Zinc, sulfur and cadmium isotopes and Zn/Cd ratios as indicators of the origin of the supergiant Broken Hill Pb–Zn–Ag deposit and other Broken Hill-type deposits, New South Wales, Australia

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Abstract
Various genetic models have been proposed for the supergiant Proterozoic Broken Hill Pb–Zn–Ag deposit largely based on geological and geochronological evidence. Here we present Zn, Cd and S isotope compositions as well as Zn/Cd ratios of sphalerite from Broken Hill and Broken Hill-type deposits (Australia) to help constrain these models but focus on syngenetic and magmatic–hydrothermal processes, since epigenetic models can be rejected because the orebodies were deformed and metamorphosed by the Olorian Orogeny. Values of δ34S

\[
\text{Svast, } \delta^{63}Zn, \delta^{114}Cd, \text{ and } \delta^{34}SVCDT
\]

for sphalerite from Broken Hill range from +0.27 to +4.73‰, -1.15 to +0.46‰ and -0.48 to +0.01‰, respectively, while those for the smaller Broken Hill-type deposits range from -5.11 to +1.28‰, -0.97 to +0.10‰ and -1.02 to +2.59‰, respectively. By combining published S isotope data of sulfides from the Broken Hill district with those obtained here, the sources of sulfur via thermochemical sulfate reduction, bacterial sulfate reduction and a magmatic origin cannot be distinguished. However, when the S isotope compositions are considered along with the broad range of Cd and Zn isotope data for sphalerite, which are among the lightest and heaviest yet reported for a sulfide deposit, the isotopic datasets are consistent with low-temperature biogenic processes associated with syngenetic deposition of sulfides. Cadmium isotope compositions when coupled with Zn/Cd ratios of sphalerite have previously been used to classify Pb–Zn deposits, including low-temperature, high-temperature and exhalative ores. However, the Zn/Cd ratios of sphalerite from Broken Hill cannot be used for such classification purposes.

1. Introduction
The Broken Hill Pb–Zn–Ag deposit (280 Mt of 10.0 % Pb, 8.5 % Zn and 148 g/t Ag; Huston et al. 2006) is the world’s largest massive sulfide deposit. It occurs in the southern Curnamona province, New South Wales (Australia), along with hundreds of minor Broken Hill-type (BHT) deposits. They are hosted in the Palaeoproterozoic Willyama Supergroup in an ~7 km thick package of multi-deformed and metamorphosed clastic sediments, bimodal (felsic and mafic) volcanic and volcaniclastic rocks, chemical sediments and granitoids (Fig. 1) (Willis et al. 1983; Burton, 1994). Metamorphic conditions reached granulite facies. Given the high metamorphic grade and extreme deformation, which have largely removed primary textures in the ore, a variety of origins have been proposed for the formation of the deposit. These ore deposit models are summarized in Greenfield (2003) and include: (1) syngenesis in which the deposit was considered to have formed by submarine exhalative/inhalative processes (Plimer, 1979; Wright et al. 1987; Parr & Plimer, 1993); (2) syntectonic (Katz, 1976; Findlay, 1994; Nutman & Ehlers, 1998); (3) post-tectonic (Andrews, 1922; Williams et al. 1996); (4) magmatic–hydrothermal (Crawford & Maas, 2009); and (5) partial melting (Mavrogenes et al. 2001; Frost et al. 2011).

In attempting to add clarity to how the Broken Hill deposit formed, we evaluate sulfur, zinc and cadmium isotopes of sphalerite along with the Zn/Cd ratios of sphalerite. Although various zinc isotopic studies have been conducted on several types of ore deposits including, Mississippi Valley-type Pb–Zn (MVT) (e.g. Pašava et al. 2014; Wen et al. 2016; Zhu et al. 2018, 2021; Li et al. 2019), Irish-type Pb–Zn (Wilkinson et al. 2005; Gagnevin et al. 2012, 2014); volcanogenic massive sulfide (VMS) (Mason et al. 2005), sedimentary exhalative (Sedex) (e.g. Kelley et al. 2009; Gao et al. 2018; Baumgartner et al. 2021; Wang et al. 2021) and active hydrothermal vents (e.g. John et al. 2008), Zn isotope studies of sphalerite in regionally metamorphosed ore deposits are
restricted to those of Matt et al. (2020, 2022) on sphalerite and zinc oxides (zincite and franklinite) from the carbonate- and evaporate-hosted Balmat Zn deposit (New York) and the marble-hosted Franklin Zn deposit, New Jersey. A preliminary Zn isotope study was also made on sphalerite from the Gamsberg Sedex Zn deposit (South Africa) by S. E. Foulkes (unpub. M.Sc. thesis, Rhodes Univ., 2014), which, along with the Balmat deposit, was metamorphosed to the amphibolite facies. The Franklin district mines, like the Broken Hill district, were metamorphosed to the granulite facies. Although not part of this study, the Zn isotope composition of galena from various unmetamorphosed Chinese Pb–Zn deposits were obtained by Wang et al. (2020, 2021).

Cadmium isotopes have been used to evaluate the source of Cd in rocks, ore deposits, unconsolidated sediments, seawater, meteorites and biological samples (e.g. Wohmbacher et al. 2003, 2004; Lacan et al. 2006; Zhu et al. 2016, 2021; Hohl et al. 2017), and to
understand geochemical processes. Wen et al. (2016) suggested that Cd isotope compositions of sphalerite when coupled with Zn/Cd ratios of sphalerite can be used to classify Pb–Zn deposits. They identified three classes of ore systems: high-temperature (i.e. skarn, VMS, porphyry, magmatic–hydrothermal), low-temperature (i.e. Sedex, seafloor hydrothermal). To date, no Cd isotope study has been done on an ore deposit subject to regional metamorphism. The criteria for deposit classification as applied by Wen et al. (2016) is discussed further in Section 5.b.

Several sulfur isotope studies have been conducted on sulfides from Broken Hill and the smaller BHT deposits (Lawrence & Rafter, 1962; Stanton & Rafter, 1966, 1967; Both & Smith, 1975; Dong et al. 1987; Spry, 1987; Parr, 1992, 1994a; Huston et al. 1995), while the major-element composition of sphalerite was determined by, for example, Both (1973), Hodgson (1975) and Lockington et al. (2014). Trace-element compositions of sphalerite are largely restricted to the studies of Both (1973) and Lockington et al. (2014). Both (1973) determined the trace-element content (including Cd) of sphalerite separates from each orebody using X-ray fluorescence spectrographic techniques, while Lockington et al. (2014) analysed two samples of sphalerite using a laser ablation inductively coupled plasma mass spectrometer. We have obtained new major- and trace-element compositions of sphalerite because individual sphalerite compositions were not provided by Both (1973) and Hodgson (1975) and only two samples were obtained by Lockington et al. (2014). Both (1973) plotted the compositions to show the ranges of Cd in sphalerite for each orebody, which is unsuitable for our purposes, while Hodgson (1975) analysed Zn, Mn, Fe and S but not Cd. The new sphalerite compositions obtained here, along with Cd isotope analyses from the Broken Hill deposit, are used to evaluate the origin of the Broken Hill deposit given the classification scheme of Wen et al. (2016). These geochemical parameters along with Zn isotope composition of sphalerite have not previously been applied to lead–zinc–silver mineralization in the Broken Hill district. The study of Zn isotopes of sphalerite from Broken Hill is particularly relevant given the partial melt model of Mavrogenes et al. (2001) and Frost et al. (2011) for the formation of the deposit, which was recently applied to the metamorphosed Balmat deposit by Matt et al. (2020) to explain the fractionation of Zn isotopes in some orebodies. The aim of the study is to utilize Zn, Cd and S isotopes and the Zn/Cd ratios of sphalerite to shed light on the controversy surrounding the origin of the Broken Hill deposit and minor BHT deposits in the Broken Hill district.

2. Geological setting

Depositional ages of the Willyama Supergroup are ~1720–1640 Ma, with the Broken Hill Group, which hosts the Broken Hill deposit, having formed at ~1695–1685 Ma (Page & Laing, 1992; Page et al. 2005) (Fig. 2). Metamorphic conditions in and adjacent to the Broken Hill deposit were ~700–800 °C and 5–6 kbar (Phillips & Wall, 1981; Powell & Downes, 1990; White et al. 2004) but decreased to the amphibolite facies in the northern part of the Willyama Domain. The minor BHT deposits studied here (11.30, Flying Doctor, Esmeralda, Henry George, Globe, Pinnacles) were all subjected to the granulite facies. The deposits were intensely deformed and affected by at least three periods of deformation. Two of these deformational episodes resulted in the Broken Hill deposit being subject to isoclinal fold events (Laing et al. 1978; Willis et al. 1983) with the structural data of Laing et al. (1978) suggesting that the deposit and the contained orebodies were overturned. The Broken Hill deposit is 8 km long and consists of at least six separate orebodies (from stratigraphic bottom to the top, they are C, B and A lodes and 1, 2 and 3 lenses; Figs 3, 4) each of which has a characteristic gangue mineralogy and metal ratio. Details of the vast array of minerals (>350) found in the Broken Hill deposit are given in Plimer (1984) and Birch (1999). The main metallic minerals consist of sphalerite and galena, with minor amounts of pyrrhotite, chalcopyrite, arsenopyrite, löllingite, tetrahedrite and various sulfosalts. The most abundant silver-bearing minerals are galena and tetrahedrite with pyrrargyrite, polybasite, stephanite, argentite, antimonal silver, allargentum, dyscrasite, argentopyrite and native silver occurring in lesser amounts (Lawrence, 1968; Both & Stumpfl, 1987). The dominant gangue minerals in each orebody are rhodonite, fluorate, quartz (3 lens), calcite, rhodonite, wollastonite (2 lens), quartz, calcite, wollastonite (1 lens), rhodonite, manganooan hedenbergite (A lode), quartz (B lode) and quartz (C lode). Based, in part, on Laing et al.’s (1978) assumption that the deposit was structurally overturned, Groves et al. (2008) identified a feeder zone system in the C lode, with cross-cutting blue quartz-gahnite ± garnet rocks serving as the metamorphosed alteration zone. However, some workers (e.g. Mavrogenes et al. 2001; Webster, 2006; Frost et al. 2011) suggested that the deposit was not overturned so that the orebodies are the correct way up with 3 lens being at the stratigraphic base of the deposit and C lode at the top. The C, B and A lodes and 1 lens are characterized by Zn > Pb, whereas the 2 and 3 lenses have Pb ≥ Zn. By invoking major partial melting of the deposit, Mavrogenes et al. (2001) and Frost et al. (2011) argued that the zinc lodes (i.e. A, B and C lodes and 1 lens) are restites of Pb-rich sulfide melts implying that these melts migrated through the stratigraphy to form the Pb-rich orebodies (i.e. 2 and 3 lenses).

