The Potential of Zn Isotopes in the Science and Exploration of Ore Deposits

Jamie J. Wilkinson

Abstract

Since the turn of the Century, the growth in development and application of zinc isotopes to multiple fields in terrestrial and planetary sciences has been exponential. The potential for the application of zinc isotope systematics to ore deposit formation processes was obvious from the outset, given that they represent the most significant concentrations of zinc on Earth and because this approach allowed, for the first time, direct assessment of zinc metal origins and transport. This contribution presents a brief summary of the notation and analytical procedures for analysis of zinc isotopes and summarizes the terrestrial data reported to date. These results show that the variation in zinc isotope composition in rocks and ore systems is in fact rather small (< 2 ‰), linked, at least in part, to the single oxidation state in which zinc occurs in nature. Based on an assessment of the literature, the principal mechanisms for causing isotopic fractionation are all relatively low temperature processes: (i) biogenic; (ii) supergene dissolution-reprecipitation; (iii) adsorption–desorption reactions; and (iv) hydrothermal precipitation. High temperature igneous processes do not appear to produce significant isotopic variations. In ore deposit studies, it currently appears unlikely that zinc isotopes can be used to constrain potential metal sources, apart from zinc derived from carbonate host rocks which tends to be isotopically heavy. However, there are a number of systems in which systematic variation in δ^{66}Zn of sulfides suggests that Rayleigh-type fractionation during ore mineral precipitation occurs, opening up the possibility of using zinc isotopes to trace flow paths and vector in towards mineralized centers. Modeling of such hydrothermal processes is currently hindered by a paucity of experimentally-determined fractionation factors, but as such work is done, our ability to better understand and utilize zinc isotopic zonation patterns for the purposes of mineral exploration will be progressively enhanced.

1 Introduction

Over the past decade and a half, new insights into metal transport pathways and mechanisms in Earth and Planetary systems have been made possible by the development and application of non-traditional stable isotopes (Albarède 2004; Johnson et al. 2004). This burgeoning field has been driven by technological developments in

J. J. Wilkinson (✉)
London Centre for Ore Deposits and Exploration (LODE), Natural History Museum, Cromwell Road, London SW7 5BD, UK
e-mail: j.wilkinson@nhm.ac.uk

Department of Earth Science and Engineering, Imperial College London, Exhibition Road, London SW7 2AZ, UK

D. Huston and J. Gutzmer (eds.), *Isotopes in Economic Geology, Metallogenesis and Exploration*,
Mineral Resource Reviews, https://doi.org/10.1007/978-3-031-27897-6_15

multicollector inductively-coupled-plasma mass spectrometry (MC-ICP-MS). Utilizing plasma ionization and multiple collection of ions, the technique has enabled small isotopic variations in poorly ionized elements to be resolved, a goal that was not achievable with traditional thermal ionization mass spectrometry (TIMS). Using MC-ICP-MS, analytical precision is typically around or below 0.05 ‰ (δ value), several tens or hundreds of times smaller than the isotopic range measured to date in terrestrial rocks, minerals and sediments for a range of elements. Nonetheless, analytical problems remain and there are many studies that have focused on their resolution (e.g. Moynier et al. 2017).

The ability to directly determine the isotopic composition of ore-forming metals has opened up a number of potential applications in studies of hydrothermal ore systems that could shed light on several key parts of the source-transport-trap cycle (Fig. 1). There is the possibility that isotope compositions may be able to pinpoint metal *sources* in contrast to conventional stable isotope systems such as O, H and S which can help to identify sources of water or sulfur but may only indirectly suggest where metals originated. Pb isotope tracing of metal sources is hindered by the complexities of correcting for radiogenic decay. Ore metal isotope studies may also help to understand the processes by which metals are *mobilized* from source rocks or magmas and what characteristics (e.g. mineralogy, pH, fO_2) of rocks and fluids contribute to efficient extraction; metal stable isotopes may be especially powerful for tracking redox changes because these are a major control of isotopic fractionation. Fertile hydrothermal fluids may leave a recognizable metal isotope imprint of their passage that could enable *flow pathways* to be identified. Finally, in the ore deposit environment itself, isotopic variations may be useful for understanding the controls of *ore mineral deposition*. Thus, the application of these stable isotopes could impact on every aspect of the source-transport-trap paradigm. In the longer term, improved understanding of these processes, especially where constrained by experimental data on fractionation behavior, will lead to refinement of deposit models and ultimately influence exploration methods. More immediately, however, the potential exists for metal isotopes to fractionate in systematic ways in hydrothermal environments, leaving either zoning patterns that can be directly utilized for vectoring towards hydrothermal centres, or a diagnostic fingerprint that may reflect efficient ore deposition—i.e. a signature of system *fertility*.

In this paper, I summarize work done to date on hydrothermal ore deposits, focusing on the transition metal Zn. This is not intended to be an exhaustive review; for this, the reader is referred to Johnson et al. (2004), Cloquet et al. (2008), Moynier et al. (2017) and Mathur and Wang (2019). Rather, I focus on findings reported in the literature and results from our own laboratory that are beginning to advance our understanding of processes of zinc transport and deposition in ore systems, particularly in relation to possible applications in mineral exploration.

2 Zinc Stable Isotopes

Zinc has five stable isotopes ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn and ^{70}Zn (Table 1) with average natural abundances of 48.63, 27.90, 4.10, 18.75 and 0.62% respectively (Rosman and Taylor 1998). δ^{66}Zn is normally reported in the literature, relating to the ^{66}Zn/^{64}Zn ratio, where the subscript "X" refers to an unknown and "STD" to a reference material:

$$\delta^{66}\mathrm{Zn_X} = \left(\frac{\mathrm{Zn_X^{66/64}} - \mathrm{Zn_{STD}^{66/64}}}{\mathrm{Zn_{STD}^{66/64}}}\right) \cdot 10^3 \qquad (1)$$

Thus, δ^{66}Zn refers to the ^{66}Zn/^{64}Zn isotope ratio relative to the standard. There is currently no universal standard for zinc isotope measurements, with some data reported with respect to IRMM 3702, some to the Johnson Matthey Corporation zinc standard used by the Lyon group (Lyon JMC 3-0749-L Zn) and, more recently, to the ETH standard AA-ETH (Archer et al. 2017). Data reported relative to IRMM

