overgrowths formed prior to sphalerite, as demonstrated by sphalerite enveloping the outermost euhedral py2 overgrowths, and minor galena inclusions occur in some py2 overgrowths (Fig. 13A). This is the same pyrite aggregate shown in Figure 11, and the pyrite crystal shown in Figure 13 is highlighted in the white box in Figure 11B. Nanoscale FIB-TOF-SIMS analysis of the py1 and py2 crystal shown in Figure 13B shows that Tl is concentrated in the py2 overgrowths, with some minor Tl in the py1 core (Fig. 13C).

In a pyrite aggregate from the same sample, but not spatially associated with sphalerite at the millimeter scale (Fig. 11B, right), Tl is concentrated in thin rims on the outer py2 overgrowth (App. 1, Fig. A5). No measurable Tl was observed in any other mineral phase in this study.

Discussion

Carbonate replacement by Zn-Pb sulfides at the HYC deposit

Laminated ore facies: It is instructive to look at nonmineralized Barney Creek Formation laminated rocks distal from the HYC ore deposit as a comparison to ore samples. Laminated dolomitic facies (App. 1, Fig. A3) are characteristic and typical of lithofacies 16; (Kunzmann et al., 2019) within the Barney Creek Formation across the southern McArthur basin, specifically in the HYC Pyritic Shale member, which was deposited in deep subtidal to slope environments. However, the lack of significant carbonate (dolomite) in high-grade ore zone samples that display otherwise identical laminated textures and sedimentary structures to the wider lithofacies, such as that shown in Figure 7 (we refer the reader to the full-resolution version of this figure in App. 1), suggests that laminated sphalerite likely occupies the position of original laminar dolomite. This is supported by the observation that the highest-grade ore samples contain the least preserved dolomite (Fig. 5A) and low-to-medium-grade samples contain measurable and visible dolomite (Fig. 6).

These observations present two possible scenarios: (1) dolomite did not precipitate during deposition or early diagenesis, uniquely in the HYC subbasin, or (2) original dolomite has been replaced by sphalerite postdeposition, preserving the various sedimentary textures on the macro and microscale. The first scenario, which is central to the synsedimentary exhalative interpretation of ore formation, we argue is unlikely for the following reasons:

1. Sphalerite only rarely occurs in the carbonaceous-pyrite beds in laminated facies, and where it does it only occurs in thin sphalerite interlaminae between pyrite laminae
Likewise, carbonaceous silt is largely absent from the sphaleritic laminae and is restricted to alternate interbeds. If laminated sphalerite deposition occurred syngenetically through exhalative processes, it must have occurred during periods of no dolomite deposition in the HYC subbasin but coevally with periods of dolomite deposition everywhere else in the wider southern McArthur basin, mimicking the macro- and microscale textures of sedimentary dolomite in the process. Sphalerite deposition would also need to have coincidentally ceased during the deposition of carbonaceous-pyritic beds. It might be argued that carbonaceous material is absent from the sphaleritic laminae because of a potential role of bacterial sulfate reduction (BSR) that oxidized organic matter, but this would not explain the absence of pyrite in these areas, which would almost certainly be present in such a case. Collectively, we argue that this scenario (or combination of scenarios) is unlikely and that the above characteristics are better explained by processes involving dissolution of laminated dolomite and subsequent dissolution of carbonaceous-pyritic beds.
sphalerite precipitation at the site formerly occupied by dolomite.

2. In the high-grade facies that display cryptocrystalline sphalerite laminae, the laminae envelop and thus postdate the nodular pyrite (Fig. 7). This implies the alteration process responsible for the late euhedral py$_2$ overgrowths in laminated ore facies preceded sphalerite deposition. This, we argue, precludes synsedimentary ore formation processes, consistent with previous observations for HYC and other deposits (Eldridge et al., 1993; Broadbent et al., 1998; Huxton et al., 2006; Polito et al., 2006; Leach et al., 2010a).