The Broken Hill deposit is intimately associated with a package of rocks that Johnson & Klingner (1975) referred to as the ‘lode horizon’, which consists of quartz garnetite, garnetite, blue quartz and blue quartz-gahnite rocks, and lode pegmatite (Spry & Wonder, 1989; O’Brien et al. 2015). Apart from metasedimentary rocks, blue quartz-gahnite rocks and quartz garnetite are the two most common rock types spatially associated with minor BHT deposits (Barnes et al. 1983). A summary of the geological setting for the deposits from which samples were analysed is given in Table 1.

3. Samples and analytical methods

3.1. Cadmium and zinc isotopes

Thirty-one samples were collected from drill core and from underground locations at the Broken Hill and Pinnacles deposits. Some of the samples were used previously in the studies of Spry & Wonder (1989) and O’Brien et al. (2015). Approximately 50 mg of sphalerite powder was dissolved in 4 ml of ultrapure heated (80 °C) aqua regia for 8 hours. Complete dissolution was visually confirmed. The solution was cut into two equal aliquots and used for chromatographic separation. The procedure for the preparation of the Cd and Zn isotopes is identical to that given by Wang et al. (2020, 2021). All reported results show mass dependence.

The Cd isotopic compositions were measured on a Neptune multicollector inductively coupled plasma mass spectrometer (MS-ICP-MS) at Rutgers University. Cadmium was purified using the anion exchange chromatograph (Cloquet et al. 2005) with...
volumetric yields for the samples greater than 94% after two rounds of column chromatography. Yield checks were measured on an Agilent 5900 ICP-optical emission spectrometer (ICP-OES) at Juniata College. Zinc and Cd concentrations were determined with standard calibration curves that ranged from 0.5 to 20 ppm, and yttrium was used as an internal standard for analysis. The chromatography for Cd involved 2 ml of wet BioRad AG MP-1 resin chloride form (100–200 mesh), which was added to a 10 ml BioRad chromatography column. The resin was sequentially cleaned with 10 ml of 2% HNO₃, 10 ml of MQ water (18.2 W) and 5 ml of 1.2 molar HCl. The sample was loaded onto the resin with 1 ml of 1.2 molar HCl and the unwanted ions were sequentially eluted with lower molality HCl and the Cd was collected in 17 ml of 0.0012 molar HCL. This process was repeated with the use of new resin for the second column to eliminate Sn. The chromatography was effective, as no 115Sn voltages were recorded above the 2 mV background. The 115Sn mass was monitored in H4 cup, with 107Ag in L4 cup, 109Ag in L2 cup, 110Cd in L1 cup, 111Cd in Ax cup, 112Cd in H1 cup, 113Cd in H2 cup, 114Cd in H3 cup and 115Sn in H4 cup. Instrumentation setup and introduction was similar to that of Wasylenti et al. (2014). All samples were doped with 150 ppb NIST 987 Ag isotope standard, which was used to correct for mass bias using the exponential fractionation correction (Maréchal et al. 1999). The 107Ag/109Ag of the NIST 987 Ag isotope standard is reported as 1.07638. Solutions were measured at 200 ppb Cd, with on-peak blank subtraction in one block of 30 ratios. The reported values are an average of two separate measurements, and the data are presented relative to the NIST SRM 3108 standard in per mil notation defined as: $\delta^{114/110}{\text{Cd}} (\%) = ((^{114}{\text{Cd}}/^{110}{\text{Cd}})_{\text{sample}}/(^{114}{\text{Cd}}/^{110}{\text{Cd}})_{\text{NIST SRM 3108}} – 1) \times 1000$ (Abouchami et al. 2013). All data cited here from the literature are converted relative to the NIST SRM 3108 standard ($\delta^{114}{\text{Cd}}_{\text{NIST SRM 3108}} = \delta^{114}{\text{Cd}}_{\text{Nancy SPEX}} – 0.11 \%o; Xu et al. 2020).

Measured errors of ratios were in the fifth or sixth decimal and do not represent a conservative estimation of error. Errors for the measured values are constrained in two ways. The variation of NIST SRM 3108 throughout the measuring session was 0.05 %o (2s, n = 27). The second means for error estimation was by measuring a High Purity Standard ICP-MS standard during the two sessions. The value of the standard is $\delta^{114}{\text{Cd}} = -0.53 \%o \pm 0.06$ (2s,

| BROKEN HILL DOMAIN | WILLYAMA SUPERGROUP | IGNEOUS ROCKS |
|---------------------|---------------------|--------------|
| Dalit Bore Metasediments | <1642 +/- 5 Ma | PARAGON GROUP |
| Bijerkerno Metasediments | <1656 +/- 4 Ma | |
| Cartwrights Creek Metasediments | | |
| King Gunnia Calc-silicate Member | | |
| **SUNDOWN GROUP** | **Silver King Formation** | **Hores Gneiss 1685 +/-3 Ma** |
| Purnamota Subgroup | | |
| 1691 +/- 3 Ma | Allendale Metasediments | |
| Himalaya Formation | | |
| Kyong Formation | | |
| Lady Brassey Fm. | Alma Gneiss 1704 +/-3 Ma | |
| Thorndale Composite Gneiss | | |
| Clevedale Migmatite | | |
| Mulculca Formation | | |
| Ednas Gneiss | | |
| Redan Gneiss | | |

Fig. 2. (Colour online) Stratigraphic column and ages of rocks in the Broken Hill domain (after Conor & Preiss, 2008). The Broken Hill and BHT deposits occur in the Hores Gneiss of the Purnamota Subgroup, while the Pinnacles deposit likely occurs in the Cues Formation stratigraphically lower in the Broken Hill domain.
n = 10) and is considered the error of measurements. All duplicate measurements fall within reported errors.

The chromatography for Zn also involved the BioRad MP-1 anion exchange resin using the protocol defined by Maréchal et al. (1999). Yields from the columns were tested volumetrically and were all greater than 95%. The mass bias corrections for Zn using Cu (NIST 976) were employed for these samples and then the corrected values were bracketed by the standards (Archer & Vance, 2004; Chapman et al. 2004, 2006; Peel et al. 2008). Solutions were measured at 150 ppb Cu and 200 ppb Zn (63Cu = 7V and 66Zn = 4V). One block was 30 ratios in the analytical session, and the Zn isotope values are reported in traditional per mil notation relative to the AA–ETH standard: δ66Zn(‰) = ((66Zn/64Zn)sample/(66Zn/64Zn)AA–ETH − 1) × 1000. All the data cited here from the literature were converted relative to the AA–ETH standard (δ66ZnAA–ETH = δ66ZnJMC3–0749L − 0.28‰; Archer et al. 2017).

Errors for Zn isotopes are calculated in a similar manner to that discussed above for Cd isotopes. Throughout the analytical sessions, the reference material AA–ETH standard compared with itself (n = 14) yielded two standard deviations of 0.06‰ (2σ) for 66Zn, which is larger than the error for each sample during the run. The value of USGS BVHO-2 δ66ZnAA–ETH is +0.02‰ ± 0.04 (2σ, n = 3). The largest error between the two methods is that of the variation of the standard in comparison to itself and is considered the error for reported samples.

3.b. Sulfur isotopes

Sphalerite was separated from ore samples by hand picking under a binocular microscope or was drilled out with a Dremel tool with a 1 mm drill tip. We followed the procedure for sulfur isotope analysis as described by Grassineau (2006). Sphalerite was pulverized in an agate mortar to a powder (1.5 mg), which was then loaded into tin capsules and burned using a Thermo Scientific Flash IRMS IsoLInk elemental analyser. The Sn capsules oxidized at ~1020 °C, and when oxygen was added it flash combusted at 1800 °C (Grassineau, 2006). The oxygen was added at a rate of 300 ml/minute for three seconds. The SO2 gas produced was purified through a gas chromatography column and then introduced via a Conflo IV Universal Interface system into a continuous flow-type dual-inlet Thermo Scientific Delta V Series Isotope Ratio mass

Fig. 3. Geological map of the Broken Hill deposit. Abbreviations: N.B.H.C. – New Broken Hill Consolidated mine (currently part of Southern Operations operated by Perilya Broken Hill Limited); Z.C. – Zinc Corporation mine (currently part of Southern Operations operated by Perilya Broken Hill Limited); B.H.S. – Broken Hill South mine; N.B.H. – North Broken Hill mine (currently North mine operated by Perilya Broken Hill Limited). Cross-section No. 62 is shown as a bold black line (see Fig. 4 for cross-section).
spectrometer under He flow. The analysis time was ~420 seconds. The 3 lens orebody is not shown here as it only occurs in the central and northern parts of the deposit, where it occurs at the stratigraphic top. The figure has been modified after Pratten (1965).