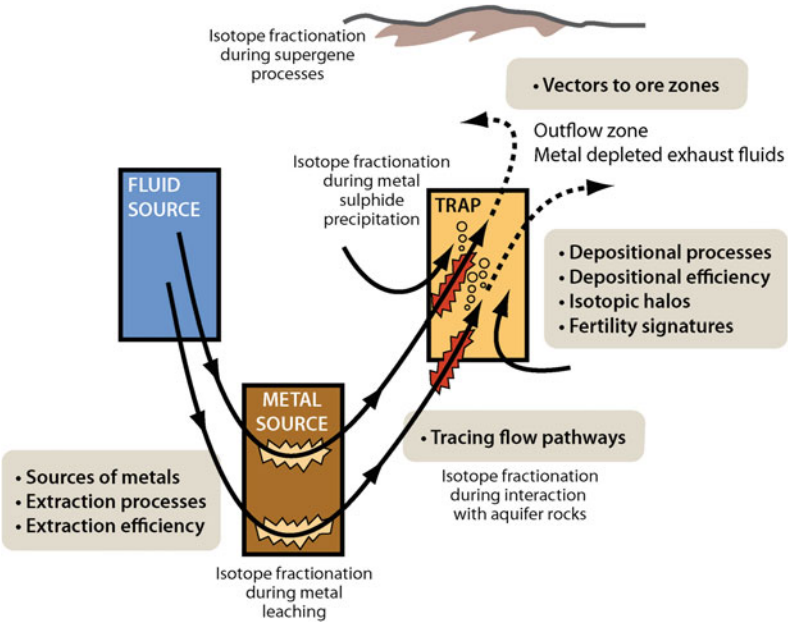

Fig. 1 Hydrothermal system schematic highlighting environments where fractionation of zinc isotopes may occur

Table 1 List of isotopes of zinc found in nature and statistics on the range of δ^{66}Zn values reported in the literature from a compilation of 483 analyses

Element	Isotopes	Delta notation	N	Mean (‰)	Min (‰)	Max (‰)	Range (‰)	Average precision (‰)
Zn	^{64}Zn (48.63%) ^{66}Zn (27.90%) ^{67}Zn (4.10%) ^{68}Zn (18.75%) ^{70}Zn (0.62%)	δ^{66}Zn (66/64)	483	0.33	−0.43	1.34	1.77	0.07

3702 (=AA-ETH) can be recalculated to Lyon JMC-Zn using the published offset between the two standards of 0.28 ‰ ($\delta^{66}\text{Zn}_{\text{IRMM 3702}} = \delta^{66}\text{Zn}_{\text{AA-ETH}} = \delta^{66}\text{Zn}_{\text{JMC-Zn}} + \quad + 0.28$ ‰; Ponzevera et al. 2006; Cloquet et al. 2008; Moeller et al. 2012; Archer et al. 2017). All analyses referred to in this paper are relative to the JMC-Zn standard.

3 Measurement of Zinc Isotopes

Zinc isotope analyses are normally carried out by introduction of a solution into the MC-ICP-MS and require a sample purification step to remove potentially interfering contaminants from the sample matrix (Albarède and Beard 2004). This is done via column chemistry separation methods using an ion exchange resin such as BioRad MP-1 or AG1X8 (Mathur and Wang 2019). Such methods can be quite involved and may need to be developed for specific sample types to avoid incomplete yields of the metal of interest as this can lead to fractionation (Sossi et al. 2015). Until recently, isotope measurements were typically made using a copper spike in the zinc solution to correct for instrumental mass bias and samples were interspersed with standards (standard-sample bracketing) in order to correct for drift. More recently, double-spike Zn isotopic measurements have been introduced and have yielded consistent results with those obtained by standard bracketing techniques (Moynier et al. 2017). Advantages of the double spike technique are that it provides high precision absolute elemental abundances together with the isotope ratios and accounts for mass discrimination during chemical separation. This has been important for the analysis of Zn in difficult matrixes such as seawater (e.g. Conway and John 2015). Expected, natural, mass-dependent fractionation relationships can be checked by comparing $^{66}Zn/^{64}Zn$ with $^{67}Zn/^{64}Zn$, $^{68}Zn/^{64}Zn$ and $^{70}Zn/^{64}Zn$ ratios, providing a useful check on data quality. Typical long-term 2σ precision of measurements is around ± 0.04 ‰ (e.g. Chapman et al. 2006; Chen et al. 2013).

4 Natural Variation in Zinc Isotopes

Overall, relatively small variations in zinc isotope compositions have been reported in terrestrial rock and mineral samples. In a compilation of over 400 analyses there is a total range of < 2 ‰ and the majority of data (25th–75th percentiles) fall in the $\delta^{66}Zn$ range 0.08–0.36 ‰ (Fig. 2). This is due, at least in part, to the single oxidation state in which zinc occurs, unlike other transition metals like molybdenum, iron and copper, for which redox changes can cause significant isotopic fractionation.

There is limited evidence for possible fractionation of Zn by igneous processes: single measurements of granite, granodiorite (Viers et al. 2007) and andesite (Bentahila et al. 2008) gave $\delta^{66}Zn$ values of 0.47, 0.41 and 0.55 ‰ respectively, mostly slightly higher than basalts that range from 0.2 to 0.5 ‰ (Cloquet et al. 2008) and which have an average of 0.32 ‰ (Fig. 2). However, the few more felsic *volcanic* rocks analyzed appear to be depleted in the heavier zinc isotopes (Fig. 2). The basalt standard BCR-1 is the most analyzed rock, with a reported mean $\delta^{66}Zn$ value of 0.25 ± 0.09 ‰ (2σ). The average igneous rock composition is 0.30 ± 0.07 ‰ (n = 77, 1σ; Moynier et al. 2017) and Bulk Earth is thought to have a $\delta^{66}Zn$ value of 0.28 ± 0.05 ‰ (Chen et al. 2013).

Clastic sedimentary rock data (as a proxy for average continental crust) fall in a similar range (average values of 0.12–0.53 ‰; Fig. 2) but carbonates tend to be shifted towards higher $\delta^{66}Zn$, e.g. 0.91 ± 0.48 ‰ (2σ) for recent deep-sea carbonates from the Pacific (Pichat et al. 2003) and 0.04–0.87 ‰ (mean = 0.34 ± 0.35 ‰, 2σ) for cap dolostones formed just after the Marinoan snowball Earth (Kunzmann et al. 2013). This is most likely due to a biogenic fractionation by marine microorganisms that preferentially take up light zinc isotopes—thereby leading to their depletion in seawater—potentially coupled with removal of light zinc isotopes by burial in organic matter (e.g. Vance et al. 2006; John et al. 2007, 2018). However, positive isotope fractionations of ~1 ‰ have been predicted by ab initio modeling for zinc carbonate relative to the parent solution (Fujii et al. 2011), so an inorganic control of part of this shift is perhaps possible.