Nodular pyrite in the laminated ore sample shown in Figure 7 locally displaces surrounding sphaleritic laminae, which has been argued as evidence for formation after sphalerite deposition (Ireland et al., 2004b). However, these displacive pyrite nodules are composed of predominantly py$_1$ with py$_2$ overgrowths. We argue that this likely reflects the original paragenesis of syngenetic-early diagenetic dolomite formation followed by or synchronous with nodular py$_1$ formation during diagenesis that displaced the dolomitic laminae during compaction. The nodular py$_1$ was later added to and recrystallized with py$_2$ precipitation during the initial oreforming process, followed finally by dolomite dissolution and replacement by sphalerite.

**Nodular dolomite ore facies:** In nodular dolomite facies (e.g., Figs. 8–10) carbonate replacement textures are more pronounced than in laminated ore. Our data show that not only does sphalerite occur on the outer margins of nodular dolomite, but millimeter- to micron-scale carbonate dissolution brecciation textures filled with sphalerite also occur across the ore lenses. All of the nodular dolomite samples analyzed during this study—even the highest-grade samples—retained some remnant dolomite, unlike some of the highest-grade laminar ore samples, which appear to have undergone total sedimentary dolomite loss. This may imply that nodular and crustiform dolomite were more competent during ore formation than thin laminated dolomite, and total dissolution of this facies (Figs. 8–10) during ore formation was less likely than in laminated facies (Figs. 6, 7). The causes of this remain unclear, but there may have been preferential porosity generation through the laminated facies. As in the laminated ore facies, sphalerite is absent in laminated carbonaceous or pyritic beds in the nodular dolomite ore facies. So again, if exhalative processes were involved in ore formation, it would appear coincidental that metal deposition only ceased during organic matter and syngenetic pyrite deposition.

The complex macrotextures of the pyritic matrix that envelops and surrounds mineralized dolomite nodules in brecclias (Fig. 8) and locally in slumped facies (Fig. 9) could be
considered evidence that py2 precipitated after sphalerite deposition in the dolomite (e.g., Ireland et al., 2004b). However, the micron-scale textures at the interface between py2 and dolomite-associated sphalerite show that sphalerite precipitated after multiple phases of py2 overgrowths (Figs. 11, 13). This demonstrates the importance of investigating these textures across a range of scales; the temporal relationship of pyrite followed by sphalerite is consistent with the observations of previous studies (Eldridge et al., 1993; Broadbent et al., 1998; Huston et al., 2006; Polito et al., 2006; Leach et al., 2010a, b). Furthermore, the spatial association with dolomite sphalerite in this facies suggests a likely chemical control on ore formation. Chemical (Mn-Fe) enrichments close to dissolution fronts (embayments) on the outer margins of nodular dolomite in contact with sphalerite (Fig. 11), sphalerite inliers, and micron-scale remnant outliers of individual dolomite crystals within the sphalerite are strong evidence of sphalerite precipitation at the former site dolomite through chemical dissolution and replacement (Fig. 11C, E). This is consistent with ore textures observed in Mississippi-Valley type (MVT) Zn-Pb deposits in which coarse-grained dolostone carbonates are favorable for carbonate replacement-style mineralization because of the enhanced fractures and secondary porosity (e.g., Leach et al., 2010b).

Our data suggest carbonate dissolution-associated replacement of dolomite by sphalerite following precipitation of py2 was the ore-forming mechanism for both nodular and laminated dolomite facies in the HYC Pyritic Shale member. This chemical process could have occurred across the subbasin throughout the entire sedimentary unit, in both undisturbed and deformed or brecciated facies, as the ore fluids reached equilibrium with the host carbonate. This would also explain the presence of mineralized laminated facies clasts in the talus breccia (Ireland et al., 2004a), as brecciated clasts would be subject to the same chemical reactions.