3.c. Major- and trace-element composition of sphalerite

Part of the dissolved separates of sphalerite in solution that were analysed for Zn and Cd isotopes from the Broken Hill deposit as well as smaller BHT deposits (11:30, Esmeralda, Flying Doctor, Henry George) were also analysed for Ag, Cd, Cu, Fe and Zn using an Agilent 5900 ICP-OES at Juniata College. Quantitative analyses of sphalerite were also performed on a JEOL JXA-8530FPlus electron microprobe at the University of Minnesota. Analytical conditions for determining sphalerite compositions used an accelerating voltage of 15 kV, beam current of 50 nA and a beam diameter of 5 microns. Elements were acquired using analysing crystals LIL for Zn kα, Mn kα, Fe kα and Cu kα, PETL for Cd kα, and PETJ for S kα and Ag kα. The standards were Mn-olivine and synthetic Mn₃SiO₅ for Mn, Cu metal for Cu, pyrite for Fe, sphalerite for Zn and S, hesstie for Ag and cadmium sulfide (CdS) for Cd. The on-peak counting time was 10 seconds for Zn kα, Mn kα, Fe kα, Cu kα and S kα, 40 seconds for Ag kα and 60 seconds for Cd kα. The mean atomic number (MAN) background intensity method was used instead of the traditional off-peak background acquisition (Donovan & Tingle, 1996; Donovan et al. 2016). The MAN background intensity data was calibrated and continuum absorption corrected for Cd kα, Zn kα, Mn kα, Fe kα, Cu kα, S kα and Ag kα. Unknown and standard intensities were corrected for dead-time. The Phi-Rho-Z matrix correction algorithm Armstrong/Love Scott (CitZAF) was used along with the mass absorption coefficients dataset FFAST (Chantler et al. 2005).

4. Results

4.a. Sulfur isotopes

Sulfur isotope compositions of 31 samples of sphalerite are in Table 2. The values of δ³⁴S from Broken Hill range from +0.27 to +4.73‰ (n = 19), while those for the following smaller BHT deposits are: Pinnacles (−3.08 to −0.94‰, n = 3), Esmeralda (+1.24 to +1.28‰, n = 2), Henry George (−1.06 to +1.17‰, n = 4), 11:30 (−5.11‰, n = 2) and Flying Doctor (−0.36‰, n = 1) (Fig. 5). Sulfur isotope compositions of sulfides from these minor deposits had not previously been obtained, except for the Pinnacles deposit, the second largest Pb–Zn–Ag deposit in the Willyama Domain, where Parr (1992, 1994a) reported a range of δ³⁴S = −3.5 to +3.7‰. Other sulfur isotope studies of sulfides from the Broken Hill area include analyses of sphalerite, galena, pyrrhotite and chalcopyrite. Both & Smith (1975) recorded δ³⁴S values of between −2.1 and +2.4‰ per mil and between −3.8 and +5.4‰ for sulfides from the main Broken Hill lode and 26 minor BHT deposits (including Pinnacles), respectively, while Spry (1987) showed a broader isotopic range for the Broken Hill deposit of −3.3 to +6.7‰. The isotopic compositions obtained by Lawrence & Rafter (1962); δ³⁴S = +0.4 to +1.7‰ and Stanton & Rafter (1966); δ³⁴S = −2.2 to +4.7‰, 1967; δ³⁴S = −1.5 to +2.8‰ for Broken Hill fall within the range given by Spry (1987).

By combining the S isotope data for sphalerite, galena, pyrrhotite and chalcopyrite of Both & Smith (1975) and Spry (1987), the latter proposed that there may be a weak increase in isotopic values from the stratigraphic footwall (C lode) through to the hanging wall (3 lens). However, by adding the S isotope data for sphalerite obtained here with these two studies it is apparent that there is no systematic increase from the footwall to the hanging wall. Instead, there is an increase in the average isotopic compositions for sphalerite in C lode (δ³⁴S = 0‰) to the top of the Zn lodes (i.e. 1 lens; δ³⁴S = +2.2‰) with a slight decrease to 1‰ in 3 lens (Fig. 6a). Although galena was not analysed here, the combined data of Both & Smith (1975) and Spry (1987) show a steady increase in the average δ³⁴S galena composition from C lode (−1.4‰) to 2 lens (+1.3‰) and 3 lens (+1.2‰). Data for the Zn mineralization from the North mine is shown in Figure 6a but was not included owing to uncertainty in its stratigraphic position (possibly 1 lens or
Table 1. Summary of geological characteristics of Broken Hill and BHT deposits (modified after O’Brien et al. 2015)

| Deposit: Lat., Long. | Grade, drilling data, tonnage*, metallic minerals† | Gangue minerals | Lode and country rocks | References |
|---------------------|-----------------------------------------------|------------------|------------------------|------------|
| Broken Hill        | 300 Mt of 10.0 % Pb, 8.5 % Zn, 0.14 % Cu and 148 g/t Ag: Gn–Sp–Ccp ± Asp ± Po ± Lo | Qz–Ghn–Rhd–Grt ± Ms ± Síl ± Amp ± Ap ± Fsp | Qz–Grt and Qz–Ghn rocks envelope orebodies in psammitic-psammopelitic–pelitic metasediments (Hores Gneiss) and quartzofeldspathic gneiss (Potosi Gneiss); Ghn–Qz ± Grt rocks are most abundant in the structural hanging wall, spatially associated with BIF | Johnson & Klingner (1975); Parr & Plimer (1993); Webster (2006) |
| 11:30 (BHT)         | 0.2 Mt @ 1 % Pb, 12 % Zn, 7 g/t Ag; Sp ± Py ± Po ± Asp ± Gn | Ghn–Qz–Grt–Bt ± Fsp | Qz–Ghn–Grt lode rocks in psammitic–psammopelitic metasediment (Broken Hill Group) occur between two plagioclase gneiss units; locally intersected by a mafic amphibolite | Perilya (2008); O’Brien et al. (2015) |
| Esmeralda (BHT)     | Unknown tonnage, 5–7 % Pb + Zn (up to 5 m drill intersection); Sp ± Po ± Py | Qz-Cal–Pmt–Wo–Grt–Mag | Qz–Cal lode rocks in psammitic–psammopelitic metasediment (lower Broken Hill Group) and is also associated with amphibolites, calc-silicate units and rare Potosi Gneiss | Heimann et al. (2013); D. Rogers (pers. comm. 2022) |
| Flying Doctor (BHT) | 1.5 Mt @ 4 % Pb, 3 % Zn, 44g/t Ag; Gt–Sp–Asp–Po–Cp ± Py | Qz–Ghn–Grt ± Bt ± Chl ± Ap | Qz–Ghn–sulphide ± Gt lode rock in pelitic to psammopelitic metasediments (Broken Hill Group) | Burton (1994); Teale et al. (2006) |
| Globe (BHT)         | 2686 t produced, with 502 kg Ag and 512 t Pb recorded; Cer–Gn–Sp–Mic ± Po | Fsp–Qz ± Chl ± Ms ± Grt ± Tur | Qz–Ghn lode rock in pelitic–psammitic metasediments (Purnamoota Subgroup) and Potosi Gneiss | Burton (1994) |
| Henry George (BHT)  | 1.3 Mt @ 1 % Pb, 8 % Zn, 14 g/t Ag; Sp–Po–Py–Gn ± Asp | Qz–Ghn–Fsp–Bt ± Grt | Qz–Ghn lode rock in pelitic to psammopelitic metasediment with minor pegmatic segregations (Broken Hill group). Lode rocks occur adjacent to amphibolite and ultramafic dyke | Perilya (2008) |
| North Mine Zinc Lode| Also known as the ‘Fitpatrick Zinc Lode’. Past production 0.04 Mt @ 9.6 % Zn, 4.6 % Pb, 187 g/t Ag; reserves: 1 Mt @ 9.0 % Pb, 7.0 % Zn, 140 g/t Ag; Sp–Po ± Gt ± Py ± Ccp | Qz–Grt–Ghn ± Síl ± Bt | Po–Sp-bearing Gt–Qz lode rocks bounded by Gt–Síl-bearing psammites–psammopelites and pelitic metasediments | Widdop (1983); Webster (2006) |
| Pinnacles (BHT)     | Second largest Broken Hill deposit. 2 Mt @ 6–11 wt % Pb, 2.5 wt % Zn, 300–500 g/t Ag; Gn–Sp–Py–Po ± Asp ± Lo ± Tr ± Po | Fsp–Ghn–Amp–Grt–Mag–Qz–Ghn ± Bt ± Ms | Three sulphide-bearing lode (two Pb and one Zn) with associated Qz–Ghn and Qz–Grt lode rock occur in pelitic and psammitic metasediment (Cues Formation) | Parr (1994) |

*Estimates of grades and tonnage supplied by Perilya Ltd for North Mine Zinc Lode, Henry George and 11:30.
†Mineral abbreviations after Whitney & Evans (2010); Amp–amphibole; Ap–apatite; Asp–arsenopyrite; Az–azurite; Bt–biotite; BIF–banded iron formation; Cal–calcite; Cer–cerussite; Ccp–chalcopyrite; Chl–chlorite; Di–diopside; Fsp–feldspar; Ghn–gahnite; Gt–garnet; Lo–löllingite; Mag–magnete; Mic–malachite; Ms–massicot; Pmt–piemontite; Po–pyritohedrite; Py–pyrite; Rhd–rhyodite; Qz–quartz; Sil–sillimanite; Sp–sphalerite; Tr–tetrahedrite; Tur–tourmaline; Wo–wollastonite.
Table 2. Zn, Cd and S isotope data and major-trace-element contents of sphalerite (ppm) from Broken Hill and minor BHT deposits

