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A global assessment of Zn isotope fractionation in secondary Zn minerals from sulfide and non-sulfide ore deposits and model for fractionation control

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Abstract

We investigated extent and direction of Zn isotope fractionation in secondary zinc minerals formed during low temperature hydrothermal and/or supergene oxidation of primary sulfide deposits. Zinc isotope data have been obtained from non-sulfide zinc mineral separates (willemite - Zn_2SiO_4 , smithsonite - ZnCO_3 , hemimorphite - $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$, hydrozincite - $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, and sauconite - $\text{Na}_{0.3}\text{Zn}_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) collected from several Zn deposits in Ireland, Belgium, Poland, Namibia, Peru, Yemen and Zambia. The data are compared with Zn isotope compositions measured on Zn sulfides collected in the same areas and/or derived from the existing literature to establish the controls of direction and likely extent of any fractionations. We find that willemite has the greatest compositional variability, with measured $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ values ranging from -0.42 to 1.39‰ , spanning the entire range of terrestrial variation in Zn isotopes recorded to date. Overall, significant fractionations in positive and negative directions are recorded relative to the precursor phase (primary sphalerite or an earlier secondary phase), with primary sphalerite falling in a relatively narrow range of isotopic values (approximately -0.1 to $+0.4\text{‰}$). Most of the data observed on willemite, hemimorphite and hydrozincite can be explained with a model of isotopic fractionation in which partial dissolution of primary sphalerite is followed by precipitation of an initial secondary phase that preferentially incorporates heavy Zn isotopes. Smithsonite, instead, preferentially incorporates light Zn isotopes. This reflects the variation in the Zn-x bond strengths of these secondary phases with respect to the original sulfides. We also observed that isotope compositions do not depend only on the difference between the fractionation factors of the involved phases but also on the amount of the secondary mineral precipitated after dissolution of primary sulfide, and that the greatest

fractionations occur when only small amounts of secondary mineral are precipitated. Progressive precipitation from migrating fluids that form phases enriched in heavy zinc isotopes would lead to a gradual decrease in the $\delta^{66}\text{Zn}$ values of such phases, and the fluids involved, in time and space. Strong negative isotopic shifts are almost only observed for late crystallizing phases, such as those in vugs. These are interpreted to reflect precipitation from residual, isotopically-light fluids that are the inevitable highly-fractionated product of the above-described process. Where a more complete replacement of primary sulfide has occurred, such as in the high-grade core of nonsulfide zinc orebodies, there is limited net isotopic fractionation because dissolved primary zinc is nearly quantitatively reprecipitated locally. In addition, in only one case (Yanque, Peru) we observed that the fringes of non-sulfide zinc deposit were characterized by isotopically fractionated compositions, with highly negative values implying extensive precipitation (earlier, or elsewhere) of isotopically heavy secondary phases. The higher-grade ore zones, where complete breakdown of primary sulfides and quantitative reprecipitation of zinc have occurred, show instead less fractionated compositions.

Keywords: Zn isotopes; isotope fractionation; supergene environment; Rayleigh-type distillation; non-sulfide zinc deposits; secondary zinc minerals.

1. Introduction

Zinc, an element with atomic number 30, which occurs in the natural environment with the +2 oxidation state, has five stable isotopes, ^{64}Zn (49.2%), ^{66}Zn (27.8%), ^{67}Zn (4.0%), ^{68}Zn (18.4%), and ^{70}Zn (0.6%) and an average relative atomic mass of 65.37777(22) (Cloquet et al., 2008; Moynier et al., 2017; Rosman, 1972). The measurement of Zn isotopic ratios by Thermal-Ionization Mass-Spectrometry (TIMS) is difficult, because the element has a high first ionization potential which leads to a low Saha constant; for this reason, most of the existing data have been produced since the late 90s, after the advent of Multiple-Collector Inductively-Coupled-Plasma Mass Spectrometry (MC-ICP-MS) (Moynier et al., 2017). In the last twenty years, several reference standards have been adopted for Zn isotopic investigations. However, many studies used a Johnson Matthey Corporation (JMC) Zn standard solution, batch 3–0749L, commonly denoted as JMC-Lyon (Maréchal et al., 1999), which is no longer available (Moynier et al., 2017). Möller et al. (2012) calibrated IRMM-3702 as the new certified Zn standard, which has a $\delta^{66}\text{Zn}$ value of +0.29 ‰ relative to the JMC-Lyon standard. Despite this, recent papers (e.g. Wanty et al., 2013) have still reported Zn isotope ratios relative to JMC-Lyon:

$$\delta^{66}\text{Zn} (\text{‰}) = \left(\left(\frac{(\frac{66\text{Zn}}{64\text{Zn}})_{\text{sample}}}{(\frac{66\text{Zn}}{64\text{Zn}})_{\text{JMC-Lyon}}} \right) - 1 \right) * 1000$$

The main processes affecting the Zn isotope composition of natural materials are evaporation–condensation processes, in which the vapor phase is depleted in the heavier isotopes relative to the solid phase, adsorption, complexation and diffusion (Cloquet et al., 2008; Moynier et al., 2017). Evaporation-condensation processes have produced the large variations in $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (–11‰ to +7‰: Moynier et al., 2011; Kato et al., 2015) observed in extraterrestrial samples such

as meteorites (Rosman, 1972; Luck et al., 2005) and in lunar rocks (Moynier et al., 2006). In terrestrial geological samples (i.e. sediments, igneous rocks and ores), $\delta^{66}\text{Zn}$ values are clustered around +0.5‰, ranging from ca. -0.5‰ to +2.5‰ (Moynier et al., 2017). This limited spread reflects the fact that Zn does not undergo redox transitions which often produce large isotope fractionations (Moynier et al., 2017). The main mechanisms causing Zn isotope fractionation at the Earth's surface are equilibrium isotope distribution between dissolved aqueous species (e.g. organic complexes) and equilibrium and kinetic effects caused by interactions between solids and aqueous solutions (e.g. sorption, precipitation). In natural waters and hydrothermal solutions, Zn occurs as the free ion, i.e. Zn^{2+} , solvated by water molecules (Ducher et al., 2018), as Zn complexed to organic ligands or humic acids (Jouvin et al., 2009; Marković et al., 2017), and complexed with inorganic ligands such as chloride. Experimental and theoretical investigations on Zn complexation by organic ligands (Ban et al., 2002; Black et al., 2011; Jouvin et al., 2009, Fuji and Albarède, 2012; Marković et al., 2017) has shown that such complexes favor in general heavy Zn isotopes controlled by the affinity constant. Other experiments on isotope fractionation associated with sorption on Fe- and Mn-oxyhydroxides (e.g. Balistrieri et al., 2008; Bryan et al., 2015; Juillot et al., 2008; Pokrovski et al., 2005) have shown that heavy Zn isotopes are preferentially adsorbed, generating a positive $\Delta^{66}\text{Zn}$ between the adsorbing phase and the solution