We argue that rather than the laminated and nodular dolomite-associated sphalerite representing two distinct paragenetic phases of ore deposition (sp1 and sp2), as proposed in previous studies (Eldridge et al., 1993; Large et al., 1998; Ireland et al., 2004b), all sphalerite in the HYC deposit was formed by the same carbonate dissolution (replacement) processes, and the two textures are controlled by that of the original stratiform dolomite.

**Zinc ore geochemistry:** The generally close range of maximum Zn grades (~20–26%) across the deposit (Figs. 4, 5), the close spatial correlation of Zn with Ag, Cu, Ge, and other trace elements (Fig. 5, Tables 1, 2), and the inverse correlation between carbonate and Zn (Fig. 4A) imply a consistent sphalerite deposition mechanism across the deposit. Thus, the principle factor in the genesis of high-grade Zn ore at HYC was probably lithological—e.g., the presence of dolomite and a lithological reductant, rather than immediate proximity to the fluid source or conduit—and argues against a spatially variable ore formation process of exhalative driven in the depocenter and carbonate replacement driven on the margins (Large et al., 1998; Ireland et al., 2004b). The decreasing Pb concentration from north to south (Fig. 4D), however, is consistent with the dominant source direction of the talus breccia, which thickens toward the south (Ireland et al., 2004a). While this would suggest the ore-forming fluid being derived from the Emu fault zone northeast of the deposit (Fig. 3A), the proximity to the fluid source did not directly affect the distribution of the main ore (sphalerite) in the deposit.

**Thallium hosted in late diagenetic pyrite**

Thallium is a highly incompatible (and toxic) trace element that is commonly associated with K-bearing mineral phases because of its primary Tl+ form, which is similar in size to the monovalent cations K+, Rb+, and Cs+ (Nielson et al., 2013). As such, Tl is readily adsorbed onto clay mineral phases and Mn oxides (Martin et al., 2018). Unlike other alkali metals, Tl has been suggested to exhibit chalcophile behavior in hydrothermal fluids and sulfur-bearing melts (McGoldrick et al., 1979). However, the behavior of Tl in these environments remains poorly understood, possibly because of limitations in petrographic analysis and the typically very low concentrations in most rock types and mineral deposits.

Thallium enrichments have been known at the HYC deposit and numerous similar ore deposits worldwide for decades. Our geochemical data show a clear relationship between Tl and pyrite (Fig. 5B), consistent with previous studies (Croxford and Jephcott, 1972; Lambert and Scott, 1973; Large et al., 2000; Mukherjee and Large, 2017). What is not known, because of previous analytical limitations, is the paragenetic distribution of Tl. Bulk geochemical data cannot distinguish if one or both pyrite phases are enriched in Tl. Previous studies using LA-ICP-MS have demonstrated that there are large variations in Tl concentrations in various pyrites from the HYC ore zone, ranging from 176 to 919 ppm (Mukherjee and Large, 2017). While these analyses are no doubt useful, what is critically lacking is a context within the ore at a scale greater than that of single pyrite grains. Therefore, it is unknown if these analyses were truly representative of Tl-rich pyrite zones and/or background syngenetic pyrite in the ore, such as the different zones shown in Figure 12.

Our macro- to nanoscale data, which show Tl enrichment in Py2 proximal to sphalerite mineralization (Figs. 12, 13), are consistent with introduction of Tl from fluids after deposition of earliest pyrite, which is a sedimentary component of the host lithology. The observation that the main ore sulfide (sphalerite) envelops the multiple euhedral overgrowths of Tl-bearing Py2 is interpreted to reflect that sphalerite precipitated following or immediately after py2 (Fig. 13A), consistent with previous observations (Eldridge et al., 1993; Broadbent et al., 1998; Polito et al., 2006). The spatial association with Tl-rich pyrite and sphalerite precipitation in nodular dolomite facies (e.g., Fig. 12A) suggests that Tl and Zn entered the host rock by the same pathway and in perhaps the same ore fluid.