We do not know much about the behavior of zinc isotopes during supergene weathering but measurable fractionations do occur. In their study of a range of secondary zinc minerals from several different base metal ore deposit types, Mondillo et al. (2018) showed that willemite has the greatest compositional variability ($\delta^{66}Zn$ −0.42 to 1.39 ‰), spanning the entire range of terrestrial variation in Zn isotopes recorded to date. Both positive and negative fractionation directions were recorded relative to the precursor phase for all the minerals studied. The observed data were explained with a model of isotopic fractionation in which partial dissolution of primary sphalerite was followed by precipitation of an initial secondary phase that preferentially incorporated heavy Zn isotopes due to the development of strong Zn–O bonds. Progressive depletion of the residual fluid by this process led to distillation effects ultimately resulting in the formation of small amounts of late-stage, isotopically-light, supergene zinc minerals.

Ferromanganese nodules also form in a surficial environment where dissolution-reprecipitation reactions, adsorption and biological activity may play a role in isotopic fractionation. Maréchal et al. (2000) concluded that the high $\delta^{66}Zn$ values observed in nodules (0.53–1.16 ‰; see Fig. 2) were related to marine biological productivity in a similar way to marine

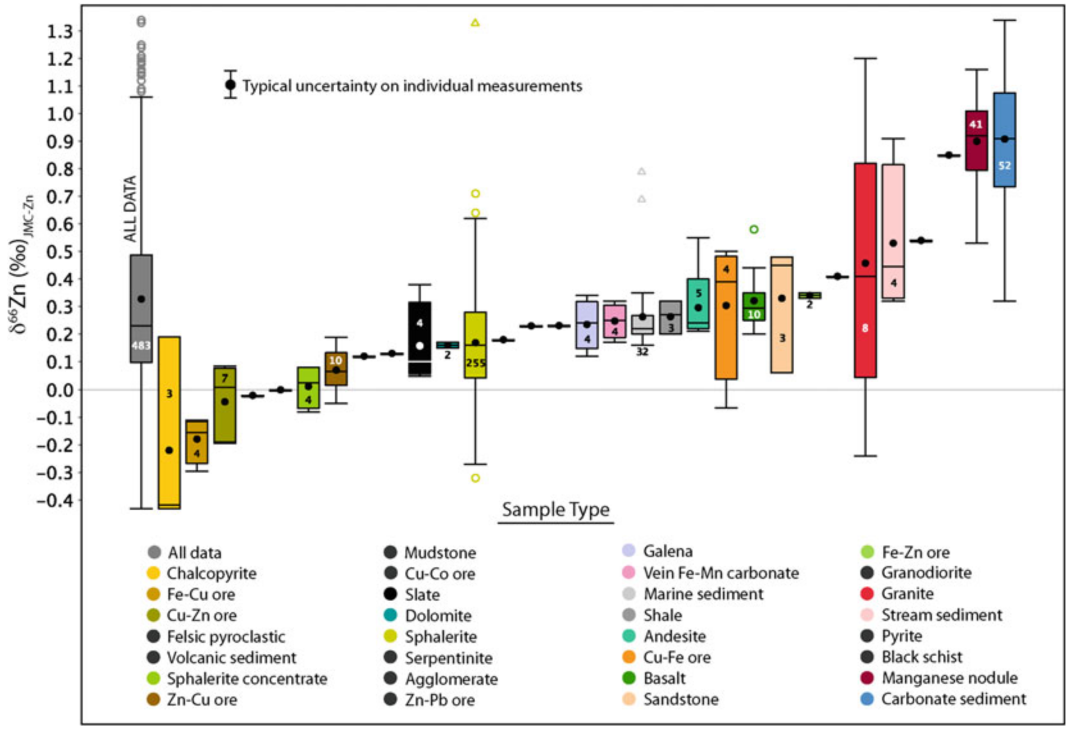

Fig. 2 Summary of terrestrial δ^{66}Zn data from rocks, ores and minerals, ordered in terms of increasing mean value. The grey box on the left represents the entire dataset. Sample types shown in black in the legend are where there is only one analysis available; for other sample types, the numbers of analyses are given on the boxes. The legend is listed in the same order as the boxes on the figure. Box boundaries = 25th and 75th percentiles; line = median; dot = mean; whiskers = the most extreme values that are not outliers; circles = outliers greater than 1.5 × the interquartile range away from the 25th or 75th percentile; triangles = outliers greater than 3 × the interquartile range away from the 25th or 75th percentile

carbonates. The observed global distribution of higher δ^{66}Zn in nodules from higher latitudes could be explained by seasonal productivity fluctuations. However, Little et al. (2014) showed that preferential uptake of heavy zinc isotopes is likely during adsorption from seawater onto manganese oxides (specifically δ-MnO$_2$) so that the coupling of different effects, both biological and inorganic, is likely.

More recently, Spinks and Uvarova (2019) showed that terrestrial Fe–Mn crusts were also enriched in isotopically heavy zinc, with those overlying unmineralized sources more enriched (by up to 0.54 ‰) than those overlying isotopically light sulfide mineralization (by up to 0.37 ‰). They suggested the difference was due to different zinc complexing behavior in the two environments and noted that the isotopic contrast could potentially be useful in mineral exploration.

Finally, zinc isotope variability has been recorded in modern submarine hydrothermal and volcanic hot spring systems indicating the likelihood of fractionation during hydrothermal ore deposit formation. Fluid δ^{66}Zn values measured at a range of submarine vent sites ranged from 0.00 to 1.04 ‰, with the higher and more variable values being linked to lower temperatures (John et al. 2008). It was suggested that subsurface precipitation of isotopically light sphalerite was the primary control of the variation in fluid composition, supported by the observation of vent chimney sulfide with lower or similar δ^{66}Zn to the fluids. A similar mechanism of sphalerite precipitation at depth was proposed to explain the high δ^{66}Zn (~0.70 ‰) of thermal spring waters at La Soufrière volcano, Guadeloupe (Chen et al. 2014), in agreement with isotopic fractionations calculated for aqueous complexes of Zn using molecular dynamics (Black et al. 2011; Ducher et al. 2018).

5 Zinc Isotopes in Ore-Forming Hydrothermal Systems

Hydrothermal processes can produce variations in sulfide δ^{66}Zn by up to 0.9 ‰ (Wilkinson et al. 2005a; Mason et al. 2005; John et al. 2008). Yet, there is still limited understanding of the controls of isotopic fractionation. Below, I consider the results reported to date from a range of hydrothermal ore deposits and summarize the current state of knowledge.