| Sample no. | Deposit | Ore body | Location or drill core | δ²⁹S ‰ | δ⁶⁸Zn ‰ | δ¹¹⁴Cd ‰ | Ag | Cd | Cu | Fe | Zn | Zn/Cd |
|------------|---------|----------|------------------------|-------|--------|-----------|----|----|----|----|----|--------|
| BH-1       | Broken Hill | 3 lens | Blackwoods pit | 2.02 | −1.15 | −0.23 | 2842 | 2769 | 4255 | 83768 | 607189 | 219    |
| BH-2       | Broken Hill | 3 lens | North mine | 0.27 | 0.04 | −0.14 | 386 | 2439 | 545 | 75201 | 1024854 | 420    |
| GT-1       | Broken Hill | 3 lens | North mine 37 level | 0.66 | 0.04 | −0.04 | 155 | 10345 | 151369 | 769324 | 3040252 | 294    |
| 532-502    | Broken Hill | 3 lens | North mine garnet rim | 1.83 | −0.35 | −0.25 | 70 | 3060 | 16818 | 142770 | 1131631 | 370    |
| 6542       | Broken Hill | 3 lens | North mine | 2.17 | −0.08 | −0.44 | 403 | 2381 | 2063 | 155596 | 780859 | 328    |
| Z3590      | Broken Hill | 2 lens | 66.9 m | 1.22 | −0.09 | 0.01 | 581 | 2451 | 10266 | 162487 | 915607 | 374    |
| 532-331    | Broken Hill | 1 lens | 4.73 | | | | | | | | | |
| Z3590      | Broken Hill | 0.6 m | 15.6 | 2.20 | −0.04 | −0.36 | 144 | 10882 | 16083 | 937588 | 3050190 | 280    |
| Z3590      | Broken Hill | 15.6 | 72.7 m | 4.47 | 0.46 | −0.08 | 32 | 181 | 1145 | 286924 | 214846 | 1189   |
| 7254       | Broken Hill | 1.29 | 88.7 m | 1.66 | −0.07 | −0.48 | 156 | 7882 | 45109 | 841379 | 2433570 | 309    |
| 7318       | Broken Hill | 2.24 | 100.5 m | 1.29 | 0.30 | −0.23 | 17 | 1435 | 11284 | 170209 | 784061 | 546    |
| 6303       | Broken Hill | 1.29 | 6.2 m | 2.24 | −0.39 | −0.12 | 17 | 2529 | 0 | 326292 | 1167979 | 462    |
| JB-10-82   | Broken Hill | 1.07 | Zinc lode | 1.22 | 0.08 | −0.33 | 18 | 5322 | 474 | 265437 | 1203836 | 226    |
| JB-10-83   | Broken Hill | 1.54 | Zinc lode | 1.54 | −0.77 | −0.12 | 324 | 2284 | 3619 | 245641 | 1001814 | 439    |
| JB-10-87   | Broken Hill | 1.54 | Zinc lode | 1.54 | −0.77 | −0.12 | 324 | 2284 | 3619 | 245641 | 1001814 | 439    |
| 6220       | Broken Hill | 1.48 | 20.0 m | 0.98 | 0.22 | 17 | 2656 | 2246 | 244523 | 815529 | 307    |
| 532-299    | Broken Hill | 1.38 | 3.7 m | 1.38 | 0.25 | −0.04 | 77 | 2242 | 1353 | 234689 | 682008 | 304    |
| 532-300    | Broken Hill | 1.66 | 3.7 m | 1.66 | 0.03 | −0.24 | 169 | 2360 | 2151 | 354074 | 1001871 | 424    |
| JB-10-52   | Esmeralda | 1.28 | PPN133 142.5 m | 1.28 | −0.76 | −0.35 | 81 | 2960 | 1664 | 222735 | 908574 | 307    |
| JB-10-53   | Esmeralda | 1.24 | PPN133 143.1 m | 1.24 | −0.97 | −0.03 | 18 | 2123 | 2928 | 263498 | 995789 | 469    |
| JB-10-100  | Flying Doctor | 1.54 | 3538 39.3 m | 0.36 | 0.10 | −0.77 | 196 | 4100 | 2684 | 331625 | 916657 | 224    |
| JB-10-X    | Henry George | 1.54 | PPN94 295 m | 0.24 | −0.24 | −0.28 | 412 | 1950 | 2464 | 147419 | 865877 | 444    |
| JB-10-23   | Henry George | −1.06 | PPN94 295.7 m | −1.06 | −0.33 | −1.02 | 29 | 2210 | 3563 | 197197 | 943294 | 427    |
| JB-10-27   | Henry George | 0.11 | PPN94 300.1 m | 0.11 | −0.38 | −0.15 | 8 | 2068 | 576 | 188590 | 1118626 | 541    |
| JB-10-34   | Henry George | 1.17 | PPN95 308.4 m | 1.17 | −0.25 | −0.38 | 532 | 1961 | 592 | 209415 | 727040 | 371    |
| JB-10-43   | 11:30 | PPN106 172.2 m | −5.11 | −0.26 | −0.04 | 57 | 2154 | 0 | 190561 | 933566 | 433    |
| JB-10-46   | 11:30 | PPN109 208.3 m | −5.11 | −0.19 | 2.59 | 55 | 1803 | 0 | 173888 | 935901 | 519    |

(Continued)
A lode; Plimer, 1979). It yields the highest average sulfur isotopic composition for sphalerite and galena for any of the orebodies.

4.b. Zinc isotopes

Values of $\delta^{66}\text{Zn}$ range from $-1.15$ to $+0.46$ ‰ ($n = 19$) for the Broken Hill deposit and from $-0.97$ to $+0.10$ ‰ ($n = 9$) for the smaller BHT deposits (Table 2). The isotopically lightest value for the smaller BHT deposits is sample JB-10-53 ($\delta^{66}\text{Zn} = -0.97$ ‰) from the Esmeralda deposit, while the isotopically heaviest sample is $\delta^{66}\text{Zn} = +0.10$ ‰ for sample JB-10-100 from the Flying Doctor deposit. Sample JB-10-53, along with samples BH-1 (3 lens), JB-10-87 (Zinc lode, North mine) and JB-10-52 (Esmeralda) have values of $\delta^{66}\text{Zn}$ of $-1.15$, $-0.77$ and $-0.76$ ‰, respectively, which are among the most negative values for sphalerite ever reported for an ore deposit, with that from sample BH-1 being the lowest value yet recorded. There appears to be no systematic variation of Zn isotopes from the stratigraphic footwall to the hanging wall of the Broken Hill deposit (Fig. 6b).

Table 2. (Continued)

| Sample no. | Deposit | Ore body       | Location or drill core | $\delta^{34}\text{S}$ ‰ | $\delta^{66}\text{Zn}$ ‰ | $\delta^{114}\text{Cd}$ ‰ | Ag | Cd | Cu | Fe | Zn | Zn/Cd |
|------------|---------|---------------|------------------------|-------------------------|--------------------------|----------------------------|----|----|----|----|----|-------|
| BH-109     | Pinnacles| Consols Lead lode |                         | $-3.08$                 |                          |                            |    |    |    |    |    |       |
| BH-113     | Pinnacles| 2 level       |                         | $-0.94$                 |                          |                            |    |    |    |    |    |       |
| BH-115     | Pinnacles| 2 level Zinc lode |                        | $-1.04$                 |                          |                            |    |    |    |    |    |       |
| ±0.14 ‰    | ±0.09 ‰ |               |                        |                         |                          |                            |    |    |    |    |    |       |

Fig. 5. (Colour online) Histogram of sulfur isotope compositions of sphalerite (this study) from the Broken Hill deposit and minor Broken Hill-type deposits (P – Pinnacles; HG – Henry George; FD – Flying Doctor; 11 – 11:30). Also shown as bar lines are the ranges of previously published sulfur isotope studies by Lawrence & Rafter (1962), Stanton & Rafter (1966, 1967), Both & Smith (1975), Spry (1987), Parr (1992, 1994) and Huston et al. (1995). Sulfur isotope compositions of sulfides from the Pinnacles deposit, minor BHT deposits and Broken Hill from these studies are shown as orange, brown and red bar lines, respectively.

Fig. 6. (Colour online) (a) Sulfur isotope compositions of sphalerite and galena as a function of stratigraphic position (with C lode in the stratigraphic footwall) in the Broken Hill deposit. Note that isotopic compositions of sphalerite in the so-called Zinc lode from the North mine is also shown but its stratigraphic position is uncertain. Plimer (1979) proposed that it equated to either 1 lens or A lode. (b) Zinc isotope compositions as a function of stratigraphic position in the Broken Hill deposit. (c) Cadmium isotope compositions as a function of stratigraphic position in the Broken Hill deposit.
Values of $\delta^{114}\text{Cd}$ for sphalerite from Broken Hill and smaller BHT deposits range from $-0.48$ to $+0.01\%$ for the Broken Hill deposit and from $-1.02$ to $+2.59\%$ for the smaller BHT deposits (Table 2). The isotopically lightest value is from the Henry George deposit, while the heaviest is from the 11:30 deposit. The range observed here for the BHT deposits are the most negative and positive yet reported for sphalerite from an ore deposit. Although it should be noted that Cd isotope compositions of native and positive yet reported for sphalerite from an ore deposit. The range observed here for the BHT deposits are the most negative and positive yet reported for sphalerite from an ore deposit. (Table 2). The isotopically lightest value is from the Henry George deposit, while the heaviest is from the 11:30 deposit. Moreover, this same sample yielded the most isotopically light sulfur isotope value lysed twice and yielded the same value (Table 2). Moreover, this same sample yielded the most isotopically light sulfur isotope value lysed twice and yielded the same value (Table 2). Moreover, this same sample yielded the most isotopically light sulfur isotope value lysed twice and yielded the same value (Table 2). Moreover, this same sample yielded the most isotopically light sulfur isotope value lysed twice and yielded the same value (Table 2). Moreover, this same sample yielded the most isotopically light sulfur isotope value lysed twice and yielded the same value (Table 2). Moreover, this same sample yielded the most isotopically light sulfur isotope value lysed twice and yielded the same value (Table 2). Moreover, this same sample yielded the most isotopically light sulfur isotope value lysed twice and yielded the same value (Table 2).