While precipitation of sphalerite after latest Py2 overgrowths precludes a syndepositional ore deposition, there are implications for the role of Tl enrichment that occurred prior to the deposition of the main-stage base metals and related trace elements such as Cu, Ag, and Ge.

**Thermodynamic modeling and paragenesis of ore**

Based on the mineralogical and geochemical data, a general paragenetic sequence of mineralization is the following: initial Tl-bearing py2 precipitation around earlier py1, followed by dissolution of laminated and nodular dolomite and sphalerite precipitation at the site of dissolution. These findings com-
bined with previous studies allow us to model the ore fluid chemistry to gain a better understanding of the ore-forming processes in this mineral system.

Thallium distribution in late pyrite suggests that both Fe and Tl were transported in the same hydrothermal fluid, particularly given the homogeneity observed in the distribution within py2 overgrowths (Fig. 13C). Our thermodynamic modeling, using the temperature (150°C) and a salinity (15 wt % NaCl equiv) constraints of Cooke et al. (2000), shows that TlCl(aq) is soluble across a wide range of pH values (0–11) above a log $f_{O_2(aq)}$ of ~45 (Fig. 14A). Similarly, FeCl-complexes are only soluble at the same temperatures below pH 4 to 5, and below log $f_{O_2(aq)}$ 45 (reducing conditions), H2S is stable (Fig. 14B). Cooke et al. (2000) noted the likely dominance of oxidized fluids in the Australian Proterozoic sediment-hosted Zn deposits. Both FeCl and TlCl complexes are transported in acidic, oxidized fluids with pH below 4 (Fig. 14A, B), in the presence of HSO4-. Such a fluid could transport Fe and Tl until reduction, which would allow precipitation of Tl-rich pyrite. Applying these principals to the HYC deposit, it is assumed that the reductant for the hydrothermal fluids was likely pyritic-carbonaceous sediment that allowed Tl-bearing pyrite overgrowths (py2) to precipitate around early framboidal py1. Our EBSD pyrite data suggest this pro-

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**Fig. 14.** Thermodynamic modeling of stability of predominant Tl, Fe, Zn, and Mn minerals and aqueous species as a function of log $f_{O_2}$ and pH at 150°C: A) Tl, B) Fe, C) Zn, and D) Mn. Boundaries between Tl, Fe, and Zn (and Mn?) species and minerals are red colored, with solid, dashed, and dash-dotted lines representing different solubilities as marked. The boundaries of sulfur species are shown with blue dashed lines in all subplots, and activities of total sulfur, carbon, and chloride are the same as Cooke et al. (2000): $a_ΣS = 0.001$ m; $a_ΣC = 0.256$ m; $a_ΣCl = 5.83$ m.
cess recrystallized the original py$_1$, as both py$_1$ and py$_2$ phases share the same crystal orientation, and therefore together they form single crystals.

An oxidized (>45 log $f_O_2$) and acidic fluid can transport Zn as ZnCl$_2$ complexes across a range of pH values (0–9). Such oxidized fluids with near-neutral pH could transport up to 1,000 ppm Zn at 200°C (Large et al., 1998, 2005), and our calculations show that at pH ~4 and oxygen fugacity just above the SO$_4^{2−}$/H$_2$S$_{aq}$ boundary, a brine with 15 wt % NaCl equiv can dissolve 0.01 m (~654 ppm) Zn at 150°C (Fig. 14C). However, following reduction, sphalerite cannot precipitate at temperatures of 150°C and pH values below ~5 (Fig. 14C), and therefore coprecipitation of pyrite and sphalerite is unlikely. Rather, the modeling indicates that Tl-rich py$_2$ probably precipitated prior to sphalerite upon initial reduction in the still- acidic fluid. Such an acidic fluid entering carbonate-rich lithologies likely resulted in rapid dolomite dissolution, which would have created additional porosity along laminae. If the ore-bearing fluids were buffered to pH values >5 following pyrite formation and acidic dissolution of dolomite, and if there was a reduced S source (H$_2$S or HS$^-$), sphalerite would precipitate. This mechanism could explain the presence of sphalerite that surround latest-stage py$_2$ overgrowths (Fig. 13A) proximal to dissolved dolomite. In this scenario, the precipitation of sphalerite may have occurred immediately after the precipitation of Tl-bearing py$_2$.