5.1 Sediment-Hosted Zn–Pb Deposits

Several studies have investigated hypogene Zn isotope variation in sediment-hosted base metal deposits. The first such study investigated possible controls on the zinc isotope composition of sphalerite in the Irish Zn-Pb orefield (Wilkinson et al. 2005a). Four possible controls on zinc isotope variation were evaluated: (1) compositional variability of the metal source terrain(s); (2) multiple zinc sources; (3) precipitation temperature; and (4) precipitation mechanism. The δ^{66}Zn values obtained ranged from −0.17 to 0.64 ‰, with one outlier at 1.33 ‰, encompassing the terrestrial variation (Fig. 2). Although largely overlapping with other sulfide data, the average composition of the Irish sphalerites (0.15 ± 0.19 ‰, 1σ; omitting outlier) is isotopically light compared to most rock samples.

This study showed that there was no clear relationship between zinc isotopic composition of sphalerite and fluid temperature, salinity or likely source rocks. Wilkinson et al. (2005a) concluded, based on the spatial variability in δ^{66}Zn, that fractionation was induced via sphalerite precipitation with an inferred negative kinetic isotopic effect during rapid supersaturation. Thus, fluids evolved to heavier isotopic compositions via a Rayleigh fractionation process as they migrated upward and outward through the ore deposits, generating late and/or distal sphalerite with high δ^{66}Zn (Fig. 3).

Gagnevin et al. (2012) followed up this work with a specific investigation of the Navan deposit in Ireland and found that δ^{66}Zn was correlated with δ^{56}Fe and δ^{34}S in sphalerite. They interpreted this to be a result of a negative kinetic Zn (and Fe) isotope fractionation during sphalerite precipitation, coupled with the linked process of fluid mixing involving fluids of contrasting δ^{34}S. Their sphalerite bulk concentrate samples gave a mean δ^{66}Zn of 0.01 ‰ confirming the relatively light average isotopic composition of Irish sphalerites and suggesting that average ore has lower δ^{66}Zn than that generally found in the coarser crystalline sphalerite grains that are more amenable to drilling out for isotopic analysis.

In a study of the Red Dog sediment-hosted Zn–Pb district, Kelley et al. (2009) reached similar conclusions regarding the control of zinc isotope fractionation in sphalerite. Samples from shale-hosted massive sulfide and stratigraphically underlying vein-breccia deposits showed a range of δ^{66}Zn values from 0.00 to 0.60 ‰. The lowest values were observed in the vein-breccias and the stratigraphically overlying (but structurally displaced) ore deposits showed a systematic trend of increasing δ^{66}Zn from south to north (Main-Aqqaluk-Paalaaq-Anarraaq). The δ^{66}Zn values were inversely correlated with sphalerite Fe/Mn and tended to be higher in low-Cu sphalerite, consistent with precipitation of sphalerite with lower δ^{66}Zn closer to the principal hydrothermal fluid conduits. It was inferred that Rayleigh fractionation during sulfide precipitation led to the preferential incorporation of light zinc isotopes in the earliest sphalerite forming at deeper levels (vein-breccias) and close to the principal fluid conduits in the orebodies. This was followed by precipitation of sulfides with higher δ^{66}Zn in shallower and/or more distal parts of the flow path.

More recently, Gao et al. (2018) reported similar trends from the giant Dongshengmiao sediment-hosted Zn–Pb deposit, China. δ^{66}Zn varied from 0.17 to 0.40 ‰ and showed a lateral trend of increasing δ^{66}Zn from southwest to

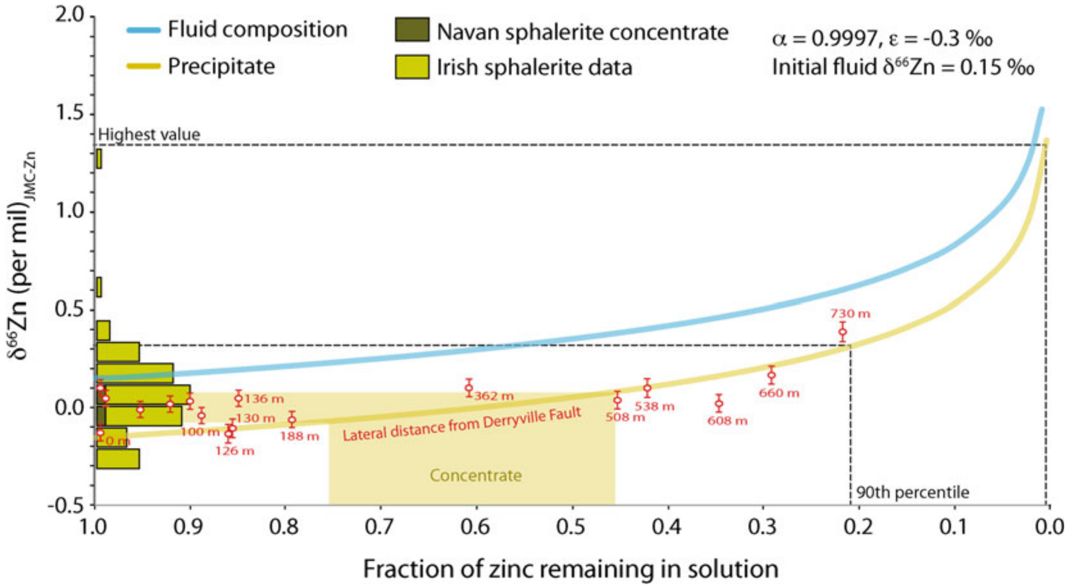

Fig. 3 Open system Rayleigh fractionation model to explain range and spatial distribution of δ^{66}Zn values of sphalerite from the Irish Zn–Pb orefield. The model is constrained by an imposed requirement to encompass the total range of measured δ^{66}Zn, assumes a starting fluid composition that is the same as that determined for Lower Paleozoic basement greywacke samples (Crowther 2007), assuming 100% extraction from these inferred source rocks (Wilkinson et al. 2005b) and an instantaneous equilibrium sphalerite-fluid fractionation factor ε ($\delta^{66}Zn_{mineral} - \delta^{66}Zn_{fluid}$) of −0.3 after the experimental data of Veeramani et al. (2015). Sample data from Wilkinson et al. (2005a; unpublished), Gagnevin et al. (2012) and Crowther (2007). The histogram shows the range of measured δ^{66}Zn for sphalerite with the 90th percentile highlighted; the majority of the ore falls within this range and, based on the model, could have formed after precipitation of between 0 and ~80% of the zinc in solution. The "ore average" compositions given by the bulk sphalerite concentrate data of Gagnevin et al. (2012) indicate that the average ore composition is consistent with having precipitated after ~25–55% of the zinc in solution had been removed. Spatially-constrained samples from a traverse away from the Derryville Zone feeder fault at the Lisheen deposit (Wilkinson, unpublished), arbitrarily plotted on a linear distance scale on the x-axis in red, can be interpreted in terms of progressive precipitation of sphalerite from batches of fluid during lateral flow, with the most distal sphalerite (at 730 m, located at the edge of the orebody) having a composition consistent with formation after about 80% of the zinc had already been precipitated from batches of fluid arriving at that point, i.e. the orebody as a whole represents a depositional efficiency of 80%. The most extreme δ^{66}Zn value measured, 1.33 ‰ from the Galmoy deposit, can be explained by relatively proximal but very late-stage precipitation of very small amounts of sphalerite in vugs from fluids that had already deposited most (~99%) of the original zinc in solution. Data plotting above the model line in proximal samples can be accounted for by rapid, disequilibrium precipitation of high proportions of the zinc in solution in the core of the ore body, with sphalerite compositions therefore approaching the initial solution δ^{66}Zn value. Although the model is subject to many uncertainties, it demonstrates how spatial and temporal trends of increasing δ^{66}Zn can be explained by Rayleigh fractionation processes during flow. The observed pattern of increasing δ^{66}Zn from the centre of hydrothermal deposits outwards thus has a firm theoretical basis and can be utilized in exploration. The discovery of minor, isotopically heavy sphalerite (or whole rocks with high δ^{66}Zn controlled by trace amounts of sphalerite) could therefore be indicative of the extensive precipitation of sphalerite elsewhere in the vicinity. A gradient of decreasing δ^{66}Zn towards ore would be predicted

