Title	Zn, Fe and S isotope fractionation in a large hydrothermal system
Authors(s)	Gagnevin, Damien, Boyce, Adrian, Barrie, Craig, Menuge, Julian, Blakeman, Robert
Publication date	2012-07-01
Publication information	Gagnevin, Damien, Adrian Boyce, Craig Barrie, Julian Menuge, and Robert Blakeman. "Zn, Fe and S Isotope Fractionation in a Large Hydrothermal System" 88 (July 1, 2012).
Publisher	Elsevier
Item record/more information	http://hdl.handle.net/10197/3869
Publisher's statement	This is the author's version of a work that was accepted for publication in Geochimica et Cosmochimica Acta. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Geochimica et Cosmochimica Acta (Volume 88, 1 July 2012, Pages 183–198) DOI:10.1016/j.gca.2012.04.031 Elsevier Ltd.
Publisher's version (DOI)	10.1016/j.gca.2012.04.031

Downloaded 2023-04-07T10:52:29Z

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa)

© Some rights reserved. For more information

Zn, Fe and S isotope fractionation in a large hydrothermal system

Gagnevin D.^{1*}

Boyce A.J.²

Barrie C.D.^{2†}

Menuge J.F.¹

Blakeman R.J.³

¹UCD School of Geological Sciences, University College Dublin, Belfield, Dublin 4, Ireland

² Scottish Universities Environmental Research Centre, East Kilbride, Glasgow G75 0QF, Scotland

³ Boliden Tara Mines Limited, Navan, County Meath, Ireland

Submitted to: *Geochimica et Cosmochimica Acta*

2 Tables, 7 Figures, 1 Appendix

* Corresponding author: Damien.Gagnevin@ucd.ie; tel (+353) 1716 2326; Fax (+353)

1283 7733

† Present Address: Isoprime Ltd., Isoprime House, Earl Road Cheadle Hulme, Cheadle,
SK8 6PT, England

ABSTRACT

The genesis of hydrothermal ore deposits is of crucial economic importance. This study investigates the extent, causes and consequences of zinc and iron isotope fractionation in a large hydrothermal system at the world-class Navan Zn-Pb orebody, Ireland. Large variations in Zn, Fe and S isotope compositions have been measured in microdrilled sphalerite (ZnS) at the millimetre scale. $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ display a well-defined positive correlation and both also correlate with $\delta^{34}\text{S}$. These relationships represent the combined effects of kinetic Zn and Fe isotope fractionation during sphalerite precipitation, and S isotope variation through mixing of hot, metal-rich hydrothermal fluids and cool, bacteriogenic sulfide-bearing brines. Combined with S isotope data, $\delta^{56}\text{Fe}$ and $\delta^{66}\text{Zn}$ data on mine concentrates confirm that hydrothermal sulfide is a minor component of the overall deposit signature. Our data suggest that incoming pulses of metal-rich hydrothermal fluid triggered sulfide mineralisation, and that rapid precipitation of sphalerite from hydrothermal fluids will lead to strong kinetic fractionation of Zn and Fe isotopes at very short time and length scales, thereby limiting the use of Fe and Zn isotopes as exploration tools *within* deposits, but revealing the possibility of detecting new deposits from isotopically heavy Zn-Fe geochemical halos.

1. INTRODUCTION

Elucidation of fluid pathways, sulfide precipitation environments and the quantification of sulfide crystallization are important, but often poorly known, factors in mineral exploration that is increasingly directed to more deeply buried targets. The extent and causes of isotope fractionation of transition metals in low to medium temperature hydrothermal systems show potential for mineral exploration (Kelley et al., 2009). Studies of Zn isotopes in hydrothermal environments suggest the incorporation of light isotopes in sulfides in deeper/hotter parts of the hydrothermal system; kinetic Raleigh isotope fractionation has been inferred to account for the evolution from light to heavy Zn isotopic composition, i.e. residual fluid and late precipitates should have heavy Zn (Wilkinson et al., 2005a; Mason et al., 2005; John et al., 2008; Sivry et al., 2008; Kelley et al., 2009; Dekov et al., 2010). In most studies, the databases are limited in terms of their sample coverage, mass balance and their ability to quantify relative fractionations.