Carbonate buffering of pH would likely have been strongest at the dissolution interface. As carbonates have retrograde solubilities, with the solubility products of Fe-Mn carbonates being lower than those of Ca-Mg–rich carbonates, the Fe-Mn carbonates may precipitate close to the site of dissolution (Chen et al., 2003). Manganese has solubility characteristics almost identical to those of Fe in the fluid model proposed (Fig. 14D), so would have been soluble in acidic, oxidized ore fluids. Manganese does not easily incorporate into sulfide minerals unless the ore fluid has H$_2$S > SO$_4^{2−}$; however, it is readily incorporated into carbonate minerals. This is consistent with the localized growth of Fe-Mn–rich rims observed at the dissolution front observed in contact with sphalerite in Figures 9C and F and 11C.

In summary, our modeling indicates the following sequence of events, which are summarized and simplified in Figure 15:

1. Oxidized and acidic metal chloride-bearing ore fluids migrate laterally from the Emu fault zone (or related structures) into the Barney Creek Formation. Fluids interact with reduced lithologies, carbonate, and H$_2$S-bearing pore fluids and become reduced below the oxidizing buffer. Simultaneously, laminated dolomite in the central zone is locally entirely dissolved and nodular dolomite is partially dissolved and undergoes Mn enrichment at the dissolution reaction front at the outer margins of the nodules.

2. Secondary Tl-rich pyrite (py$_2$) precipitates around earlier diagenetic pyrite (py$_1$).

3. Fluid pH buffering allows sphalerite to precipitate at the site of carbonate dissolution, possibly immediately after step 2.

**Fluid pathways and fault permeability**

It is important to consider the stratigraphic relationship between the HYC orebody and the overlying bituminous black shales within the HYC Pyritic Shale member (Fig. 2; App. 1, Fig. A2), which is anomalously thick at HYC compared to that observed regionally in the broader Batten fault zone. This relationship highlights the need to discuss a potential role of this black shale unit on the formation of the orebody.

A syngenetic ore formation process would require that the Emu fault and associated structures on the eastern side of the Batten fault zone (Figs. 1–3) were permeable all the way from the fluid source region to the seafloor, allowing the ore fluid to escape onto the seafloor (Fig. 16A; Cooke et al., 1998; Large et al., 1998; Garven et al., 2001; Williford et al., 2011). However, the diagenetic-epigenetic replacement interpretation implies that the ore fluid deviated out of the fault zone into the Barney Creek Formation before reaching the seafloor (Fig. 16B), which implies that the fault switched from being a fluid pathway to a fluid barrier at some depth within the Barney Creek Formation. Such a switch from high to low permeability with decreasing depth can be explained by a change in degree of consolidation of the sediments, which affects their behavior during faulting. High-porosity rocks and unconsolidated sediments tend to deform in a ductile fashion, resulting in permeability reduction, whereas consolidated, lower-porosity rocks behave in a more brittle fashion, resulting in permeability enhancement. Thus, faults in consolidated, well-cemented sedimentary rocks tend to act as fluid pathways, whereas those in unconsolidated, highly