**4.c. Cadmium isotopes**

**4.d. Composition of sphalerite and Zn/Cd ratios**

Samples were analysed for Ag, Cd, Cu, Fe and Zn using the Agilent 5900 ICP-OES but only the Ag, Cd and Cu concentrations are accurate since the Zn and Fe are major elements (per cent levels) and thus not suitable for analysis by ICP-OES analysis, given the ppm level concentrations of Zn and Fe in the standard. The Ag, Cd and Cu concentrations of sphalerite from Broken Hill (17–2842 ppm Ag, 181–10 882 ppm Cd, 0–151 369 ppm Cu), Esmeralda (18–81 ppm Ag, 2123–2960 ppm Cd, 1664–2928 ppm Cu), Flying Doctor (196 ppm Ag, 4100 ppm Cd, 2684 ppm Cu) and Henry George (8–532 ppm Ag, 1950–2210 Cd, 576–3563 ppm Cu). To further explore the concentrations of both major- (Zn, Fe and S) and trace-element (Ag, Cd, Cu and Mn) compositions of sphalerite, a suite of ore samples containing sphalerite from the main Broken Hill deposit, as well as minor BHT deposits (Flying Doctor, Globe, Henry George) were analysed by electron microprobe (Fig. 7; Table 3). Note that samples analysed here are not the same as those analysed for Zn, Cd and S isotopes owing to the limited sample size. The Zn and Cd concentrations in sphalerite from 14 samples from the Broken Hill deposit range from 52.93 to 58.73 wt % Zn and 1740 to 2810 ppm Cd, respectively, for Zn/Cd ratios of 203 to 303 with an average of 220 (Fig. 7). The narrow range of ratios obtained by electron microprobe analysis is remarkable given the enormous sized localities. Samples of sphalerite were analysed from Globe and Cu concentrations of sphalerite from Broken Hill (17–2842 ppm Ag, 181–10 882 ppm Cd, 0–151 369 ppm Cu), Esmeralda (18–81 ppm Ag, 2123–2960 ppm Cd, 1664–2928 ppm Cu), Flying Doctor (196 ppm Ag, 4100 ppm Cd, 2684 ppm Cu) and Henry George (8–532 ppm Ag, 1950–2210 Cd, 576–3563 ppm Cu). To further explore the concentrations of both major- (Zn, Fe and S) and trace-element (Ag, Cd, Cu and Mn) compositions of sphalerite, a suite of ore samples containing sphalerite from the main Broken Hill deposit, as well as minor BHT deposits (Flying Doctor, Globe, Henry George) were analysed by electron microprobe (Fig. 7; Table 3). Note that samples analysed here are not the same as those analysed for Zn, Cd and S isotopes owing to the limited sample size. The Zn and Cd concentrations in sphalerite from 14 samples from the Broken Hill deposit range from 52.93 to 58.73 wt % Zn and 1740 to 2810 ppm Cd, respectively, for Zn/Cd ratios of 203 to 303 with an average of 220 (Fig. 7). The narrow range of ratios obtained by electron microprobe analysis is remarkable given the enormous sized localities. Samples of sphalerite were analysed from Globe (n = 1), Flying Doctor (n = 2) and Henry George (n = 1) and yield compositions considerably more variable than those from Broken Hill (i.e. Globe, 56.99–58.63 wt % Zn, 42–70 ppm (average Zn/Cd ratio of 1111); Flying Doctor, 51.05–56.66 wt % Zn, 2400–3420 ppm (average Zn/Cd ratios of 153 to 226); Henry George, 54.94–55.44 wt % Zn, 2410–2550 ppm Cd (average Zn/Cd ratio of 221)). The Zn/Cd ratio of 1111 for the Globe sample is anomalous relative to all other samples of sphalerite from the Broken Hill district. This is likely due to the low Fe content of the sphalerite, which is consistent with sphalerite not being buffered by a member of the system Fe–S. The Fe, Mn and Cu concentrations of sphalerite from Broken Hill range from 7.12 to 11.89 wt % Fe (average = 10.35 wt %), 0.08 to 1.02 wt % Mn (average = 0.34 wt %) and 0 to 0.09 wt % Cu (average = 0.03 wt %). Up to 0.08 wt % Ag was also obtained. The range of concentrations of Fe, Cu and Ag in sphalerite is similar to the ranges of these elements in the minor BHT deposits (6.85 to 12.93 wt % Fe, 0 to 0.04 wt % Cu, up to 0.06 wt % Ag). However, the Mn concentration is considerable lower (0.01 to 0.08 wt % Mn) in the minor BHT occurrences. The concentrations of Cd and the Zn/Cd ratios derived from electron microprobe analysis are evaluated further in this contribution rather than those obtained by ICP-OES.

**5. Discussion**

**5.a. Previous genetic models**

The origin of the Broken Hill deposit and the minor BHT deposits is controversial with a variety of origins having been proposed in the vast literature on the deposit (see Greenfield, 2003). Essentially these disparate views can be distilled down to syngenetic, epigenetic and magmatic–hydrothermal models. For the syngenetic models, sulfide formed by subaqueous hydrothermal processes and subsequently underwent high-grade metamorphism, deformation and possibly partial melting (e.g. Johnson & Klingner, 1975; Laing et al. 1978; Mavrogenes et al. 2001). For the syngenetic models, there has been debate regarding whether or not the BHT deposits are Sedex deposits (e.g. Goodfellow et al. 1993; Sangster, 2020), a separate class of deposit (e.g. Walters, 1996; Walters et al. 2002; Spry & Teale, 2021) or deposits that are possibly transitional between Sedex and VMS deposits (e.g. Walters, 1998; Leach et al. 2005; Spry et al. 2010).

Epigenetic models revolve around the introduction of metals during peak metamorphism or by post-tectonic replacement (e.g. Nutman & Ehlers, 1998; Gibson & Nutman, 2004). Crawford & Maas (2009) proposed a magmatic–hydrothermal
model where they argued that the ore-forming components were derived from fractionated rift-related ferrotholeiite magmas in which fractional crystallization of Fe-rich oxide gabbros separated Cu from Pb and Zn. They suggested that magmatic fluid evolved from these magmas transported Pb and Zn in a saline-rich hydrothermal fluid and deposited metals below the seafloor.

Of these models, the epigenetic (i.e. syntectonic and post-tectonic models) of formation can be rejected since the orebodies were deformed and metamorphosed by the Olarian Orogeny. However, the syngenetic and magmatic–hydrothermal models will be considered further based on the geochemical data obtained here.

### 5.b. Zn/Cd ratios and Cd isotopes of sphalerite as an indicator of ore genesis

Wen et al. (2016) pointed out that the Cd content of sphalerite is dependent on a variety of physicochemical parameters including temperature (T), the nature and concentration of ligands in the ore fluid that bond to Zn and Cd, pH and the total sulfur in solution. Wen et al. classified Pb–Zn deposits into three groups: low-temperature (i.e. MVT deposits), high-temperature (i.e. porphyry, magmatic–hydrothermal, skarn and VMS deposits) and exhalative systems (i.e. Sedex, seafloor hydrothermal sulfides). Distinctions between the three classes of deposits were based on Cd concentrations and Zn/Cd ratios in sphalerite as well as a plot of Cd isotopes versus Zn/Cd ratios. However, an issue with Wen et al.’s study is that it was based on only ten occurrences, four of which were MVT deposits with single examples of a Sedex (i.e. Langshan) and a VMS deposit (i.e. Gacun).

There are several difficulties with the categorization technique proposed by Wen et al. (2016). Their study evaluated low- and high-temperature classes of deposits, which include different types of deposits that form under very different ore-forming conditions. For example, Wen et al.’s (2016) high-temperature deposits include both VMS and porphyry-style deposits, yet VMS deposits form at much lower temperatures (up to ~400 °C) than those of porphyry-style deposits that form above magmatic solidus temperatures (~600–750 °C) (Franklin et al. 2005; Seedorff et al. 2005). Volcanogenic massive sulfide deposits also generally form from low salinity fluids (i.e. equivalent to seawater compositions), although higher salinity fluids are reported in some deposits that have a magmatic component (Franklin et al. 2005). Metals from porphyry-style deposits are either carried in the vapour phase or from highly saline fluids (commonly >50 wt % NaCl). Finally, Wen et al. (2016) also provided a simplistic set of physicochemical conditions of formation for Sedex deposits proposing that they formed under reducing conditions, which is characteristic of Selwyn-type Pb–Zn Sedex deposits. Cooke et al. (2000) recognized the McArthur River-type Sedex deposits form from more oxidized fluids at T generally <200 °C, while Selwyn-type deposits form from reduced fluids at T >200 °C. These concerns notwithstanding, Wen et al. (2016) demonstrated that competing physicochemical conditions produce different Cd concentrations and Zn/Cd ratios.

### Table 3. Zn and Cd concentrations and Zn/Cd ratios of sphalerite from Broken Hill and BHT deposits

| Deposit                  | Sample no. | No. analyses | Zn (wt %)     | Cd (ppm) | Zn/Cd (average) |
|--------------------------|------------|--------------|---------------|---------|-----------------|
| **Broken Hill**          |            |              |               |         |                 |
| Broken Hill C lode, NBHC | JB10-140A  | 6            | 54.10–54.26   | 2260–2370| 234             |
| Broken Hill B lode, NBHC | JB10-125   | 6            | 53.51–54.89   | 1740–1860| 303             |
| Broken Hill Zinc lode, NM| JB10-82    | 18           | 53.70–54.70   | 2300–2610| 221             |
| Broken Hill A lode, ZC   | SJT-308    | 6            | 58.09–58.73   | 2470–2550| 233             |
| Broken Hill A lode, ZC   | JB32-313   | 6            | 52.93–53.68   | 2080–2190| 280             |
| Broken Hill A Lode NBHC  | JB32-283   |              | 53.70–54.33   | 1850–1990| 280             |
| Broken Hill SE A Lode    | JB10-130A  | 6            | 53.68–54.23   | 1840–1950| 287             |
| Broken Hill 1 lens, NBHC | JB32-11    | 6            | 56.51–56.70   | 2220–2290| 254             |
| Broken Hill Lead lode, NBHC | JB32-35H  | 6            | 58.09–58.73   | 2450–2550| 233             |
| Broken Hill Lead lode, NBHC | JB32-34   | 6            | 54.80–55.23   | 2290–2430| 234             |
| Broken Hill 3 lens, NBHC | JB32-357   | 6            | 54.78–56.07   | 2640–2790| 204             |
| Broken Hill 3 lens, NBHC | JB32-35    | 6            | 56.40–56.89   | 2470–2570| 225             |
| Broken Hill 3 lens, NM   | JB32-45    | 6            | 55.89–55.97   | 2420–2480| 227             |
| Broken Hill 3 lens, NM   | JB32-73    | 6            | 53.60–54.10   | 2530–2810| 203             |
| **Broken Hill-type**     |            |              |               |         |                 |
| Globe                    | JB10-65C   | 6            | 56.99–58.63   | 42–70   | 1111            |
| Flying Doctor             | JB10-100   | 6            | 51.05–52.19   | 3300–3420| 153             |
| Flying Doctor             | JB10-101   | 6            | 55.39–56.66   | 2400–2510| 226             |
| Henry George              | JB10-34    | 6            | 54.94–55.44   | 2410–2550| 221             |