A variety of processes are considered as possible explanations for the isotopic variability of Zn in hydrothermal ore systems, including source-rock control, temperature, and kinetic or equilibrium fractionation during precipitation (Albarède, 2004; Archer and Vance, 2002; Kelley et al., 2009; Maréchal et al., 1999, 2000; Mason et al., 2005; Pašava et al., 2014; Pichat et al., 2003; Wilkinson et al., 2005). For example, the variability in Zn isotopic data observed for

sphalerite in the Irish ore field is likely generated by kinetic fractionation and Rayleigh distillation during progressive sulfide precipitation from the hydrothermal fluids (Wilkinson et al., 2005). Low temperature water-rock interaction imparts measurable Zn isotope fractionation (Balistrieri et al., 2008; Bermin et al., 2006; Borrok et al., 2008; Fernandez and Borrok, 2009; Lv et al., 2016; Opfergelt et al., 2017). To date, the majority of the Zn isotope studies on surficial environments have focused on how the isotopes can trace metal contamination (Araújo et al., 2017; Bigalke et al., 2010, 2016; Cloquet et al., 2008; John et al., 2008; Kelley et al., 2009; Mattielli et al., 2009; Sivry et al., 2008; Sonke et al., 2008; Wanty et al., 2013; Weiss et al., 2007).

Several experimental and natural studies have provided important insights into the controls of Zn isotope fractionation. Fernandez and Borrok (2009) observed that “continuous batch leaching of sphalerite at pH=2 and pH=4 was characterized by a modest (0.2‰) initial increase in the $\delta^{66}\text{Zn}$ of the leachate relative to the sphalerite, which quickly dissipated and the $\delta^{66}\text{Zn}$ of the fluid began to reflect the $\delta^{66}\text{Zn}$ of the sphalerite”. The initial fractionation was explained by the transient formation of a surface coating composed of Zn-sulfates that, changing the bonding environment for Zn, incorporated preferentially the heavier Zn isotopes. Wanty and co-workers (2013) studied the isotopic effects related to the precipitation of hydrozincite in a Zn-polluted river in Sardinia and observed that $\delta^{66}\text{Zn}$ values of hydrozincite samples were consistently about 0.35‰ heavier than the waters with which they were in contact. Thus, it was concluded that hydrozincite preferentially incorporated the heavier isotope, after a biologically-mediated mineralization process, leaving the residual waters depleted in ^{66}Zn and leading to lower $\delta^{66}\text{Zn}$ values in downstream water samples. Isotopic fractionation of Zn, associated with a solution isotopically lighter than the parent material, was also observed during experimental leaching of a

biotite granite with oxalic and hydrochloric acid solutions which, at the early stages, produced a solution ca. 1‰ lighter than the original sample (Weiss et al., 2014).

Ducher et al. (2016) reported theoretical studies of Zn isotope fractionation in Zn-bearing minerals. They investigated the isotope fractionation properties of Zn in several minerals at equilibrium using density functional theory (DFT). Assuming that equilibrium, mass-dependent isotopic fractionation arises mainly from the vibrational motions of atoms, the equilibrium isotopic properties of the element were determined by the calculation of the reduced partition function ratio, also called the β -factor, by computing vibrational frequencies using a harmonic approach. The β -factor is defined as the ratio at equilibrium of the isotope ratio of the substance of interest to the isotope ratio of a perfect gas of atoms (Bigeleisen and Mayer, 1947), which in this case is represented by monatomic Zn:

$$\beta_{Zn-phase}^{^{66}Zn/^{64}Zn} = \frac{(^{66}Zn/^{64}Zn)_{Zn-phase}}{(^{66}Zn/^{64}Zn)_{Zn}}$$

The β -factors are useful to our aims because there is a relationship between the equilibrium isotopic fractionation factor α (a, b, Y) between two phases a and b for an element Y (in this case Zn), and the reduced partition function ratios of a and b:

$$\alpha(a,b,Y) = \beta(a,Y) / \beta(b,Y)$$

This allows simple approximation of the β -factors with the δ values, which are normally measured on natural samples:

$$10^3 \ln \alpha(a,b,Y) \approx \Delta = \delta_a - \delta_b$$

As the calculated β -factors are very close to 1, they are presented as logarithmic quantities ($\ln\beta$) expressed in per mil units (‰). Ducher and co-workers (2016) demonstrated that at ambient temperature gahnite, hemimorphite and hydrozincite are amongst the minerals having the highest logarithmic values of the reduced partition function ratio ($\ln \beta^{^{66}Zn/^{64}Zn}$ of 4.18‰, 3.78‰ and

3.19‰ at 22 °C, respectively), whereas smithsonite and sphalerite have the lowest β -factors ($\ln \beta$ $^{66}\text{Zn}/^{64}\text{Zn}$ of 2.30‰ and 2.40‰ at 22 °C, respectively). This means that, at equilibrium, an alteration process that releases Zn from sphalerite and reprecipitates it into secondary minerals could produce either positive or negative fractionations: hemimorphite and hydrozincite would be isotopically heavier than parental sphalerite (at 22 °C $\Delta_{\text{hem-sph}}(\text{‰}) = +1.38$, $\Delta_{\text{hydr-sph}}(\text{‰}) = +0.80$), whereas smithsonite would be isotopically lighter (at 22 °C $\Delta_{\text{sm-sph}}(\text{‰}) = -0.10$). Crystal-chemical parameters control these isotopic properties (Ducher et al., 2016): indeed, excellent linear correlations exist between $\ln \beta$ and Zn interatomic force constants, and β -factors increase when the Zn-first neighbor bond lengths decrease and charges on atoms involved in the bonding increase and vice versa.

The present study sought to determine the controls of Zn isotope fractionation during sphalerite dissolution and formation of oxidized secondary Zn minerals in sulfide and non-sulfide ore deposits, and to establish a preliminary model for Zn isotope fractionation for this process. To this end, Zn isotope compositions were measured on 28 secondary zinc minerals (willemite - Zn_2SiO_4 , smithsonite - ZnCO_3 , hemimorphite - $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$, hydrozincite - $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, sauconite - $\text{Na}_{0.3}\text{Zn}_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) collected from several localities in Ireland, Belgium, Poland, Namibia, Peru, Yemen and Zambia (Fig. 1), and compared, where possible, with the Zn-isotopic ratios measured on primary sulfides (9 samples of sphalerite and one galena) from the same areas. Of particular interest was the behavior of the Zn silicate, willemite, which is observed in some of the deposits (Belgium, Namibia, Zambia) that may have either a supergene or hypogene genesis.