Fe isotopes may be significantly fractionated by redox processes (e.g. Dauphas and Rouxel, 2006, and references therein), yielding a greater range in Fe isotopic composition in natural environments (up to 5‰), compared to Zn (<0.5‰ in most cases) for which redox processes are unimportant, as Zn has only one common oxidation state, Zn^{2+} . Abiotic kinetic Fe isotope fractionation has been demonstrated in a range of hydrothermal settings and sedimentary environments (Rouxel et al., 2003; 2004; Matthews et al., 2004; Markl et al., 2006; Busigny and Dauphas, 2007; Dekov et al., 2010). Studies of the effects of sulfide precipitation on Fe isotopic systems are largely restricted to Fe and Fe-Cu sulfides (e.g., Rouxel et al., 2003; 2004; Butler et al., 2005; Guilbaud et al., 2010; 2011). Sulfides formed at low to medium hydrothermal temperatures (100-320°C) at the seafloor contain isotopically light Fe (Rouxel et al., 2003; 2004). However, there remain few metal stable

isotopic data from low to medium temperature ore systems, especially for economic sulfides in large economic deposits. Furthermore the potential value of combined Zn-Fe isotopic data, on which our study focuses, has not previously been explored.

This study examines the world-class Navan Zn-Pb ore deposit (Fig. 1) to elucidate spatial and temporal variations of Zn and Fe isotopes within a large hydrothermal system. These data are coupled with new data on S isotopes, whose behavior in Irish-type ore systems is already well established (e.g. Fallick et al., 2001). Navan comprises stratabound sphalerite-galena-Fe sulfide lenses precipitated primarily via carbonate replacement, with subordinate open space filling, during normal faulting (Ashton et al., 2003). By taking samples of layered sphalerite, bulk Zn concentrates (Fallick et al., 2001) and potential source rocks (Walshaw et al., 2006), we are able to examine processes of metal isotopic fractionation ranging from millimeter to kilometer scales. Layered textures are common in sphalerite across a range of ore deposit styles (Barrie et al., 2009a, and references therein) and where colloform in nature (Roedder 1968) faithfully record ore crystallization at a fine scale. Bulk concentrates, representing several thousand tonnes of ore, offer insight into the behavior of the large-scale ore system, and constrain mass balance.

2. GEOLOGY OF THE NAVAN ORE DEPOSIT

Ireland is host to several significant carbonate-hosted, base metal ore deposits which together currently represent the greatest concentration of Zn, per square kilometer, on Earth (Singer, 1995). The Navan ore deposit (Fig. 1) is the largest of these Irish-type base metal deposits, a deposit class commonly considered to be part of a larger group of carbonate-hosted base metal deposits that has affinities to both Mississippi Valley-type (MVT) (Leach and Sangster, 1993) and SEDEX deposits (Blakeman et al., 2002). In almost continuous

production since 1977, and currently the largest zinc producer in Europe, the ore already extracted at Navan plus reserves together amount to more than 105 million tonnes at an average grade of ~8.3 % zinc and ~2.1% lead (Ashton et al., 1986, 2003). Improved understanding of the Navan ore deposit is the key to understanding Irish-type ore deposits and hence will support mineral exploration strategies.

In the Navan area, Lower Carboniferous sedimentary rocks lie unconformably on deformed Lower Palaeozoic rocks of the Longford-Down Inlier. The NE-trending Ordovician succession includes sedimentary and basic to intermediate volcanic rocks and is enclosed to the NW and SE by Silurian greywackes, sandstones, siltstones and mudrocks (Vaughan, 1991). Faunal, structural, isotopic and geophysical evidence suggest that the Lower Palaeozoic rocks lie just above the northward-dipping Iapetus Suture (Phillips, 2001). A Precambrian gneissic basement at 3-4 km depth has been proposed on geophysical evidence (Williams and Brown, 1986), but there are no exposures of Precambrian rocks.