NBHC – New Broken Hill Consolidated mine; NM – North mine; ZC – Zinc Corporation mine.
if there are differences in these concentrations and ratios between sphalerite in Sedex and VMS deposits. Table 3 lists the Cd concentrations and Zn/Cd ratios of sphalerite in the Broken Hill area that were analysed by electron microprobe. The highest concentrations of Cd are generally associated with the 3 lens and Lead lode (i.e. undifferentiated 2 and 3 lenses), which is consistent with the findings of Both (1973) who determined the trace-element compositions of sphalerite concentrate in the Broken Hill orebodies. Although the Cd concentrations overlap in the current study for the various orebodies, Both (1973) found a decline in Cd content of sphalerite from 3 lens to A lode. This was not observed in the current study but is likely a result of the fewer number of samples analysed here. Given that Broken Hill and minor BHT deposits occur in metasedimentary rocks spatially associated with metagneous rocks, it is not surprising that both sets of data for these deposits have Cd isotope compositions and Zn/Cd ratios that overlap the compositions of both Sedex and VMS deposits (Figs 7, 8).

The only magmatic–hydrothermal deposit for which there are Cd isotope compositions and Zn/Cd ratio data is the Shagou deposit, China, which has Zn/Cd ratios of 154–191 and values of δ114Cd = −0.05 to 0 ‰. These values overlap those for MVT deposits with the Zn/Cd ratios being lower than the range observed for the Broken Hill and the minor BHT deposits. Although the number of data are limited, the range of values obtained by Wen et al. (2016) cannot be used to support a magmatic–hydrothermal model for the Broken Hill and minor BHT deposits.

5.c. Cd, Zn and S isotopes and the origin of Broken Hill and minor BHT deposits

By incorporating data from the present study with those of Lawrence & Rafter (1962), Stanton & Rafter (1966, 1967), Both & Smith (1975), Spry (1987), Parr (1992, 1994a) and Huston et al. (1995), sulfur isotope compositions of sulfides in the Broken Hill and minor BHT deposits show ranges of δ34S = −3.3 to +6.7 ‰ and −5.1 to +5.4 ‰, respectively. Plimer (1985), in recognizing that the sulfur isotope compositions were centred around 0 ‰, proposed a single primordial source of sulfur, while Parr (1992) suggested that the values near 0 ‰ were the result of sulfide formation from a modified magmatic–hydrothermal source of sulfur in which hydrothermal fluids mixed with reduced sulfur source or that magmatic sulfur was oxidized. The scenarios proposed by Plimer (1985) and Parr (1992) are supportive of a magmatic source associated with the magmatic–hydrothermal model of Crawford & Maas (2009).

Alternatively, Spry (1987) suggested an inorganic source of sulfur in which thermochemical considerations at a $T$ of ~350 °C show that the range of isotopic compositions observed for Broken Hill and the minor BHT deposits occur along the pyrrhotite–magnetite join, which is the dominant assemblage in the system Fe–S–O in the Broken Hill district, although rare primary pyrite is also present (e.g. Parr, 1994b). A log $\delta^{18}$O–pH diagram incorporates the current S isotope data along with those of previously published S isotope data (Fig. 9). The temperature used here is higher than that proposed by Large et al. (1996) who suggested that BHT deposits were derived from slightly acid or near neutral, high salinity fluids between 100 and 250 °C. The upper temperature limit was largely based on solubility constraints of chalcopyrite. However, it should be emphasized that minor amounts of chalcopyrite are present throughout the deposit but its paucity may simply be due to the limited amount of Cu in the source rocks. Regardless, if thermochemical sulfate reduction (TSR) is assumed,
Table 4. Cd concentrations and Zn/Cd ratios of sphalerite in MVT, VMS and Sedex deposits

| Deposit          | Type       | No. analyses (samples) | Zn (wt %) | Cd (ppm) | Zn/Cd (average) | References          |
|------------------|------------|------------------------|-----------|----------|-----------------|---------------------|
| Fule             | MVT        | 14 (8)                 | 51.7–62.8 | 5238–34981 | 17.0–119.9 (43) | Wen et al. (2016)   |
| Tianbaoshan      | MVT        | 28 (3)                 | 39.3–49.5 | 1998–4887 | 93.8–228.1 (140)| Wen et al. (2016)   |
| Jinding          | MVT        | 5 (4)                  | 54.1–66.3 | 3184–22826 | 24–189 (126)    | Wen et al. (2016)   |
| Dadongla         | MVT        | 5 (4)                  | 58.7–65.1 | 16536–26215| 24–36 (30)      | Wen et al. (2016)   |
| Fankou           | MVT        | 10 (7)                 | 55.97–62.7 | 1400–2700 | 216–389 (324)   | Xuesin (1984)       |
| Beichang         | MVT        | 23 (23)                | 51.5–60.3 | 3160–14695 | 38–189 (84)     | Li et al. (2019)    |
| Nanchang         | MVT        | 9 (9)                  | 54.0–58.4 | 5625–22750 | 24–96 (46)      | Li et al. (2019)    |
| Maoping          | MVT        | 23                     | 47–61     | 1869–3344 | 156–294         | Wu et al. (2021)    |
| Gacun            | VMS        | 4 (4)                  | 51.5–63.9 | 2828–3476 | 169–213 (193)   | Wen et al. (2016)   |
| Bankshapa        | VMS        | 5                      | 60.24–62.12 | 1518–1569 | 391–407 (398)   | Mishra et al. (2021)|
| Jangalderi       | VMS        | 9                      | 56.30–57.62 | 378–1217 | 470–674 (558)   | Mishra et al. (2021)|
| Biskhan          | VMS        | 5                      | 55.57–57.64 | 1070–1168 | 477–512 (498)   | Mishra et al. (2021)|
| Bhuyari          | VMS        | 6                      | 54.53–56.07 | 1036–1187 | 463–530 (492)   | Mishra et al. (2021)|
| Bukit Botol      | VMS (massive) | 54 (7)                     | 65.72–66.13 | 5100–5700 | 115–130 (123)   | Basori et al. (2021)|
| Bukit Botol      | VMS (stringer) | 24 (7)                  | 53.48–62.35 | 2200–2800 | 216–267 (240)   | Basori et al. (2021)|
| Bukit Ketaya     | VMS (massive) | 45 (9)                  | 64.70–66.63 | 1800–2500 | 265–371 (320)   | Basori et al. (2021)|
| Bukit Ketaya     | VMS (stringer) | 48 (8)                  | 64.57–66.08 | 2700–5200 | 125–246 (218)   | Basori et al. (2021)|
| Arminius         | VMS        | 16 (8)                 | 57.80–67.00 | 1000–3000* | 195–670 (274)  | D. J. Sandhaus (unpub. MS thesis, Virginia Polytechnic Institute and State Univ., 1981) |
| Cofer            | VMS        | 35 (20)                | 55.80–64.70 | 1000–3100* | 77–656 (312)   | D. J. Sandhaus (unpub. MS thesis, Virginia Polytechnic Institute and State Univ., 1981) |
| Geco             | VMS        | 14 (2)                 | 58.54–58.72 | 2400–4700 | 125–244 (185)   | P. G. Spry (unpub. Ph.D. thesis, Univ. Toronto, 1984) |
| Attu             | VMS        | 25 (10)                | 55.83      | 1900     | 294             | Hangala (1987)      |
| Pontide          | VMS (Zone A) | 16 (2)                 | 61.80–66.40 | 2639–8957 | 78–249 (177)   | Revan et al. (2014) |
| Pontide          | VMS (Zone B) | 1 (1)                  | 62.7       | 2773     | 226 (226)       | Revan et al. (2014) |
| Pontide          | VMS (Zone C) | 2 (10)                 | 61.84–66.00 | 2260–3765 | 174–278 (219)  | Revan et al. (2014) |
| Langshan         | Sedex      | 4 (3)                  | 1.1–34.2   | 34–996   | 316–393 (350)   | Wen et al. (2016)   |
| Bleikvassil      | Sedex      | ?                     | 58.4       | 1100     | 531             | Vokes (1976)        |
| Aclare           | Sedex      | 1 (1)                  | 57.4       | 2000     | 287             | Spyri et al. (1988) |
| Kanmantoo        | Sedex      | 29 (4)                 | 51.94–56.99 | 1200–2800 | 198–461 (320)  | H. Arbon (unpub. B.Sc. Honors thesis, Univ. Adelaide, 2011) |
| Mt Isa           | Sedex      | 357 (13)               | 53.08–63.86 | 1464–4492 | 135–436 (264)  | Cave et al. (2020)  |
| Sullivan         | Sedex      | 222 (5)                | 56.20–59.72 | 500–3200†  | 180–398 (345)  | Lydon & Reardon (2000) |
| Gamsberg         | Sedex      | 8 (8)                  | 51.48–52.46 | 900–1700  | 326–580 (393)  | Höhn et al. (2021)  |

* below detection limits (0.11 wt % Cd) were not included.
† below detection limits (0.05 wt % Cd) were not included.

it is not possible to obtain the observed range of isotopic compositions along the pyrrhotite–magnetite join for geologically reasonable values of ionic concentrations, pH and δ¹⁸S in the ore fluid at the temperatures proposed by Large et al. (1996). While the range of sulfur isotope values can be explained by TSR, the range in isotope data can also be accounted for by reduced sulfur produced by TSR that is mixed with magmatic sulfur or that sulfate from seawater was reduced by biogenic processes at low temperatures (Spry, 1987). It should be noted that Both & Smith (1975) suggested that sulfur isotopic differences among BHT deposits are due to differences in the relative proportion of biogenic sulfur contributed to each deposit.