2. Geological settings and mineralization of the sampled areas

2.1. Ireland

The zinc sulfide deposits in Ireland (carbonate-hosted SEDEX, Mississippi Valley-type (MVT) and vein-type deposits) occur mainly in the Lower Carboniferous of the Central Midlands (e.g. Wilkinson et al., 2003; Wilkinson and Hitzman, 2015). Locally, nonsulfide zinc-lead mineralization was developed above these deposits (Balassone et al., 2008), and represents an example of supergene oxidation of primary sulfide ores, with local redeposition and preservation under glacial till. The dominant composition of these oxidized ores is relatively simple: smithsonite, hemimorphite, cerussite and Cu-carbonates. Prior to the 1960s, lead and zinc were also mined from low temperature hydrothermal veins throughout much of Ireland. These veins are hosted by Lower Paleozoic rocks which, in the case of the Glendalough and Old Luanus deposits, comprise Caledonian granite. Supergene minerals in these occurrences probably relate to exhumation and exposure of the deposits between 36-10 Ma.

2.2. Belgium

In the Liège Zn-Pb-Ba mining district (NE Belgium), primary zinc-lead sulfides (MVT) and secondary nonsulfides are the main typology of deposits (Dejonghe et al., 1993). Sulfide mineralogy includes sphalerite, galena, and pyrite/marcasite with collomorphic and brecciated textures. The mineralized veins cut the Palaeozoic rocks folded during the Hercynian orogeny, and the main mineralizing event dates back to the end of the Jurassic (~150 Ma). The Belgian nonsulfide ores mainly represent the supergene oxidation products of primary sulfides. Nonsulfide ores consist of an association of smithsonite, hydrozincite, hemimorphite, willemite

and Zn-clays, with a variable content of Pb minerals. The extensive occurrence of the Zn-silicate willemite (Fig. 2A), which appears to be the first deposited nonsulfide mineral directly replacing sphalerite, is a peculiarity of the Belgian ores and its genesis has not been fully resolved. In fact, willemite may have formed during a hydrothermal event (Brugger et al., 2003) with moderate temperatures, high silica activities and deeply reaching O-rich fluids, possibly active in the deposit area between the Jurassic and Cretaceous, as well as the first product of sulfide weathering, post Cretaceous (Coppola et al., 2008). By contrast, smithsonite and hemimorphite have all the characteristics of supergene products, and were commonly developed at the expense of primary sulfides as well as of willemite (Coppola et al., 2008).

2.3. Poland

Sulfide ores from Upper Silesia (Poland) are hosted by the so-called Ore Bearing Dolomite, a hydrothermal alteration product corresponding to the epigenetic replacement of Muschelkalk (Triassic) carbonates. Two important kinds of mineralization have been described: (a) replacement bodies and (b) in-filling of open spaces in fractures and breccias. The mineral association in the sulfide deposits includes sphalerite, galena, marcasite, pyrite and sulfoarsenides (Kucha, 2005). The age of mineralization is controversial and both early Mesozoic and Tertiary have been proposed (Heijlen et al., 2003; Leach et al., 1996). The nonsulfide ores are commonly associated with horst features delimited by Tertiary faults (Coppola et al., 2009) and were formed by weathering of primary Zn-Pb sulfides. Their prevailing mineralogical association comprises smithsonite, cerussite, hemimorphite and Fe-(hydr)oxides (Fig. 2B).

2.4. Namibia

The Otavi Mountain Land (OML) in Namibia broadly coincides with the Neoproterozoic carbonate platform of the Damara Orogen. In the OML, several ore deposits and prospects (both sulfides and nonsulfides) are hosted in the carbonate successions of the Otavi Group. The primary sulfide ores have been subdivided into the ‘Berg Aukas-type’ (Zn-Pb MVT) and ‘Tsumeb-type’ (Pb-Cu-Zn pipes) deposits (Pirajno and Joubert, 1993). A maximum age for the ‘Tsumeb-type’ sulfide ores in the OML is 530 Ma, whereas the ‘Berg Aukas-type’ ores seem to be older, possibly related to fluids expelled during the Damaran orogeny. In the Namibian occurrences, willemite is in several generations (Fig. 2C). It commonly replaces sphalerite, but may also occur as a newformed phase or as a direct replacement of the carbonate host rocks (Schneider et al., 2008). The willemite concentrations in the Namibian deposits (Berg Aukas, Abenab West, Baltika etc.) have been interpreted to be mainly of hydrothermal origin (Hitzman et al., 2003; Schneider et al., 2008). Smithsonite, hemimorphite and descloizite commonly follow willemite and have been interpreted as late, weathering-derived supergene phases.

2.5. Zambia

The Zambian Zn-Pb deposits occur in metasedimentary rocks of the Late Proterozoic Katangan Supergroup. The most important orebodies are located in the Kabwe area, and contain both sulfides and nonsulfides hosted in dolomite. The Zn-Pb sulfide mineralization has been interpreted as having been formed before the last Lufilian deformational phase (ca 650 - 500 Ma) (Kamona and Friedrich, 2007), and would be broadly in the same age range as the OML sulfides. Similar to the OML, several willemite generations of possibly hydrothermal origin (Fig. 2D) are

present at Kabwe (Mondillo et al., 2018), which are clearly followed by supergene phases, like smithsonite, cerussite, hemimorphite, descloizite and tarbuttite (Fig. 2E).

2.6. Yemen

The Jabali mixed sulfide-nonsulfide Zn mineralization is located about 110 km east of Sana'a (Yemen) (Mondillo et al., 2014a). The host rocks of both ore types are intensively dolomitized Jurassic carbonates. The primary sulfide deposit shows the general features of MVT ores, and its formation age was attributed to Early Cretaceous (Ostendorf et al., 2015). Smithsonite (Fig. 2F) is the most abundant economic mineral in the nonsulfide mineralization, where it replaces both the host dolomite and sphalerite (Fig. 2G). It is associated with minor hydrozincite, hemimorphite, acanthite and greenockite. The Jabali smithsonite shows $\delta^{18}\text{O}$ values substantially lower and with a larger variability in comparison with other smithsonites considered supergene in the literature (Gilg et al., 2008), suggesting that this Zn carbonate could have been precipitated from fluids with a temperature between 30 and 65 °C, probably derived from the mixing of local groundwaters with low-temperature hydrothermal waters (Mondillo et al., 2014a).