The Lower Carboniferous succession (Philcox, 1984; Strogon et al., 1996) has been ascribed to a northerly marine transgression. The Courceyan Navan Group comprises thin red beds which pass upwards into a varied sequence of locally dolomitised, shallow marine carbonates, with lesser amounts of sandstone and shale (Anderson et al., 1998). The ore deposit is hosted primarily in the Pale Beds which dominate the Courceyan sequence in the mine, and which comprise pale to medium grey micrites, oolitic and bioclastic calcarenites, dolomite, calcareous sandstones and minor shale-silt layers. The main orebody at Navan consists of a stacked series of stratabound lenses divided into several zones by major NE to ENE-trending faults (Anderson et al., 1998; Ashton et al., 2003). The Pale Beds are overlain successively by the Courceyan Shaley Pales, which also contain economic

mineralisation, and the Courceyan to Chadian Argillaceous Bioclastic Limestones and Waulsortian Limestones, which do not contain significant ore at Navan, but do so elsewhere in Ireland (Hitzman, 1995). Mineralisation is spatially and temporally associated with Courceyan to Chadian extensional faulting, though the exact relationship between faulting and mineralisation remains contentious, as does the timing of ore deposition (e.g. Anderson et al., 1998; Peace and Wallace, 2000; Blakeman et al., 2002; Symons et al., 2002).

The economic minerals of the Navan deposit comprise sphalerite and galena; gangue minerals include pyrite, marcasite, barite, calcite and dolomite. Broadly, the main ore stage generally consists of massive and banded sphalerite, commonly accompanied by galena and iron sulphides, with calcite and sometimes dolomite both pre- and post-dating ore (Hitzman, 1995; Braithwaite and Rizzi, 1997). Textures of the main ore stage minerals predominantly result from carbonate replacement, but laminated ores filling open cavities and fractures are also common (Ashton et al., 1986, 2003; Anderson et al., 1998).

Published fluid inclusion data indicate fluids with homogenisation temperatures (T_h) ranging from 75 – 170 °C and salinities of 6 – 18 wt. % NaCl equiv. (Wilkinson 2010). Sulfur in the Navan ore deposit, as with other Irish-type economic deposits, has a dual source resulting from mixing of a deep, relatively hot hydrothermal fluid and a shallow, relatively cool surface brine, bearing two distinct S sources (Boyce et al., 1983; Anderson et al. 1998; Fallick et al. 2001; Wilkinson et al., 2005b). At Navan, the hydrothermal end-member is characterised by $\delta^{34}\text{S}$ values clustering around $+10 \pm 10\%$, which is isotopically consistent with the dominant range of $\delta^{34}\text{S}$ in diagenetic pyrite in Lower Palaeozoic rocks regionally (Anderson et al. 1989; Fallick et al. 2001; Blakeman et al. 2002). The shallow

brine is an evaporated seawater, dominated by isotopically light bacteriogenic sulfide, derived from the open-system (with respect to sulfate) bacterial reduction of Lower Carboniferous seawater sulfate, with $\delta^{34}\text{S}$ typically around $-15 \pm 10\text{‰}$ during ore deposition. (Anderson et al., 1998; Fallick et al., 2001; Blakeman et al., 2002). Compared with the bacteriogenic sulfide, basement-derived hydrothermal sulfide is volumetrically minor ($<10\%$ total ore sulfide; Fallick et al. 2001), a continuous source of bacteriogenic sulfide being essential for the development of the giant ore deposit at Navan (Anderson et al. 1998; Fallick et al. 2001). Ore precipitation is known to have occurred where the two fluids met. Blakeman et al. (2002) showed that extensional faults, active during and after deposition of the Pale Beds, acted as conduits for the hydrothermal fluids, characterised by positive $\delta^{34}\text{S}$ values and relatively coarse sulfide textures. They also showed that bacteriogenic sulfide dominated outwith 3m of the footwall of these faults.

Pb isotope analysis of Navan galena, and other Irish-type deposit sulfides, provides strong evidence of derivation of the Pb, and presumably Zn and Fe, from local underlying Silurian and Ordovician sedimentary and volcanic rocks (LeHuray et al., 1987; Mills et al. 1987; Dixon et al., 1990). Furthermore, leaching experiments of typical Lower Palaeozoic lithologies also indicate release of Pb, Zn and Fe in ratios similar to those found within the overlying ore deposits (Bischoff et al., 1981). Thus, there is compelling evidence that the hydrothermal fluid carried all the metals, and some sulfide, with the latter having a distinct ^{34}S -enriched character, compared to the surface fluid. By contrast, whilst the surface fluid carried what was to be the critical bacteriogenic sulfide source, there is little evidence that this fluid, buffered overwhelmingly by carbonates, with minor clastics, carried any Zn, Pb or Fe (Walshaw et al., 2006). Thus, whilst a two component mixing model is essential to understand S isotope variations, it is not justified to account for any Zn, Pb or Fe isotope variations in the deposits.