In an attempt to further evaluate ore-forming processes that may be gleaned from the sulfur isotopes obtained here, we plotted δ¹⁸S versus δ¹¹⁵Cd (Fig. 10) and δ³⁴S versus δ¹³⁵Cd (Fig. 11). However, these isotope pairs involving S show no systematic
variation suggesting that Zn, Cd and S were decoupled from each other. This is further demonstrated by the lack of correlation between δ66Zn and δ114Cd (Fig. 12). Two exceptions exist for one sample (Z359O 15.6 m) from A lode at Broken Hill and one from 11:30. The former shows the highest Zn (δ66Zn = +0.46‰) and S (δ34S = +4.47‰) isotope compositions in the deposit, while sample JB-10-46 from 11:30 shows the highest Cd (δ114Cd = 2.59‰) and lowest S (δ34S = −5.11‰) isotope values for the samples analysed here.

The range of δ66Zn for sphalerite from the Broken Hill deposit is among the largest (1.61‰) yet reported, being exceeded only by sphalerite from the Yuhuang-1 hydrothermal field (1.67‰; Liao et al. 2019). Fourteen of the 18 samples of sphalerite samples from Broken Hill have values of δ66Zn that range from −0.39 to +0.46‰, which overlap most Zn isotope compositions reported from previous studies of MVT, Sedex and VMS deposits (Fig. 13), as well as the compositions of most igneous and sedimentary rocks (e.g. Mârčel et al. 2000; Toutain et al. 2008; Telus et al. 2012). A question remains as to why the remaining four Zn isotope isotopic compositions, two from Broken Hill and two from the Esmeralda deposit, yield the very negative values of δ66Zn between −1.15 and −0.76‰.

Variations in Zn isotopes in a given hydrothermal orebody can result from a variety of processes including (Li et al. 2019): Rayleigh fractionation (e.g. Wilkinson et al. 2005; Kelley et al. 2009; Wang et al. 2020); biological processes (Li et al. 2019); equilibrium fractionation related to T (Mason et al. 2005); different Zn species in the hydrothermal fluid (Fuji et al. 2011); volatilization/evaporation/boiling (e.g. Paniello et al. 2012; Wang et al. 2021); and mixing of different sources of Zn (Wilkinson et al. 2005). Although the effects of metamorphism on the fractionation of Zn isotope compositions in natural systems have received limited attention, Xu et al. (2021) showed that basalt metamorphosed to the greenschist, amphibolite and eclogite facies showed no detectable fractionation. This contrasts with the observations of Pons et al. (2016) who showed that small isotopic variations (up to 0.16‰) occur in subducted Alpine serpentinites that were metamorphosed from greenschist to blueschist through to the eclogite facies. They ascribed the decrease in δ66Zn to the release of oxidized Zn sulfate-rich fluids to the mantle wedge. Regardless, metamorphism to high grades would appear to only produce a very small amount (i.e. <0.2‰) of fractionation. Relatively small isotopic ranges were reported by S. E. Foulkes (unpub. M.Sc. thesis, Rhodes Univ., 2014) for sphalerite from the Gamsberg (δ66Zn = −0.22 to −0.08‰, n = 7) and by Matt et al. (2020) for sphalerite from the Balmat deposits (δ66Zn = −0.30 to 0.28, n = 47) that were both metamorphosed to the amphibolite facies. This further supports the idea that the metamorphism does not modify the original Zn isotopes in the Broken Hill district and is not the cause for the wide isotopic range in the Broken Hill district. Owing to the intense deformation at Balmat, Matt et al. (2020) showed there was a δ66Zn fraction of up to 0.4‰ down the length of some ore bodies. They ascribed this to syntectonic isotopic fractionation that resulted from the interaction between the ore and sulfide melts that were fluxed by H2S. Peak metamorphic conditions at Balmat reached ~640 °C and 6.5 kbar. However, given that sulfide in the Balmat deposit primarily consists of sphalerite with only minor to trace amounts of other sulfides/sulfosalts (e.g. arsenopyrite, bournonite, tetrahedrite, galena, pyrite, tennantite, chalcopyrite, jordanite, realgar; P. Matt, unpub. MS thesis, City Univ. New York, 2019) to potentially lower the melting point of a sulfide mix, there is some question regarding whether or not there was sufficient quantity of these minerals to lower the melting point to the metamorphic conditions reached at Balmat given the high melting point of sphalerite (i.e. 1827 °C). Regardless of whether or not there was a sulfide melt, or whether
Mechanisms involving Rayleigh fractionation may not produce the large fractionation in Zn isotopes observed in the Broken Hill and the minor BHT deposits, although it may account for the Zn isotopic compositions >0‰ at Broken Hill. Nonetheless, ab initio calculations by Fuji et al. (2011) show that negative values of $\delta^{66}$Zn of up to 0.6‰ can occur in sulfides in high pH fluids (likely associated with carbonates) at low temperatures but a considerably smaller fractionation occurs under neutral to acidic fluids at higher temperatures. Regardless, Rayleigh fractionation is inconsistent with the isotopic compositions in the Esmeralda deposit and two samples from Broken Hill that have values of $\delta^{66}$Zn < −0.7‰ since they are hosted in clastic metasedimentary rocks rather than marbles (although carbonates are relatively common in 2 lens at Broken Hill). It is, therefore, unlikely that high pH ore fluids were associated with the formation of deposits in the Broken Hill district (including Broken Hill) and cannot account for the observed wide isotopic range.

The largest Zn isotopic variations in the solar system are associated with devolatilization processes related to the formation of terrestrial bodies where variations of several per mil have been reported (e.g. Luck et al. 2005; Creech & Moynier 2019). Wang et al. (2021), in evaluating the Zn isotopic compositions of sphalerite in the Keyue and Zhaxikang Sedex deposits, showed that vapour–liquid–solid partitioning from hydrothermal fluids would result in lighter Zn and Cd isotopes in the vapour and heavier Zn and Cd isotopes in the solid phase (i.e. sphalerite). Given the possibility that the Broken Hill and minor BHT deposits may have formed from magmatic–hydrothermal fluids (i.e. possibly in the range of 400–700 °C, see Williams-Jones & Heinrich, 2005) rather than the lower temperature fluids (i.e. <350 °C) associated with the previously discussed syngenetic model, then a vapour phase may have been generated. However, Wang et al. (2021) also showed that when the fraction of the initial Zn and Cd partitioned into the volatile phase is extremely high (i.e. >0.8), the resultant sphalerite precipitated from the vapour can produce very light isotopic values.

This scenario could conceivably account for the very negative Zn isotopes observed in sphalerite from the Esmeralda deposit and two samples from the Broken Hill deposit even though such high partitioning of metals such as Zn and Pb into the vapour can produce very light isotopic values.

The light Zn isotopes fractionate due to deformation in a fluid-bearing or fluid-free environment remains uncertain. However, a similar question was raised by Spry et al. (2008) regarding whether a partial sulfide melt was produced at Broken Hill and whether or not it was possible to produce the Pb lode ore bodies as a result of sulfide migration from the restite Zn lodes as proposed by Mavrogenes et al. (2001). Despite these uncertainties, fractionation of S isotopes in veins due to deformation was reported by Spry (1987) at Broken Hill and it may be the same mechanism that is responsible for some of the light Zn isotopes in the Broken Hill district where isoclinal folding exists for the first two phases of deformation that affected the Broken Hill deposit and which caused the migration of sulfides into fold hinges (e.g. Laing et al. 1978; Parr & Plimer, 1993).

![Fig. 11](Colour online) A plot of $\delta^{66}$Zn versus $\delta^{34}$S for sphalerite from the Broken Hill deposit and minor BHT deposits.

![Fig. 12](Colour online) A plot of $\delta^{66}$Zn versus $\delta^{114}$Cd for sphalerite from the Broken Hill deposit and minor BHT deposits.

Fractionation of Cd isotopes can be large with extreme values of between −8 and +16‰ being reported for meteorites as a result of condensation and evaporation processes (e.g. Woebbeling et al. 2003, 2004, 2008). Previous studies of hydrothermal ore deposits show ranges of −0.74 to +1.01‰ in sphalerite based on studies of the Zhaxikang VMS and Fule MVT deposits (Wen et al. 2016; Wang et al. 2020). Cadmium isotope compositions of igneous and sedimentary rocks are essentially indistinguishable with $\delta^{114}$Cd values generally around 0 ± 0.2‰ (e.g. Woebbeling et al. 2003; Schmitt et al. 2009; Liu et al. 2019). Values of $\delta^{114}$Cd for sphalerite from Broken Hill and smaller BHT deposits range from −0.48 to +0.01‰ for the Broken Hill deposit and from $\delta^{114}$Cd = −1.02 to 2.59‰ for the smaller BHT deposits (Fig. 14). Although values of $\delta^{114}$Cd for sphalerite from Broken Hill overlap those of igneous and sedimentary rocks, 10 of the 17 samples analysed range from $\delta^{114}$Cd = −0.48 to −0.23‰ suggesting that some mechanism other than hydrothermal processes,
where Cd was extracted from the meta-igneous and metasedimentary package associated with the Zn–Pb deposits in the Broken Hill district, was responsible. In a Cd, S and Zn isotope study of the Broken Hill deposit and minor Broken Hill-type deposits. Also shown as bar lines are the ranges of δ⁶⁶Zn for sphalerite from the Xiaobaliang VMS deposit, Yang district, was responsible. In a Cd, S and Zn isotope study of the Xiaobaliang deposit; the Alexandrinka (Gao et al. 2018) and Xiaobaliang (Yang et al. 2022) VMS deposits; the Cantabria (Palavia et al. 2014), Cévennes (Albarède, 2004), Jinding (Deng et al. 2017; Li et al. 2019), Maoping (Wu et al. 2021) and Wuishe (Zhu et al. 2018) MVT deposits; Irish-type deposits including Navan (Wilkinson et al. 2005; Gangevin et al. 2012) and the Balmat (Matt et al., 2020), Banbangqiao, Tianqiao (Zhou et al. 2014b), Daliangzi, Fusheng, Jinshachang, Mazou, Tianbaoshan (Xu et al. 2020) and Shanshulin (Zhou et al. 2014a) carbonate-hosted Pb–Zn or Zn deposits. Note that the anomalous value of sample of δ⁶⁶Zn = +1.05 ‰ for late-stage sphalerite that was obtained by Wilkinson et al. (2005) from the Galmoy Irish-type Zn–Pb deposit is not shown on this figure. The reader can view the individual data points for most of the deposits shown here in Wang et al. (2018, 2021).