2.7. Peru

The Yanque nonsulfide Zn(Pb) prospect is located in the Cuzco area (southern Peru, Mondillo et al., 2014b). The primary sulfides are considered to represent polymetallic mineralization genetically related to the emplacement of the Andahuaylas–Yauri batholith (Middle Eocene to Early Oligocene, ca. 48–32 Ma). However, these sulfides have been totally weathered, and the economic concentrations in the prospect consist prevailingly of supergene Zn(Pb) nonsulfides, mostly hosted in siliciclastic conglomerates. The mineral association contains sauconite,

hemimorphite, smithsonite and cerussite. Remnants of the primary sulfides are represented by moderate amounts of galena and pyrite, but residual sphalerite is very rare. Sauconite, the most abundant ore mineral in the Yanque deposit, formed after a process of supergene wall-rock replacement (Fig. 2H; sensu Hitzman et al., 2003), where the Zn released from the complete dissolution of sphalerite precipitated as a newformed mineral after the reaction of Zn-bearing solutions with the silicatic country rock. The process likely started in the center of the present orebody, and progressively propagated southward from surficial zones into more deeply buried strata (Mondillo et al., 2014b).

3. Sample locations and descriptions

The samples from the Glendalough Mine, Glendalough (BM1964R-6305) and from the Old Laganure mine, Glendasan (BM1964R-6307), originate from the Mineralogy Collection of the Natural History Museum (London), and consist of two sphalerite-smithsonite pairs. In the Glendalough sample, the sphalerite occurs as nice, idiomorphic crystals, with smithsonite in globular concretions that have overgrown and partly replaced it. In the Old Laganure sample, the smithsonite is commonly green-yellow, possibly due to the presence of Cd, and appears to have overgrown sphalerite. The samples from the Galmoy mine were collected underground from the CW orebody (Doyle et al., 1992; Balassone et al., 2008) and consist of vug-filling, late-stage, greenish sphalerite, overgrown by smithsonite.

Samples from the mines of Fossey (RN2300) and La Calamine (R2B35/3925) in Belgium (Coppola et al., 2008) originate from the Royal Belgian Institute of Natural Sciences in Brussels

and consist of two willemite-smithsonite pairs (Table 1). In both samples, rhombohedral crystals of smithsonite have overgrown partially-altered, anhedral crystals of willemite that have replaced the original sphalerite. The sample (RN5011) from the Moresnet old mine (a subsidiary of La Calamine) consists of crystalline willemite, which has replaced collomorphic sphalerite; galena from this sample was also analyzed to provide an indication of the Zn isotopic composition of primary sulfides in the deposit.

The samples from the Polish mines (Coppola et al., 2009) were collected on site, from old mine workings. They are represented by a sphalerite-smithsonite pair (sample CV05-71, Chrzanów), and by a sphalerite-hemimorphite pair (sample CV05-80, Pomorzany) (Table 1). In the Chrzanów sample, smithsonite occurs as globular concretions around massive sphalerite (complete replacement of sphalerite by smithsonite was not observed), whereas in the Pomorzany sample, hemimorphite has overgrown collomorphic sphalerite.

The Namibian samples (Schneider et al., 2008) are from two different localities. Two generations of willemite were collected from the Berg Aukas mine (generation 1 BA2003-4: botryoidal yellow willemite that has replaced the carbonate host rock; generation 2 BA2003-13.2: white needles of late willemite in vein and cavity fillings; Terracciano, 2008). A sphalerite-willemite pair was also sampled at the small Baltika prospect near Otavi. The sample NARO427A-1 consists of black-reddish sphalerite, and sample NARO427A-2 contains an early generation of willemite that has partly replaced sphalerite.

The Zambian samples originate from the Kabwe mining area (Terracciano, 2008). The first sample consists of a sphalerite-willemite pair from the Kabwe 5/6 pit (ZA0502-D: black-grayish sphalerite; ZA0502-M: early, botryoidal willemite that has replaced the carbonate host rock). The other specimen contains a smithsonite-hemimorphite pair sampled from the outcropping gossan of Kabwe pit 2 (ZA0511-2: brownish smithsonite crystals in cavity; ZA0511-1: white hemimorphite needles that have overgrown the smithsonite).

The samples from the Jabali deposit originated from drill core J125, which encounters the mineralization at ~50 m depth below a thick cover of carbonate rocks, and from two outcrops located on the side of a valley which cuts the sedimentary rocks hosting mineralization. Sphalerite samples J125-5 and J125-7 represent two specimens of vein-type sphalerite, texturally associated with saddle dolomite (Mondillo et al., 2014a). Sample J125-9 contains smithsonite that has directly replaced the vein-type sphalerite, whereas the concretionary smithsonite sample J125-32 came from the deeper zones of the Jabali mineralization and is not texturally associated with any sphalerite. Smithsonite sample JS-MON-6 and hydrozincite sample JS-MON-22B were collected from the best mineralized outcrops occurring at Jabali: JS-MON-6 represents an outcropping part of the smithsonite orebody, sampled alongside the J125-9 specimen, whereas the hydrozincite is a late phase formed from the supergene alteration of the former smithsonite generations.

Seven sauconite samples were selected from drill cores in the Yanque deposit (Peru). The samples consist of massive sauconite that formed from Zn precipitation from Zn-bearing groundwaters, produced by leaching of an original sulfide body, and reacting with a quartz-

feldspar-mica siliciclastic rock. The samples are texturally similar, but originate from different parts of the deposit, which locally crops out in the north of the prospect area and plunges southward with a dip of $\sim 30^\circ$. Three near-surface samples (<20 m) are YA13-SAM12, collected from the northern limb of the ore body, YA17-SAM16 from the central part of the ore body and YA20-SAM19 from its eastern side. The samples YA31-SAM24, YA34-SAM25, YA40-SAM29 and YA45-SAM32 originate from the southernmost limb of the ore body and at greater depths (120-160 m); they are separated by around 100 m and are sequentially located along a traverse to the south (i.e. YA45-SAM32 most distal from the deposit core).

4. Analytical methods

Samples from Ireland, Belgium, Poland, Namibia and Zambia were analyzed at the MAGIC Laboratories, Imperial College London, UK. Samples from Yemen and Peru were analyzed at the University of Arizona, USA. The Zn minerals were handpicked from each specimen, powdered and sieved to <500 micron. At the University of Arizona, 0.02-0.04 g of sample was weighed into 15 ml Teflon beakers, and dissolved/leached at 120°C for greater than 12 hours 4 ml in ultrapure *aqua regia*. 0.5 ml of the resulting solution was then taken and dried. At Imperial College London, sample digestion was carried out following the procedure described in Chapman et al. (2006). In both the laboratories, the Zn in the resulting salts was then separated using two subsequent passages through an anion exchange resin as outlined in detail by Chapman et al. (2006).