northeast within the main ore body. The lead isotopic homogeneity of ore sulfides suggested that there was only one significant source for metal, thus precluding mixing of multiple metal sources as a control of this pattern. It was concluded that the most likely control on spatial variations was Rayleigh fractionation during hydrothermal fluid flow, with lighter Zn isotopes preferentially incorporated into the earliest sulfides to precipitate.

Zhou et al. (2014a, b) studied the Tianqiao, Banbanqiao and Shanshulin carbonate-hosted Pb–Zn deposits from the Sichuan–Yunnan–Guizhou Pb–Zn metallogenic province, southwest China. These deposits are associated with dolomitization related to reverse faults and are probably of the Mississippi Valley-type. Sphalerite from successive stages of deposition in all three deposits exhibited increasing δ^{66}Zn values in the range −0.26 to 0.71‰. Furthermore, δ^{66}Zn values in the core of the Tianqiao No. 1 orebody were lower than those on the periphery. Both trends are consistent with a kinetic Rayleigh fractionation effect during progressive precipitation, with earlier/deeper sphalerite being preferentially enriched in lighter zinc isotopes.

5.2 Volcanic-Hosted Massive Sulfide Deposits

In their study of the undeformed Devonian Alexandrinka volcanic-hosted massive sulfide (VHMS) deposit in the Urals, Mason et al. (2005) found that chalcopyrite-rich samples from vein stockwork had lower δ^{66}Zn by ~0.4 ‰ (−0.43 to −0.10 ‰) relative to sphalerite-bearing samples (−0.03 to 0.08 ‰) and attributed this to equilibrium partitioning of isotopically light Zn into chalcopyrite during its precipitation. Alternatively, it is possible that the zinc measured in the chalcopyrite-rich samples (“Cu–Zn ore”; Fig. 2) was principally contained within minor sphalerite; in this case, the lower δ^{66}Zn could be explained by preferential precipitation of light zinc isotopes in more proximal and higher temperature stockwork sphalerite. In a vent chimney sample, δ^{66}Zn increased toward the chimney rim by 0.26 ‰ (−0.03 to 0.23 ‰), which may have been caused by changing temperature (hence fractionation factor), or Rayleigh distillation. Clastic sulfide samples, mostly containing < 15% sphalerite, were isotopically light (−0.30 to −0.05 ‰) possibly due to chalcopyrite predominance as a Zn host, or post-depositional seafloor oxidative dissolution and re-precipitation which led to systematic negative shifts in δ^{66}Zn relative to the primary sulfides.

5.3 Vein-Hosted Zn–Pb Deposits

The only vein-type deposit to have been investigated is the Zhaxikang Sb–Pb–Zn–Ag deposit in Southern Tibet (Wang et al. 2017, 2018). The origin of this fault/vein-controlled deposit is controversial with both magmatic-hydrothermal (Duan et al. 2016) and magmatic-hydrothermally overprinted SEDEX (Wang et al. 2017) origins being proposed. δ^{66}Zn values of sulfides range from −0.03 to 0.38 ‰ (Fig. 2) and cannot distinguish between these alternatives. A trend of decreasing δ^{66}Zn through part of the paragenetic precipitation sequence was noted, although the proposed explanation of boiling coupled with mineral precipitation as a control (Wang et al. 2018) is inconsistent with the Rayleigh distillation models presented and no independent evidence of phase separation was recorded.

5.4 Porphyry-Type and Other Ore Deposits

To date, only a single determination of δ^{66}Zn has been made in a porphyry system, from a chalcopyrite separate from Chuquicamata, Chile. This returned a typical crustal value of 0.19 ‰ (Maréchal et al. 1999). In porphyry deposits, the focus has been on the primary ore metals, Cu and Mo (see Cooke et al. 2014; Mathur and Zhao 2023). At the time of writing, no other deposit types containing zinc as a major or minor component have been investigated.

6 Discussion

6.1 Identifying Metal Sources

Despite suggestions to the contrary, it is not considered here very likely that—at least at the present time—zinc isotope measurements can be used to identify the source of metals for hydrothermal ore deposits. The principal reason is because of the narrow compositional variability of terrestrial reservoirs and the apparently greater variability that is introduced during depositional processes. Added to this, there is almost no information on how zinc isotopes may be fractionated during extraction from a source by hydrothermal fluids or potentially modified during transport. Thus, it is difficult to identify the primary source signal from samples where various fractionation steps may have occurred along the system flow path (Fig. 1). The one exception might be where zinc is sourced from carbonate rocks because these tend to have a fairly distinctive, isotopically heavy composition (Fig. 2). Consequently, questions such as the possible importance of host rock sourcing of metals for skarn deposits and the potential derivation of metals from different aquifer compositions as an influence on the metal tenor of MVT deposits—in particular the apparent relationship between carbonate aquifers and more Zn-rich deposits (Sverjensky 1984)—may be tractable.