5.d. A biological syndepositional model for the formation of the Broken Hill deposit and minor BHT deposits

Although the S isotopic compositions of sphalerite can be interpreted in the light of a magmatic–hydrothermal or a syngenetic model, where TSR occurs at a temperature of around 350 °C, neither model can account for the wide range of Zn and Cd isotope compositions of sphalerite. Microbially mediated dissimilatory sulfate reduction to H₂S produces isotopically light H₂S with Δ¹⁵NSO₄-H₂S up to 72 ‰ (e.g. Canfield & Teske, 1996; Balci et al. 2007). However, biological processes are also likely to be important for Zn and Cd (e.g. Li et al. 2019). Although fractionation factors associated with biological processes are not large (1.0002 to 1.0008; Abouchami et al. 2013), biological partial assimilation of Cd from seawater can generate a range of δ¹¹⁴Cd of 7 ‰ in surface waters as a result of the uptake of dissolved Cd by photosynthesis (e.g. Lacan et al. 2006; Ripperger et al. 2007; Schmitt et al. 2009; Wen et al. 2016), while a range of δ⁶⁶Zn of up to ~0.7 ‰ occurs as a result of biological processes (e.g. Conway & John, 2014; Conway & Conway 2014; Zhao et al. 2014) (Fig. 15). Theoretical calculations and experimental studies of Fuji et al. (2011) and Marković et al. (2017), respectively, show that organic compounds (e.g. Zn-carboxylate) generally have heavier isotopic compositions than Zn⁺², which can result in sphalerite having very low δ⁶⁶Zn values in a low T solution (i.e. <100 °C). Li et al. (2019) suggested that Cd, like Zn, may have bonded to carboxylate molecules in hydrothermal solutions resulting in light isotopic values for sphalerite.

However, two features of the Zn and Cd isotope ranges for sphalerite from Broken Hill need to be addressed: why there is no apparent linear relationship between Zn and Cd isotopic compositions of sphalerite from the Broken Hill deposit and minor Broken Hill-type deposits. Also shown as bar lines are the ranges of δ⁶⁶Zn for sphalerite from the Dongshengmiao (Gao et al. 2018), Gamsberg (S. E. Foulkes, unpub. M.Sc. thesis, Rhodes Univ., 2014), Keyue (Wang et al. 2021), Red Dog (Kelley et al. 2009) and Zhaxikang (Wang et al. 2018, 2021) Sedex deposits; the Alexandrinka (Gao et al. 2018) and Xiaoabaliang (Yang et al. 2022) VMS deposits; the Cantabria (Palavia et al. 2014), Cévennes (Albarède, 2004), Jinding (Deng et al. 2017; Li et al. 2019), Maoping (Wu et al. 2021) and Wuishe (Zhu et al. 2018) MVT deposits; Irish-type deposits including Navan (Wilkinson et al. 2005; Gangevin et al. 2012) and the Balmat (Matt et al., 2020), Banbangqiao, Tianqiao (Zhou et al. 2014b), Daliangzi, Fusheng, Jinshachang, Mazou, Tianbaoshan (Xu et al. 2020) and Shanshulin (Zhou et al. 2014a) carbonate-hosted Pb–Zn or Zn deposits. Note that the anomalous value of sample of δ⁶⁶Zn = +1.05 ‰ for late-stage sphalerite that was obtained by Wilkinson et al. (2005) from the Galmoy Irish-type Zn–Pb deposit is not shown on this figure. The reader can view the individual data points for most of the deposits shown here in Wang et al. (2018, 2021).

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compositions (see Fig. 12) and why the range of isotopic values for Cd is smaller than that for Zn isotopes. Cadmium and Zn behave differently with regards to biological productivity. While Zn can be adsorbed and assimilated by phytoplankton, the scavenging of isotopically heavy Zn onto biological particles, which sink through the water column, leave the remaining fluid characterized by lighter Zn isotope compositions (John et al. 2017). Scavenging/ad sorption can lower the Zn isotope compositions by ~0.3 to ~0.6 ‰ (Li et al. 2019). Therefore, the sum of values related to preferential uptake of light isotopes during biological processes is as much as ~1.3 ‰ (i.e. the sum of values for biological assimilation (up to 0.7 ‰; Conway & John, 2014) and scavenging/adsorption (~0.3 to ~0.6 ‰; Li et al. 2019)). On the other hand, Cd is not scavenged by biological particles but is controlled by biological assimilation as it substitutes for P. If Zn in the Broken Hill area was released from organic material during decay to form sphalerite this process could result in the light Zn and Cd isotopic compositions of both Zn and Cd. Alternately, sphalerite formation from the residual seawater would not account for the Cd isotope composition because surface seawater trends to high values of δ114Cd.

A similar explanation for the small range in Cd isotopes compared to Zn isotopes, a feature observed in sphalerite from the Broken Hill area, was proposed by John et al. (2017) for the Neoproterozoic dolostones from the Nuccaleena Formation, South Australia. In the Nuccaleena dolostone, Cd was buried in biological material (i.e. phytoplankton) to produce light Cd isotope compositions, while scavenging of heavy Zn left surface seawater with light Zn isotope compositions. Organic matter formed in surface seawater when buried will produce a larger isotopic range for Zn than Cd.

A mechanism involving Zn and Cd being bonded to organic molecules best accounts for the light Zn and Cd isotopic compositions in the Broken Hill district, including the light isotopic values from the Flying Doctor (δ114Cd = −0.77 ‰) and Henry George (δ114Cd = −1.02 ‰). This scenario is analogous to biogenic processes proposed by Li et al. (2019) to explain similar Zn, Cd and S
isotope compositions for sulfides from the giant Jinding MVT deposit, China, and by Yang et al. (2022) to account for the isotopically light Cd and S isotope values of sphalerite in the Xiaoabaliang Cu–Au VMS deposit, China. Fractionation by biogenic sulfate reduction (BSR) is consistent with the process proposed by Both & Smith (1975) to explain the differences in S isotopes in the district. To this end, Heimann et al. (2013) also reported C and O isotopes values in calcite from the Esmeralda and Broken Hill deposits (the two deposits that show the most negative values of $\delta^{66}Zn$; Table 2), which range from $-25$ to $-21 \%$ for $\delta^{13}C_{VPDB}$ and $+10$ to $+11.0 \%$ for $\delta^{34}S_{SMOW}$, respectively. The low carbon isotope values also overlap ($\delta^{13}C_{VPDB} = -26$ to $-14 \%$) for graphite in graphitic schists in the southern Curnamona province (including the Broken Hill deposit) and calcite at the RW Iron Clad and Little Broken Hill BHT prospects (M. Schuler et al., The Broken Hill Line of Lode Study, unpub. report to Pasminco Mining Company, 1993; Bierlein et al. 1996). Biogenic processes occur at low temperatures (i.e. <100 °C). Notwithstanding the proposal here that biological processes are important in producing the Zn, Cd and S isotopic compositions reported for sphalerite in the Broken Hill district, the cause of the outlier value of $\delta^{114}Cd = +2.59 \%$, coupled with the isotopically lightest value of $\delta^{48}S$ of $-5.11 \%$, for the samples studied here from the small 11:30 deposit remains unknown. However, these anomalous isotopic values may be due to kinetic and/or equilibrium effects similar to those responsible for the isotopically anomalous value of $\delta^{66}Zn > +1.0 \%$ reported by John et al. (2008) for sulfides in active hydrothermal vents on the seafloor.

6. Conclusions

Geological and geochemical considerations suggest that the Broken Hill deposit as well as minor BHT deposits likely formed by either syngenetic processes at $T < 350 \degree C$ or from magmatic-hydrothermal fluids at a $T$ of between 400 and 700 °C. Although S isotope studies are compatible with either process, Cd and Zn isotope studies are incompatible with high $T$ processes because both the lighter isotopes for both isotopic systems will fractionate into the vapour phase leaving sphalerite exhibiting heavy isotopic compositions. Even though the S, Cd and Zn isotope values show no correlation with each other, suggesting they were decoupled, the isotopic ranges are commensurate with fractionation being caused by low-temperature biogenic processes. The Zn and Cd isotope variations for sphalerite from the Broken Hill deposit and minor BHT deposits are among the largest yet reported. Although biogenic processes appear to be the most likely explanation for the isotopically light values reported for both isotopes, fractionation caused by mechanical processes whereby the lighter isotope Zn and Cd isotopes migrate more easily in a fluid assisted or depleted system is uncertain, but this remains a possibility given the extreme deformation that resulted in two isoclinal fold episodes at Broken Hill and the migration of sulfides into fold hinges.

Syngenetic scenarios for the Broken Hill deposit have previously considered it being a VMS or Sedex deposit. Although Cd isotopes have been combined with the Zn/Cd isotope ratio of sphalerite to classify Pb–Zn deposits in the past and may have helped in distinguishing these two deposit models, such an exercise is fraught with problems. Although MVT deposits tend to have lower Zn/Cd ratios in sphalerite than those formed by high-temperature (e.g. VMS) and exhalative (Sedex) systems, the Zn/Cd ratios for VMS and Sedex deposits overlap and cannot be used to distinguish between these deposit types. Sphalerite from the Broken Hill and BHT deposits have average Zn/Cd ratios for sphalerite that range from 203 to 303 and fit within the overlap region for Sedex and VMS deposits. This is hardly surprising given the spatial association of sulfide mineralization with bimodal mafic and felsic igneous rocks within a thick package of metasedimentary rocks.

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