At Imperial College London, isotope measurements were made using an IsoProbe MC-ICP-MS (Thermo Instruments, U.K.), following the analytical procedures described in detail by Gioia and co workers (2008) and by Araújo et al. (2016). A Cetac Aridus desolvating nebulizer (Cetac Technologies, Omaha) was used for sample introduction. The instrument was used in the “hard extraction” mode and signal contributions from the cone were insignificant. Instrumental background and acid matrix blank corrections were performed using on-peak acid blank measurements taken before every sample and standard (Gioia et al., 2008). Measurements are quoted relative to the Zn standard JMC 3-0749 L (JMC-Lyon). The procedural blank was around 5 ng which was insignificant compared to the amount of Zn processed through the samples. Accuracy and precision of the Zn isotope ratio measurements following our ion exchange procedure were assessed using a well-characterized synthetic element solution from our laboratory (RomilZn), certified (for concentrations) reference materials BCR-027 (blende ore) and G-2 (granite) and the in-house standard HRM-24 (granite). Possible isotope fractionation during the ion exchange separation procedure was tested comparing the isotopic compositions of the synthetic element solutions before and after the passage through the ion exchange columns. We did not find significant isotope fractionation during the passage of the ion exchange column and $\delta^{66}\text{Zn}_{\text{Lyon}}$ values of RomilZn, G-2 and BCR-027 agreed within error with published data using a variety of different analytical procedures (Möller et al., 2012). The in-house standard HRM-24 showed values for $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ of $+0.267 \pm 0.05\text{‰}$ (2SD and $n=3$). These ratios fall well within the range observed for granites and andesite (Moynier et al., 2017). Repeated measurement of RomilZn over the study period (36 months) showed an external precision of $\pm 0.05\text{‰}$ pamu.

At the University of Arizona, isotopic measurements were also made on an IsoProbe (MC-ICP-MS). Solutions were diluted to approximately 260 ppb for Zn prior to measurement, which generated a ^{66}Zn signal between 3-4 V. Sample intensities matched the standard intensities within 20%. The reported data are the average of 2 separate measurements of a block of 25 ratios. Isotope variations were determined using IRMM 3702 and then recalculated to standard delta notation relative to JMC-Lyon, summing at the IRMM 3702 values the published offset between the two standards of +0.29‰ (Cloquet et al., 2008; Ponzevera et al., 2006; Moeller et al., 2012).

5. Results

The $\delta^{66}\text{Zn}$ values for the analyzed European sulfide and non-sulfide samples are given in Table 1 and summarized in Figure 3. The $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ values for all the primary sphalerites samples fall in the relatively narrow range between -0.06 to $+0.41$ ‰, typical of hydrothermal sphalerite from low-moderate temperature ore deposits (e.g. Wilkinson et al., 2005; Moynier et al., 2017). The minerals that generally occur as the earliest overgrowth/replacement of primary sulfides (excluding the Pomorzanj hemimorphite) are willemite and smithsonite. Differently from Araújo et al. (2017), we found that willemite has the greatest compositional variability, with measured $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ values ranging from -0.42 to 1.39 ‰, spanning the entire range of terrestrial variation in Zn isotopes recorded to date. The majority of the willemite samples (with the exception of the second willemite generation from Berg Aukas, Namibia) show a distinct positive isotopic shift from the precursor sulfide (Fig. 4), with the most extreme fractionation observed in the Belgian samples (shift larger than 0.5 ‰). Likewise, apart from the samples from

Glendalough and Old Liganure (Ireland), all the smithsonite samples show a positive shift in $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ relative to the primary sulfide of up to $\sim 0.5\text{‰}$ (Jabali, Yemen). The single case where hemimorphite was observed as the first secondary phase (Pomorzanj, Poland) also shows a positive isotopic shift of $+0.23\text{‰}$ (Fig. 4). Although primary sphalerites have not been measured from Yanque (Peru), based on the assumption that it is likely to have typical hydrothermal compositions in the range of -0.1 to 0.4‰ , it can be inferred that the sauconite formation also involved zinc isotope fractionation with an increase in $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$.

For the secondary minerals that replaced the earlier non-sulfide zinc phases (Table 1, Fig. 2) the pattern is the opposite. Smithsonite formed after willemite in the case of the Belgian deposits shows a strong negative shift (up to -0.87‰) relative to the willemite that it has overgrown and partly replaced (Fig. 3). Hydrozincite after smithsonite in the Jabali deposit (Yemen) shows a shift of -0.18‰ in $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$. Late hemimorphite after smithsonite from the Kabwe deposit (Namibia) shows a shift of -0.66‰ and the late acicular willemite from Berg Aukas (Namibia) a shift of -0.50‰ relative to the earlier willemites.

6. Discussion

The analyzed sphalerites have $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ values in the same range as those of hydrothermal sphalerites occurring in other deposits (Albarède, 2004; Archer and Vance, 2002; Kelley et al., 2009; Maréchal et al., 2000; Mason et al., 2005; Sonke et al., 2008; Wilkinson et al., 2005; Weiss et al., 2007; Zhou et al., 2014). The primary sphalerite displays a relatively narrow

compositional range (−0.06 to +0.41‰) in comparison with the replacing secondary minerals (Table 1).

From the Zn isotope data on secondary Zn-minerals analyzed for this study (Table 1), it is evident that the mobilization of zinc via dissolution and reprecipitation in various oxidized minerals results in measurable zinc isotope fractionation. Whether the initial replacement is hydrothermal, as may be the case for some of the willemites (e.g. Kabwe specimens; Mondillo et al., 2018), or supergene for the other phases (e.g. Pomorzanj hemimorphite; Coppola et al., 2009), there is a common pattern of enrichment of heavy zinc isotopes in the newly-formed phase. A similar positive shift of $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ compositions in secondary minerals deriving from sulfide alteration was observed in the previous studies of non-sulfide zinc minerals, which were focused on sphalerite and hydrozincite from several small deposits of the Cantabrian region in Northern Spain (Pašava et al., 2012), and on hydrozincite precipitation in the Naracauli river cross-cutting an old mining area in SW Sardinia (Italy) (Wanty et al., 2013). In the latter case, the groundwaters flowing into the river had previously leached waste dumps and hidden Zn-sulfide bodies (Wanty et al., 2013). The isotopic compositions of primary sphalerites from the above studies ($\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ −0.80 to 0.15‰) are similar to the compositions measured in other hydrothermal deposits and to those reported from our samples. In addition, the hydrozincite samples show a comparable shift to higher values, i.e. +0.01 to +0.30‰ (Pasava et al., 2012; Wanty et al., 2013). In regard to Sardinia, Wanty and co-workers (2013) argued that “complete sphalerite dissolution yields a solution with the same $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ as the precursor sulfide”, and that it is in the following precipitation step that the fractionation occurs, with the preferential incorporation of heavy zinc isotopes in the secondary Zn minerals, producing residual fluids with progressively lighter isotopic signature. However, considering that, in the upper reaches of the

stream, hydrozincite precipitates in a biologically-mediated environment, facilitated by microalgae and cyanobacteria, and that synthetic hydrozincites produced without bacteria had $\delta^{66}\text{Zn}$ identical to the dissolved Zn, the above authors concluded that the Zn isotopic fractionation between hydrozincite and waters was a biologically-mediated mineralization process (Wanty et al., 2013).