6.2 Precipitation Efficiency

If source fluid compositions are known, or can be inferred, the isotopic composition of precipitated ore minerals could provide a clue to depositional efficiency—a key parameter in ore studies, yet one that has been almost impossible to constrain to date. Any fractionation between fluid and mineral will generate a progressive shift in isotopic composition of the mineral being deposited. Because of the reservoir effect, locally high degrees of precipitation in an ore body from a batch of fluid will result in the average isotopic composition of the ore approaching the input fluid composition (Fig. 3). By contrast, lower degrees of precipitation could produce a broad, highly-skewed distribution, which, with a negative $\Delta_{\text{fluid-mineral}}$ fractionation would produce proximal ore with a lower δ^{66}Zn than the input fluid and more distal ore, precipitated later, with higher δ^{66}Zn than the initial fluid. For example, in the Irish sediment-hosted Zn–Pb deposits described above, the dispersion in zinc isotope compositions and slight bias towards isotopically heavy compositions within an ore lens could reflect intermediate precipitation efficiency in an open system.

6.3 Hypogene Isotopic Zonation

From the global compilation presented in Fig. 2, it is possible to make the general observation that δ^{66}Zn from copper-bearing ores (mixed mineralogy samples), dominated by Fe–Cu or Cu–Zn sulfides is consistently low. Given that chalcopyrite separates from the Alexandrinka VHMS deposit returned some of the lowest δ^{66}Zn values measured to date (Mason et al. 2005), one could conclude that Zn substituted into the chalcopyrite structure may be in a bonding environment that favours the light isotopes. This would mean that measurements of Cu–Zn ores may show a systematic shift to lower δ^{66}Zn towards the core of systems due to an increase in chalcopyrite abundance at higher temperatures. As a tool, this has limited use because assay and sulfide zonation patterns would be simpler and cheaper ways to observe the same trends. However, if it is trace sphalerite in such samples that is controlling the signature then it implies that sphalerite can record a systematic zoning from the high temperature cores of hydrothermal systems out into the typically lower temperature domains where sphalerite becomes dominant.

Based on existing studies of low temperature, sediment-hosted Zn–Pb systems, it appears that Zn isotopes are fractionated systematically in this way during ore formation. In all case studies completed to date, it has been inferred that light zinc isotopes are preferentially incorporated into sphalerite ($\alpha_{\text{sphalerite-fluid}} < 1$) so that fluids—and later sphalerite precipitated from them—evolve towards heavier compositions in time and space (Figs. 3, 4). This behavior is consistent with what has been observed in modern hydrothermal environments (e.g. John et al. 2008). Such systematic fractionation provides a theoretical basis for the development of exploration tools that can utilize zonation patterns of δ^{66}Zn in sphalerite (and possibly altered rocks containing trace sphalerite or other zinc-bearing minerals) around ore bodies (Fig. 4). In the case of the Irish ore system, there is evidence that δ^{66}Zn varies both vertically up through the systems and laterally across individual orebodies, a trend that can be modeled using a Rayleigh-type fractionation approach (Fig. 3).

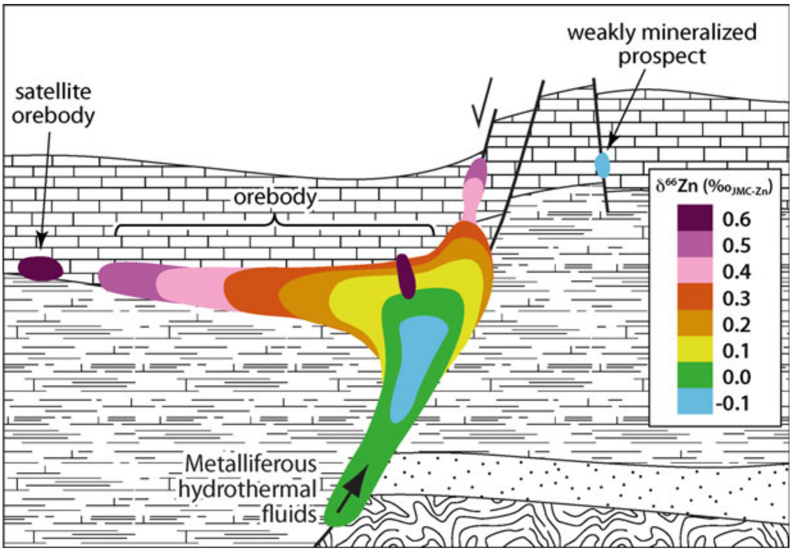

Fig. 4 Cartoon cross-section illustrating possible zinc isotope zonation that might develop in a hydrothermal zinc deposit. Geology based loosely on a SEDEX-type system, but trends would be applicable to vein-hosted hydrothermal deposits. Color scale illustrates pattern of δ^{66}Zn that may be observed in sphalerite mineral separates, or in whole rock where major to trace sphalerite dominates the Zn budget of the sample. Distal mineralization, at the margin of the orebody or developed along escape structures, is fractionated towards heavier isotopic compositions. Late-stage, overprinting mineralization may also be isotopically heavy. Weakly-mineralized satellite prospects may have compositions similar to proximal sphalerite from an orebody if they are formed by limited precipitation from similar source fluids

6.4 Supergene Isotopic Zonation

Similarly, in the supergene modification of pre-existing sulfide deposits, the prediction of an increase in δ^{66}Zn in most supergene minerals where Zn is tetrahedrally-coordinated in relatively strong Zn–O bonds ($\alpha_{\text{secondary mineral-sphalerite}} > 1$) can produce a supergene ore that is isotopically heavy but has peripheral or paragenetically-late supergene Zn minerals that have low δ^{66}Zn values because of the preferential removal of heavy zinc isotopes from the fluid by earlier precipitation (Mondillo et al. 2018).

7 Summary and Conclusions

The study of non-traditional stable isotopes in general and as applied to ore deposits in particular remains at a fledgling stage. It has become apparent that wider variations in isotopic compositions are present in hydrothermal ore deposits than in any other terrestrial environments; this makes them particularly interesting for further investigation. Several studies have inferred the probability of Rayleigh distillation processes in the systematic fractionation of zinc during precipitation of ore minerals. If this general process is confirmed it will open up many possible applications, with the isotope systematics potentially tracking flow pathways through deposits and out into the “exhaust” region (Fig. 1), the domain of spent ore fluids.

At the present time, models to explain isotope fractionation patterns of ore metals are underconstrained, particularly because of the limited experimental data on fluid-mineral fractionations and lack of knowledge on whether equilibrium or kinetic fractionations are likely to prevail. There is the additional complication of biologically-mediated fractionation of Zn in low temperature systems (e.g. Wanty et al. 2013). Consequently, current interpretations are somewhat speculative and well-designed experimental studies to measure isotopic fractionations under relevant hydrothermal conditions of metal extraction, transport and metal sulfide deposition (Fig. 1) are needed. Once these are available, quantitative modeling will be better able to test alternative hypotheses for natural datasets.