**Fig. 15.** Thermodynamic modeling summary of the stages of the fluid chemistry, mobility, and precipitation of metals on the McArthur River mineral system. 1) oxidized and acidic metal chloride-bearing ore fluids migrate laterally from the Emu fault zone (or related structures) into the Barney Creek Formation. Fluids interact with reduced lithologies, carbonate, and H$_2$S-bearing pore fluids and become reduced below the oxidizing buffer. Simultaneously, laminated carbonate in the central zone is locally entirely dissolved and nodular dolomite is partially dissolved and undergoes Mn enrichment at the dissolution reaction front at the outer margins of the nodules. 2) Secondary Tl-rich pyrite (py$_2$) precipitates around earlier diagenetic pyrite (py$_1$). 3) Fluid pH buffering at the site of carbonate dissolution allows sphalerite to precipitate at the site of carbonate dissolution, possibly immediately after step 2.
porous sediments tend to act as barriers to fluid flow (e.g., Fisher et al., 2003; Barnicoat et al., 2009). It is therefore reasonable to assume that the faults that carried the ore fluid had high permeability where they intersected consolidated sediments of the Tawallah Group (which includes the inferred fluid source region) and lower McArthur Group but had low permeability at shallow depths where they intersected relatively unconsolidated sediments of the Barney Creek Formation (Barnicoat et al., 2009). This is consistent with ductile and soft-sediment deformation observed in the HYC Pyritic Shale member (Figs. 6–10; Hinman, 1995).

The bituminous black shale unit overlying the HYC orebody (App. 1, Fig. A2), which likely represents the maximum flooding surface of sequence B1 (Kunzmann et al., 2019), would have had very low permeability where it interacted with the faults due to development of shear bands and clay smears. Furthermore, if lithified, the black shale likely had lower permeability than the surrounding siltstones; hence, it potentially acted as a barrier to upward fluid flow within the HYC Pyritic Shale member. Thus, in this scenario mineralization is expected to occur directly beneath black shale units in the diagenetic-epigenetic replacement interpretation (Fig. 16B; Kunzmann et al., 2019). The transition from high to low permeability in the fault may have coincided with the black shale, or it may have occurred at greater depth, in which case fluids would have percolated up through the Barney Creek Formation until they reached the black shale and were forced to deviate laterally. In the syngenetic interpretation, the black shale is interpreted to act as a chemical trap on the seafloor (Fig. 16A; Kunzmann et al., 2019; Sheldon and Schaub, 2019). However, given the association between mineralization and dolomite facies and the strong evidence for diagenetic-epigenetic replacement-style mineralization presented in this study, we postulate that mineralization occurred beneath the black shale unit potentially when at least some of the Barney Creek Formation was still relatively unconsolidated, such that the faults did not act as fluid pathways all the way to the seafloor.

**Implications for formation of the HYC Zn-Pb orebody**

In the context of previous work conducted at the HYC deposit and elsewhere in the Carpentaria Zn belt, our findings provide new insights into the genesis of the sediment-hosted HYC Zn-Pb deposit. Table 3 shows a summary of observations at HYC that have been used by previous studies as evidence for either syndepositional-syngenetic or diagenetic-epigenetic...
Table 3. Summarized Constraints on the Contrasting Syndepositional-Exhalative Versus Diagenetic-Epigenetic Genetic Models based on Key Lines of Evidence and Observations (modified after Huston et al., 2006)