Fernandez and Borrok (2009) conducted an experimental investigation on Zn isotopic fractionation during oxidative dissolution of pure sphalerite, and observed a modest (ca. 0.2‰) initial increase in the $\delta^{66}\text{Zn}$ of the leachate relative to the sphalerite separate, which they explained invoking a change in the bonding environment for Zn in the altered surface layer of the sphalerite. In detail, as the surface coating was composed of Zn-sulfates, the oxygen-bonding would favor the preferential incorporation of the heavier Zn isotopes in the Zn-sulfate relatively to the solution that has the same composition of the original Zn-sulfide (Fernandez and Borrok, 2009). The observations of Fernandez and Borrok (2009) (and also of Wanty et al. [2013], if we exclude the biological mediation) are in agreement with the theoretical models of Ducher et al. (2016), which yielded positive $\Delta^{66}\text{Zn}$ between hydrozincite and sphalerite (+0.80‰), and between the hydrous Zn-sulfate (gunningite) and sphalerite (+0.26‰), at ambient temperature (22 °C), and attribute these differences to the crystal-chemical parameters and the Zn interatomic force constants of the considered mineral phases. In detail, β -factors are higher when the Zn-first neighbor bond lengths is smaller and charges on atoms involved in the bonding are higher and vice versa (Ducher et al., 2016).

Broadly, the observed $\Delta^{66}\text{Zn}$ shifts for all the oxidized phases analyzed for this study from the precursor sulfides are in agreement with the theoretical calculations of Ducher et al. (2016), which predicted, at equilibrium, positive $\Delta^{66}\text{Zn}$ between several oxidized minerals (e.g.

hydrozincite and hemimorphite) and sphalerite, and negative $\Delta^{66}\text{Zn}$ between smithsonite and the Zn-sulfide, on the basis of the “changing bonding environment of the Zn atoms from sulfide to non-sulfide minerals and the different crystal-chemical parameters and Zn interatomic force constants between the different phases” (Ducher et al., 2016). There are apparent exceptions to this general pattern in our data set. For example, an isotopically lighter smithsonite than the original sulfide only observed in the Irish Glendalough and Luganure samples, whereas in all the other smithsonite samples from Zambia, Poland and Yemen this Zn-carbonate shows positive shifts in $\delta^{66}\text{Zn}$ relative to the different precursor sphalerites ($\Delta^{66}\text{Zn}_{\text{sm-sph}}$ is +0.42‰ at Kabwe-Zambia, +0.22‰ at Chrzanów-Poland, and +0.61‰ at Jabali-Yemen). These positive shifts can be explained (i) by a lack of direct relationship between sphalerite breakdown and smithsonite formation, for example by the involvement of an isotopically heavy intermediate phase; or (ii) by unusual zinc complexation that favored the enrichment of heavy isotopes (for example, on organic complexes; Ban et al., 2002; Black et al., 2011; Jouvin et al., 2009; Fuji and Albarède, 2012; Marković et al., 2017). The lack of a direct relationship between sphalerite breakdown and smithsonite formation can be suggested for the Belgian smithsonites, which do not directly derive from sulfide alteration but have an intermediate willemite precursor (Coppola et al., 2008). In this case, the Belgian smithsonites are characterized by $\delta^{66}\text{Zn}$ lower than their willemite precursor ($\Delta^{66}\text{Zn}_{\text{sm-will}}$ is between -0.5‰ and -0.9‰) and therefore fit the theoretical equilibrium Zn isotope fractionation model (Ducher et al., 2016). A similar argument can also be made for the Zambian samples where willemite is intermediate between sphalerite and smithsonite (Fig. 4). The best example suggesting an effect/influence of soil-derived organic ligands in the Zn isotopic fractionation is in the Polish samples. The smithsonites from Poland are mostly characterized by isotopically light carbon, reflecting derivation of organic carbon

from C3-vegetated soils overlying the deposits (Gilg et al., 2008; Coppola et al., 2009). It is therefore well plausible that organic complexes were present in the waters percolating through the vegetated soils, and that these were responsible for alteration of sulfides, Zn transportation and secondary Zn mineral precipitation (McPhail et al., 2003).

Assessing the other minerals, several important conclusions can be drawn. In the Namibian Berg Aukas and Baltika specimens, the first willemite generations (NAR0427A-2 and BA2003-4) formed after sphalerite alteration have compositions (+0.07‰, +0.08‰) slightly heavier than the precursor sulfide (−0.06‰). Although β -factors for willemite do not exist (Ducher et al., 2016), because Zn is tetrahedrally coordinated with oxygen in willemite like in hemimorphite, it is likely that the β -factors for these phases would be comparable. Thus, willemite formation from sphalerite might be expected to produce a positive $\Delta^{66}\text{Zn}$ relative to the original sulfide, as is observed in the Namibian willemite 1 samples. The second willemite generation (BA2003-13.2), however, is strongly depleted relative to willemite 1 ($\Delta^{66}\text{Zn}_{\text{w2-w1}}$ is −0.35‰). Considering that the observed fractionation concerns specimens of the same mineral species, likely formed at similar temperatures from similar fluids (Schenider et al., 2008; Terracciano, 2008), it is not possible to explain their diverse composition by simply using equilibrium isotope fractionation mechanisms. In this case, it is possible to explain the depleted compositions of the paragenetically late willemite via a Rayleigh-type distillation model. It is envisaged that initial dissolution of sphalerite and the formation of a Zn-bearing solution with initial composition equal to the original sulfide is followed by Zn re-precipitation into a series of secondary oxide phases. As long as Zn reprecipitation is incomplete, the formation of isotopically-heavy, neo-

formed Zn minerals will produce a depleted fluid that can progressively evolve back towards the primary sulfide composition, or even pass it (Fig. 5A). The equation describing this process is:

$$\frac{R_{pm}}{R_{dm0}} = \alpha f^{\alpha-1}$$

where, R_{dm0} is the isotope ratio of the initial solution corresponding to the isotope ratio of the original dissolved mineral (assuming its complete dissolution), and R_{pm} is the isotope ratio of the precipitated mineral; f is the fraction of residual metal in solution and the fractionation factor α is given by R_{pm} / R_{dm} . In this model, a solution with starting $\delta^{66}\text{Zn}$ bulk composition of 0.1‰, resulting from the complete dissolution of a sphalerite with the same composition ($\delta^{66}\text{Zn}_{\text{sph}} = 0.1\text{‰}$ is the median value of all the sphalerite shown in Fig. 4), will produce precipitates with different $\delta^{66}\text{Zn}$ compositions using a α -fractionation factors between the mineral and the fluid, and the mass percent of metal precipitated (Fig. 5). For example, an α -fractionation factor of 1.0015 (which is ca. the α -fractionation factor between hemimorphite and sphalerite at $T = 22^\circ\text{C}$; Ducher et al., 2016) reproduces both the highest (which are formed from the first small amounts of precipitation), and the lowest (which form when about 75% of the metal has been deposited) $\delta^{66}\text{Zn}$ values occurring in our dataset (that are $\delta^{66}\text{Zn} = 1.39\text{‰}$ La Calamine-Belgium willemite, $\delta^{66}\text{Zn} = -0.42\text{‰}$ Berg Aukas-Namibia willemite 2). However, at any point, sudden supersaturation of the solution could dump out the total Zn with the same composition of the fluid at that point (i.e. no further fractionation occurs). This model is consistent with the nature of the isotopically-light samples from Namibia, Zambia and Yemen which all occur as paragenetically late phases (willemite, hemimorphite and hydrozincite respectively; see Figure 4). In detail, from this model, the Kabwe hemimorphite could have been precipitated once about 70% of the metal had been deposited from a fluid with an initial $\delta^{66}\text{Zn}$ value of 0.1‰ (i.e. the composition of the dissolved precursor willemite). Assuming an initial $\delta^{66}\text{Zn}$ value of about

0.60‰ for the fluid sourcing the Jabali hydrozincite (corresponding to the mean value of precursor smithsonites), the model predicts a precipitation of the hydrozincite (0.25‰) after almost 75% of the metal in solution had been already deposited (Fig. 5B).

The $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ values (comprised between 0.14‰ to 0.61‰) of the sauconite samples from the Yanque deposit (Peru) show that significant isotopic variability also occurs in the same secondary mineral within one system. There is evidence of zonation in the orebody with the highest isotopic values in the center and a trend towards lower values towards the southern limits of the deposit at depth, as well as a decrease upwards and outwards (see Table 1 for sample positions and compositions). The genetic model of the Yanque deposit proposed by Mondillo et al. (2014b) suggests that sauconite formed after a process of supergene wall-rock replacement (*sensu* Hitzman et al., 2003), where Zn released from the complete dissolution of sphalerite precipitated as sauconite after the reaction of Zn-bearing solutions with the silicatic country rock. The process likely started in the center of the present orebody, and progressively propagated southward from surficial zones into more deeply buried strata (Mondillo et al., 2014b). In line with this model, the observed $\delta^{66}\text{Zn}$ zonation in the analyzed Yanque sauconites can be explained by preferential incorporation of heavy Zn isotopes in earlier formed sauconite in the core of the system, with fluids depleted in these isotopes generating the lower values in peripheral areas (e.g. YA 45 SAM 32). Thus, this spatial variation is consistent with the Rayleigh-type distillation model proposed above that can also account for a temporal (paragenetic) evolution from initial isotopically heavy phases, toward later, isotopically light ones.

7. Conclusions

The results of this study clearly indicate that supergene and hydrothermal processes on Zn mineralizations produce more significant fractionation of zinc isotopes, than previously observed (e.g. Wanty et al., 2013). The variation in Zn isotope composition through the different minerals/sampled sites can be explained by a combination of equilibrium isotope fractionation (Ducher et al., 2016) and open system Rayleigh distillation during incomplete dissolution-reprecipitation reactions. We also observed that zones where more complete replacement of primary sulfide occurs will result in minor fractionation, as the majority of mobilized zinc is redeposited without significant removal of the light zinc isotopes.

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Figure captions

Figure 1 – Locations of the nonsulfide Zn deposits sampled for this study.

Figure 2 – Typical ore samples from the studied localities. A. Belgium. Willemite from the La Calamine deposit. B. Poland. Sphalerite concretions directly replaced by smithsonite (from Coppola et al., 2009). C. Namibia. Willemite 1 directly replacing sphalerite, and cross-cut by veins and geodes filled by willemite 2 (Berg Aukas). D. Zambia. Willemite directly replacing sphalerite (Kabwe). E. Zambia. Supergene smithsonite concretions, with hemimorphite overgrowths (Kabwe). F. Yemen. Smithsonite concretions in drillcore J125 (Jabali) (from Mondillo et al., 2014a). G. Yemen. Galena and sphalerite oxidized to cerussite and smithsonite in drillcore J125 (Jabali) (from Mondillo et al., 2014a). H. Peru. Massive sauconite in drillcore YA20 (Yanque) (from Mondillo et al., 2014b). Hm = hemimorphite, Sau = sauconite, Sm = smithsonite, Sp = sphalerite, Will = willemite.

Figure 3 – Diagram showing the distribution of $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ compositions of the studied Zn minerals, compared with literature data. ¹ = data from Pašava et al. (2012); ² = data from Wanty et al. (2013); ³ = data from Araújo et al. (2017); ⁴ = data from Wilkinson et al. (2005) and Wilkinson (unpublished); ⁵ = data from Archer and Vance (2002), Albarède (2004), Kelley et al. (2009), Maréchal et al., (1999), Mason et al. (2005), Pašava et al. (2014), Zhou et al. (2014).

Figure 4 – Paragenetic relationships between the studied Zn minerals in the various districts. * = data from Sonke et al. (2008); # = data from Wilkinson et al. (2005) and Wilkinson

(unpublished): 5th, 25th, 75th, and 95th percentiles are whiskers and box, the star is the median value. Grey field is the range of primary sulfides.

Figure 5 - Rayleigh-type distillation model predicting the composition of the precipitating phase, assuming progressive precipitation from an evolving solution composition. A) The starting (bulk) $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ composition of the solution is 0.1‰ - based on the assumption of initial dissolution of sphalerite with bulk composition (the median value of all the sphalerites shown in Figure 4) - and the curves for a range of different α -fractionation factors are shown. $\alpha=1.0015$ reproduces the heaviest (which are formed from the first small amounts of precipitation) and the lightest values (which form when about 75% of the metal has been deposited) occurring in our dataset. At any point, the supersaturation of the solution could dump out the total Zn with the same composition of the fluid at that point (i.e. no further fractionation). B) The starting (bulk) $\delta^{66}\text{Zn}_{\text{JCM-Lyon}}$ composition of the solution is 0.6‰, representing the fluid sourcing the Jabali hydrozincite (corresponding to the mean value of the precursor smithsonites): the model predicts precipitation of a hydrozincite with a composition of 0.25‰, after almost 75% of the metal in solution had been already deposited. [1] = α -fractionation factors for the pairs hemimorphite-sphalerite, hydrozincite-sphalerite, and smithsonite-sphalerite (Ducher et al., 2016) – here we assume that the precipitating fluid has the same $\delta^{66}\text{Zn}$ composition of dissolved sphalerite. [2] = α -fractionation factor for the pairs hydrozincite-smithsonite (Ducher et al., 2016) – here we assume that the precipitating fluid has the same $\delta^{66}\text{Zn}$ composition of dissolved smithsonite.