Despite the current limitations, the data summarized here for zinc provide an indication of the types of new insights that studies of ore metal stable isotopes may provide. In time, these isotope systems are likely to provide powerful new tools for testing models of metal transport and deposition and thereby improve the ore deposit models that essentially underpin all modern mineral exploration. More directly, the operation of Rayleigh distillation processes may produce patterns that help to unravel complex flow paths and produce isotopic gradients that can be utilized for vectoring towards the centre of hydrothermal systems. It may be possible to identify mixing between magmatic and country rock-derived metals on the fringes of magmatic-hydrothermal systems if there is an isotopic contrast, such as for magmas intruding carbonate sequences.

Notwithstanding these opportunities, the fact remains that for a geochemical tool to achieve widespread take up in the mineral exploration industry it needs to be cheap, rapid and not require a high level of technical knowledge to apply. Zinc isotopes measurements and the subsequent interpretation of the data do not presently meet these requirements. This means that it is unlikely that vectoring using zinc isotope zonation will become a widely utilized method for the foreseeable future. Even effective tools based on mineral trace element chemistry, that are far easier to apply, are still only being taken up gradually by major explorers (e.g. Cooke et al. 2020a,b; Wilkinson et al. 2020) because they are perceived to be relatively high cost and slow to implement (~6 week turnaround time). Probably the most significant contribution that zinc isotopes can make to studies of hydrothermal systems in the immediate future is to help resolve outstanding questions about hydrothermal processes that conventional datasets have been unable to solve, such as understanding extraction of metals from source rocks, tracing flow paths and identifying the controls of depositional efficiency.

Acknowledgements The author would like to thank the numerous researchers involved in the development and application of zinc isotopes to ore systems in the MAGIC Laboratories, Imperial College London, without whom this review would not have been written, namely: Prof. Dominik Weiss, Prof. Mark Rĕhkamper, Dr. Thomas Mason, Barry Coles and Dr. Helen Crowther. Their contributions are acknowledged; however, any mistakes or shortcomings in this paper are my own. Finally, I would like to thank Marcus Kunzmann and Ryan Mathur for their helpful reviews that improved the manuscript.

References

Albarède F (2004) The stable isotope geochemistry of copper and zinc. Rev Mineral Geochem 55:409–427

Albarède F, Beard BL (2004) Analytical methods for nontraditional isotopes. Rev Mineral Geochem 55:113–152

Archer C, Andersen MB, Cloquet C, Conway TM, Dong S, Ellwood M, Moore R, Nelson J, Rehkämper M, Rouxel O, Samanta M, Shin K-C, Sohrin Y, Takano S, Wasylenki L (2017) Inter-calibration of a proposed new primary reference standard AA-ETH Zn for zinc isotopic analysis. J Anal at Spectrom 32:415–419

Bentahila Y, Ben Othman D, Luck J-M (2008) Strontium, lead and zinc isotopes in marine cores as tracers of sedimentary provenance: a case study around Taiwan orogen. Chem Geol 248:62–82

Black JR, Kavner A, Schauble EA (2011) Calculation of equilibrium stable isotope partition function ratios for aqueous zinc complexes and metallic zinc. Geochim Cosmochim Acta 75:769–783

Chapman JB, Mason TFD, Weiss DJ, Coles BJ, Wilkinson JJ (2006) Chemical separation and isotopic variations of Cu and Zn from five geological reference materials. Geostand Geoanal Res 30:5–16

Chen H, Savage P, Teng FZ, Helz RT, Moynier F (2013) No zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth. Earth Planet Sci Lett 369:34–42

Chen J-B, Gaillardet J, Dessert C, Villemant B, Louvat P, Crispi O, Birck J-L, Wang Y-N (2014) Zn isotope compositions of the thermal spring waters of La Soufrière volcano, Guadeloupe island. Geochim Cosmochim Acta 127:67–82

Cloquet C, Carignan J, Lehmann M, Vanhaecke F (2008) Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: a review. Anal Bioanal Chem 390:451–463

Conway TM, John SG (2015) The cycling of iron, zinc and cadmium in the North East Pacific Ocean—insights from stable isotopes. Geochim Cosmochim Acta 164:262–283

Cooke DR, Hollings P, Wilkinson JJ, Tosdal RM (2014) Geochemistry of porphyry deposits. In: Treatise on geochemistry, 2nd edn, vol 13, pp 357–381

Cooke DR, Agnew P, Hollings P, Baker M, Chang Z, Wilkinson JJ, Ahmed A, White NC, Zhang L, Thompson J, Gemmell JB, Chen H (2020a) Recent advances in the application of mineral chemistry to exploration for porphyry copper–gold–molybdenum deposits: detecting the geochemical fingerprints and footprints of hypogene mineralization and alteration. Geochem Environ Explor Anal 20:176–188. https://doi.org/10.1144/geochem2019-039

Cooke DR, Wilkinson JJ, Baker M, Agnew P, Phillips J, Chang Z, Chen H, Wilkinson CC, Inglis S, Martin H (2020b) Using mineral chemistry to aid exploration—a case study from the Resolution porphyry Cu-Mo deposit, Arizona. Econ Geol 115:813–840

Crowther HL (2007) A zinc isotope and trace element study of the Irish Zn-Pb orefield. Unpublished PhD thesis, Imperial College, University of London, 361 p

Duan J, Tang J, Lin B (2016) Zinc and lead isotope signatures of the Zhaxikang Pb-Zn deposit, South Tibet: implications for the source of the ore-forming metals. Ore Geol Rev 78:58–68

Ducher M, Blanchard M, Balan E (2018) Equilibrium isotopic fractionation between aqueous Zn and minerals from first-principles calculations. Chem Geol 483:342–350

Fujii T, Moynier F, Pons ML, Albarède F (2011) The origin of Zn isotope fractionation in sulfides. Geochim Cosmochim Acta 75:7632–7643

Gagnevin D, Boyce AJ, Barrie CD, Menuge JF, Blakeman RJ (2012) Zn, Fe and S isotope fractionation in a large hydrothermal system. Geochim Cosmochim Acta 88:183–198

Gao Z, Zhu K, Sun J, Luo Z, Bao C, Tang C, Ma J (2018) Spatial evolution of Zn-Fe-Pb isotopes of sphalerite within a single ore body: a case study from the Dongshengmiao ore deposit, Inner Mongolia, China. Mineral Deposita 53:55–65

John SG, Geis RW, Saito MA, Boyle EA (2007) Zinc isotope fractionation during high-affinity and low-affinity zinc transport by the marine diatom Thalassiosira oceanica. Limnol Oceanog 52(6):2710–2714

John SG, Rouxel OJ, Craddock PR, Engwall AM, Boyle EA (2008) Zinc stable isotopes in seafloor hydrothermal vent fluids and chimneys. Earth Planet Sci Lett 269:17–28