<table>
<thead>
<tr>
<th>Observation</th>
<th>Syndepositional-exhalative model literature</th>
<th>Diagenetic-epigenetic model literature</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laminated ore textures (in central zone of deposit)</td>
<td>Consistent with deposition of sulfides as chemical sediments from water column (Large et al., 1998; 2005; Ireland et al., 2004b)</td>
<td>Can be produced by sulfide replacement of layered-laminated sedimentary sedimentary-diagenetic carbonate (Eldridge et al., 1993; Broadbent et al., 1998; Polito et al., 2006); nodular carbonate also replaced by sphalerite (Ireland et al., 2004b; Large et al., 2005)</td>
<td>Textures observed in this study show that both laminated and nodular carbonate were subject to partial to full dissolution and replacement by base metal sulfides; EBSD analyses of carbonate (dolomite) show that the outer edges are Mn altered where in contact with replacive sphalerite (Figs. 9F, 11C)</td>
</tr>
<tr>
<td>Laminated ore clasts within intraformational breccias</td>
<td>Consistent with early syndepositional mineralization prior to breccia flows (Ireland et al., 2004a)</td>
<td>Can be produced by the same carbonate replacement geochemical processes as the main orebody, well after deposition</td>
<td>Can be produced by the same carbonate replacement geochemical processes as the main orebody, well after deposition</td>
</tr>
<tr>
<td>Timing of sphalerite and galena mineralization (post-latest diagenetic pyrite overgrowths; py2)</td>
<td>Not consistent</td>
<td>Deposition of base metal sulfides after latest diagenetic pyrite overgrowths indicate diagenetic-epigenetic model (Eldridge et al., 1993; Broadbent et al., 1998; Huston et al., 2006; Polito et al., 2006; Leach et al., 2010a)</td>
<td>Sphalerite and galena mineralization occurs after the latest pyrite overgrowths (Fig. 13), with some minor galena occurring as micron-scale inclusions in some pyrite overgrowths; fluid modeling demonstrates that initial acidic, oxidized ore fluids may have transported metal chloride complexes, followed by reduction, allowing precipitation of Tl-rich pyrite overgrowths; carbonate dissolution could have pH buffered the fluid to pH &gt; 5, allowing later precipitation of sphalerite</td>
</tr>
<tr>
<td>Thallium (Tl) lithogeochemical anomalousal (100s ppm)</td>
<td>Enrichment of Tl up to 200 m above ore zone could result from low-temperature fluid after main-stage mineralization (Large et al., 2000)</td>
<td>Enrichment of Tl up to 200 m above ore zone indicates fluid flow after deposition of ore-hosting sediments, low-temperature fluid after main-stage mineralization (Huston et al., 2006)</td>
<td>Ultrahigh-definition mapping of large samples shows Tl enrichments are hosted in late-stage pyrite bands, proximal to sphalerite deposition associated with carbonate replacement (Fig. 12); nanometer-scale quantitative analyses show that Tl is hosted in late-stage pyrite overgrowths that precipitated before base metal sulfides (Fig. 13); fluid modeling shows sphalerite may have precipitated immediately after Tl-rich pyrite overgrowths due to pH buffering following carbonate dissolution (Figs. 14, 15); enrichment in Tl up to 200 m above ore zone (Large et al., 2000), by this mechanism, would confirm fluid flow well after deposition of ore-hosting sediments</td>
</tr>
<tr>
<td>Manganese enrichment in carbonate</td>
<td>Represent exhalation of early connate brine prior to exhalation of base metal-bearing ore fluid (Large et al., 1998)</td>
<td>Manganese concentrations of ~1.5% in Mesoproterozoic shelf dolomite are typical and reflect uptake of Mn(^{2+}) in dolomite from Mn-bearing anoxic seawater (Spinks et al., 2018)</td>
<td>Manganese is omnipresent in the nodular carbonate throughout the ore zone (Fig. 9C); however, clear enrichments occur at the dissolution front in nodules proximal to sphalerite mineralization (Figs. 9F, 11C); this reflects Mn enrichment during sphalerite precipitation</td>
</tr>
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</table>

In summary, our findings provide strong evidence for a subsurface carbonate replacement-style mineral system at the McArthur River deposit.
overgrowths that precipitated (perhaps immediately) before sphalerite.

Fluid modeling suggests precipitation of initial Ti-bearing pyrite overgrowths by reduction of metals transported by acidic (pH <3) oxidized fluids. Acidic dissolution of carbonate allows additional porosity and creates a pH buffering effect, raising fluid pH above 5, allowing precipitation of sphalerite at the site of carbonate dissolution.

Findings provide strong evidence for a diagenetic-epigenetic carbonate replacement origin for the McArthur River mineral system and preclude syngenetic ore formation. This has implications for future exploration strategies for these Proterozoic sediment-hosted base metal deposits.

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