Table 1. Zn isotopic compositions of the analyzed samples.

Sample ID	Location	$\delta^{66}\text{Zn}/^{64}\text{Z}$		$\delta^{66}\text{Zn}/^{64}\text{Z}$		$\delta^{67}\text{Zn}/^{64}\text{Z}$		$\delta^{68}\text{Zn}/^{64}\text{Z}$		$\delta^{68}\text{Zn}/^{64}\text{Z}$	
		n	±	n	±	n	±	n	±	n	±
		‰ IRMM 3702	2 S.D.	‰ Lyon JMC 3- 0749L	2 S.D.	‰ Lyon JMC 3- 0749L	2 S.D.	‰ IRMM 3702	2 S.D.	‰ Lyon JMC 3- 0749L	2 S.D.
RN5011 Galena	Belgium - Moresnet mine			0.34	0.19	0.52	0.28			0.71	0.35
RN5011 Willemite	Belgium - Moresnet mine			0.98	0.09	1.51	0.22			2.24	1.46
RN2300 Willemite	Belgium - Fossey mine			1.31	0.13	1.83	0.33			2.39	0.32
RN2300 Smithsonite	Belgium - Fossey mine			0.44	0.06	0.50	0.55			0.75	0.54
R2B35/3925 Willemite	Belgium - La Calamine mine			1.39	0.07	2.02	0.03			2.70	0.03
R2B35/3925 Smithsonite	Belgium - La Calamine mine			0.85	0.08	1.30	0.22			1.61	0.39
BM1964R-6305 Sphalerite	Ireland - Glendalough mine, Glendalough, Co Wicklow.			0.31	0.25	0.44	0.35			0.55	0.28
BM1964R-6305 Smithsonite	Ireland - Glendalough mine, Glendalough, Co Wicklow.			-0.15	0.08	-0.19	0.27			-0.27	0.21
BM1964R-6307 Sphalerite	Ireland - Old Luganure mine (dump), Glendasan, Co Wicklow.			0.24	0.04	0.39	0.12			0.55	0.18
BM1964R-6307 Smithsonite	Ireland - Old Luganure mine (dump), Glendasan, Co Wicklow.			-0.09	0.07	-0.12	0.09			-0.14	0.08
CW-1 Sphalerite	Ireland - Galmoy			0.33	0.078						
CW-1 Smithsonite	Ireland - Galmoy			0.353	0.147						
CW-AF Smithsonite	Ireland - Galmoy			0.455	0.071						

CV05-80 Sphalerite	Poland - Pomorzanj mine	-0.01	0.05	-0.13	0.57	-0.01	0.16
CV05-80 Hemimorphite	Poland - Pomorzanj mine	0.22	0.07	0.34	0.15	0.45	0.15
CV05-71 Sphalerite	Poland - Chrzanów	0.26	0.12	0.41	1.04	0.36	0.51
CV05-71 Smithsonite	Poland - Chrzanów	0.48	0.06	0.67	0.12	0.83	0.21
NAR0427A-1 Sphalerite	Namibia - Baltika mine	-0.06	0.02	-0.06	0.08	-0.19	0.12
NAR0427A-2 Willemite	Namibia - Baltika mine	0.08	0.12	0.16	0.14	0.09	0.26
BA2003-4 Willemite I	Namibia - Berg Aukas mine	0.07	0.05	0.07	0.01	0.18	0.09
BA2003-13.2 Willemite II	Namibia - Berg Aukas mine	-0.42	0.07	-0.70	0.10	-0.92	0.11
ZA0502-D Sphalerite	Zambia - Kabwe mine Pit 5/6	-0.02	0.01	-0.10	0.05	-0.15	0.05
ZA0502-M Willemite I	Zambia - Kabwe mine Pit 5/6	0.10	0.01	0.15	0.02	0.14	0.00
ZA0511-1 Hemimorphite	Zambia - Kabwe mine Pit 2	-0.26	0.04	-0.35	0.09	-0.40	0.07
ZA0511-2 Smithsonite	Zambia - Kabwe mine Pit 2	0.40	0.11	0.67	0.17	0.77	0.14
$\delta^{66}\text{Zn}/^{64}\text{Z}$ n calculate d to ‰ JMC- Lyon (+0.29‰) *							
J125-5 Sphalerite	Yemen - Jabali	-0.05	<0.17	0.24		0.02	<0.17

J125-7 Sphalerite	Yemen - Jabali	0.11	<0.17	0.40	0.16	<0.17
J125-9 Smithsonite	Yemen - Jabali	0.56	<0.17	0.85	1.19	<0.17
J125-32 Smithsonite	Yemen - Jabali	0.23	<0.17	0.52	0.36	<0.17
JS MON 6 Smithsonite	Yemen - Jabali	0.14	<0.17	0.43	0.25	<0.17
JS MON 22B						
Hydrozincite	Yemen - Jabali	-0.04	<0.17	0.25	-0.02	<0.17
YA 13 SAM 12 Sauconite	Peru - Yanque - northern limb of the orebody (surficial)	-0.04	<0.17	0.25	-0.21	<0.17
YA 17 SAM 16 Sauconite	Peru - Yanque - central part of the orebody (surficial)	0.24	<0.17	0.53	0.38	<0.17
YA 20 SAM 19 Sauconite	Peru - Yanque - eastern side of the orebody (surficial)	-0.15	<0.17	0.14	-0.36	<0.17
YA 31 SAM 24 Sauconite	Peru - Yanque - southern limb of the orebody (deep)	0.32	<0.17	0.61	0.70	<0.17
YA 34 SAM 25 Sauconite	Peru - Yanque - southern limb of the orebody (deep)	0.25	<0.17	0.54	0.44	<0.17
YA 40 SAM 29 Sauconite	Peru - Yanque - southern limb of the orebody (deep)	0.15	<0.17	0.44	0.25	<0.17
YA 45 SAM 32 Sauconite	Peru - Yanque - southern limb of the orebody (deep)	0.07	<0.17	0.36	-0.01	<0.17

* correction value from Moeller et al. (2012)

Highlights

- Zinc isotope data from nonsulfide zinc mineral separates (willemite, smithsonite, hemimorphite, hydrozincite, sauconite) collected from seven major ore deposits worldwide
- Significant fractionations both in positive and negative directions are recorded relative to the precursor phase
- Partial dissolution of primary sphalerite is followed by precipitation of a secondary phase preferentially incorporating heavy Zn isotopes
- Negative isotopic shifts are only observed for late crystallizing phases, and are interpreted to reflect precipitation from residual, isotopically light fluids

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5