John SG, Helgoe J, Townsend E (2018) Biogeochemical cycling of Zn and Cd and their stable isotopes in the Eastern Tropical South Pacific. Marine Chem 201:256–262

Johnson CM, Beard BL, Albarède F (eds) (2004) Geochemistry of non-traditional stable isotopes. Rev Mineral Geochem 55:454

Kelley KD, Wilkinson JJ, Chapman JB, Crowther HL, Weiss DJ (2009) Zinc isotopes in sphalerite from base metal deposits in the Red Dog district, northern Alaska. Econ Geol 104:767–773

Kunzmann M, Halverson GP, Sossi PA, Raub TD, Payne JL, Kirby J (2013) Zn isotope evidence for immediate resumption of primary productivity after snowball Earth. Geology 41:27–30

Little SH, Sherman DM, Vance D, Hein JR (2014) Molecular controls on Cu and Zn isotopic fractionation in Fe–Mn crusts. Earth Planet Sci Lett 396:213–222

Maréchal CN, Télouk P, Albarède F (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. Chem Geol 156:251–273

Maréchal CN, Nicolas E, Douchet C, Albarède F (2000) Abundance of zinc isotopes as a marine biogeochemical tracer. Geochem Geophys Geosyst 1:1015. https://doi.org/10.1029/1999GC000029

Mason TFD, Weiss DJ, Chapman JB, Wilkinson JJ, Tessalina SG, Spiro B, Horstwood MSA, Spratt J, Coles BJ (2005) Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulfide (VHMS) ore deposit, Urals, Russia. Chem Geol 221:170–187

Mathur R, Wang D (2019) Transition metal isotopes applied to exploration geochemistry: insights from Fe, Cu and Zn. In: Decree S, Robb L (eds) Ore deposits: origin, exploration and exploitation. Wiley, New York, pp 167–183

Mathur R, Zhao Y (2023) Copper isotopes used in mineral exploration. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)

Moeller K, Schoenberg R, Pedersen R-B, Weiss D, Dong S (2012) Calibration of the new certified reference materials ERM-AE633 and ERM-AE647 for copper and IRMM-3702 for zinc isotope amount ratio determinations. Geostand Geoanal Res 36:177–199

Mondillo N, Wilkinson JJ, Boni M, Weiss DJ, Mathur R (2018) A global assessment of Zn isotope fractionation in secondary Zn minerals from sulfide and non-sulfide ore deposits and model for fractionation control. Chem Geol 500:182–193

Moynier F, Vance D, Fujii T, Savage P (2017) The isotope geochemistry of zinc and copper. Rev Mineral Geochem 82:543–600

Pichat S, Douchet C, Albarède F (2003) Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka. Earth Planet Sci Lett 210:167–178

Ponzevera E, Quétel CR, Berglund M, Taylor PDP, Evans P, Loss RD, Fortunato G (2006) Mass discrimination during MC-ICPMS isotopic ratio measurements: investigation by means of synthetic isotopic mixtures (IRMM-007 series) and application to the calibration of natural-like zinc materials (including IRMM-3702 and IRMM-651). J Am Soc Mass Spectr 17:1413–1428

Rosman KJR, Taylor PDP (1998) Isotopic compositions of the elements. Pure Appl Chem 70:217–235

Sossi PA, Halverson GP, Nebel O, Eggins SM (2015) Combined separation of Cu, Fe and Zn from rock matrices and improved analytical protocols for stable isotope determination. Geostand Geoanal Res 39:129–149

Spinks SC, Uvarova Y (2019) Fractionation of Zn isotopes in terrestrial ferromanganese crusts and implications for tracing isotopically-heterogeneous metal sources. Chem Geol 529:119314

Sverjensky DA (1984) Oilfield brines as ore-forming solutions. Econ Geol 79:23–37

Vance D, Archer C, Bermin J, Kennaway G, Cox EJ, Statham PJ, Lohan MC, Ellwood MJ (2006) Zn isotopes as a new tracer of metal micronutrient usage in the oceans. Geochim Cosmochim Acta 70:A666

Veeramani H, Eagling J, Jamieson-Hanes JH, Kong L, Ptacek CJ, Blowes DW (2015) Zinc isotope fractionation as an indicator of geochemical attenuation processes. Environ Sci Technol Lett 2:314–319

Viers J, Oliva P, Nonelle A, Gelabert A, Sonke J, Freydier R, Gainville R, Dupre B (2007) Evidence of Zn isotopic frationation in a soil-plant system of a pristine tropical watershed (Nsimi, Cameroon). Chem Geol 239:124–137

Wang D, Sun X, Zheng Y, Wu S, Xia S, Chang H, Yu M (2017) Two pulses of mineralization and genesis of the Zhaxikang Sb–Pb–Zn–Ag deposit in southern Tibet: constraints from Fe–Zn isotopes. Ore Geol Rev 84:347–363

Wang D, Zheng Y, Mathur R, Wu S (2018) The Fe–Zn isotopic characteristics and fractionation models: implications for the genesis of the Zhaxikang Sb–Pb–Zn–Ag deposit in southern Tibet. Geofluids 2197891. https://doi.org/10.1155/2018/2197891

Wanty RB, Podda F, De Giudici G, Cidu R, Lattanzi P (2013) Zinc isotope and transition-element dynamics accompanying hydrozincite biomineralization in the Rio Naracauli, Sardinia, Italy. Chem Geol 337–338:1–10

Wilkinson JJ, Weiss DJ, Mason TFD, Coles BJ (2005a) Zinc isotope variation in hydrothermal systems: preliminary evidence from the Irish Midlands ore field. Econ Geol 100:583–590

Wilkinson JJ, Everett CE, Boyce AJ, Gleeson SA, Rye DM (2005b) Intracratonic crustal seawater circulation and the genesis of subseafloor zinc-lead mineralization in the Irish orefield. Geology 33:805–808

Wilkinson JJ, Baker MJ, Cooke DR, Wilkinson CC (2020) Exploration targeting in porphyry Cu systems using propylitic mineral chemistry: a case study of the El Teniente deposit, Chile. Econ Geol 115:771–791

Zhou J-X, Huang Z-L, Zhou M-F, Zhu X-K, Muchez P (2014a) Zinc, sulfur and lead isotopic variations in carbonate-hosted Pb–Zn sulfide deposits, southwest China. Ore Geol Rev 58:41–54

Zhou J-X, Huang Z-L, Lu Z-C, Zhu X-K, Gao J-G, Mirnejad H (2014b) Geology, isotope geochemistry and ore genesis of the Shanshulin carbonate-hosted Pb–Zn deposit, southwest China. Ore Geol Rev 63:209–225