3. SAMPLES

Five representative drill-core samples (21643B, 21642E, 21642C, 21644A and NO1663-NV3, hereafter named D1, D2, D3, D4 and D5, respectively; Fig. 2) were collected from the north-east of the deposit in the 5-lens, the stratigraphically lowest and largest ore lens (Fig. 2; Blakeman et al., 2002; Ashton et al., 2003). Sample details can be found in the Appendix.

Although mineralogy at Navan is relatively simple, paragenesis is complex (Fig. 2). Common textures include: 1) well-defined, sometimes colloform, layers of sphalerite (Fig. 3a); 2) widespread skeletal/dendritic galena (Fig. 3a) and 3) various combinations of individual sulfide grains and textures with a chaotic, clastic arrangement (Fig. 2). Details of the layered sphalerite textures are illustrated in Fig. 3, along with inferred growth directions. Sphalerite in samples D3 and D4 has very similar individual layer thickness (>0.3 mm), moderate variation in colour and occurrence of resorbed galena within the layered zones (Fig. 3a, c). In contrast, sample D1 is characterised by extremely fine layering (mean = 0.2 mm, but often <0.1 mm; Fig. 2a), greater colour contrasts and the absence of galena. The texture in sample D2 differs from the other three as it consists of a sequence of thick layers of more granular, fine-grained sphalerite intergrown with barite (Fig. 2b).

Sample D5 (Fig. 2e) was also investigated, since a bacteriogenic sulfur signature was determined in sphalerite from this sample (minimum $\delta^{34}\text{S}$ of -15.5‰; Barrie et al., 2009b). The texture in D5 closely resembles that of sample D2, with layering instead of fine rhythmic banding, the absence of galena associated with sphalerite, and the widespread occurrence of barite finely intergrown with sphalerite.

Four mine concentrates from the U-Lens and 1-Lens at Navan were also analysed for their Zn, Fe and S isotopic compositions. In addition, six basement samples from the U9555 core drilled beneath the Navan orebody on the footwall of the B-fault (Fig. 2) were analysed. These basement samples span a range of mineral and chemical compositions, including felsic tuff, agglomerate, volcanogenic sediment, altered shist and mudstones.

One previous significant study has been published on Zn isotopes in the Irish orefield, that of Wilkinson et al. (2005a), which was essentially a pathfinder study, and one of the first ever papers publishing ore deposit Zn isotope data. One sample was from Navan, and was specified as being from the orebody, the remaining samples being a variety of sphalerites from Lower Palaeozoic hosted veins, other producing ore deposits and prospects. In contrast, our study focuses fully on the Navan deposit, which is at least 5 times larger than any Irish-type deposit discovered to date. We also provide a view from a variety of well characterised scales, from both bulk mine concentrates and sub-millimetre textures.

4. ANALYTICAL PRODECURE

4.1. Microsampling

Sampling of individual sphalerite layers for Zn and Fe isotope analysis has been carried out using a New Wave computer-controlled micromill, at a spatial resolution of 100-300 μm . The zone for microdrilling was targeted on the basis of both adequate textural features (including minimal amount of barite inclusions) and, in some cases, the reported $\delta^{34}\text{S}$

results (sample D5; Barrie et al., 2009b). Care was taken to sample individual sphalerite bands that were visually free of other minerals. An example is shown in Fig. 4 on sample D1. Minute crystals of barite could not be avoided during microsampling of samples D2 and D5. These were not removed by chemical treatment, to avoid increasing the Fe blank. However, petrographic observations suggest that barite represents a minor proportion of the sulfide fraction analysed in both samples (<10%). 10% barite would have negligible effect on Zn, Fe and Pb isotope ratios.

4.2. Chemistry

Prior to Zn, Fe and Pb isotopic analysis, sphalerite micro-samples were chemically purified on small columns containing 1 mil of pre-cleaned 200-400 mesh AG1-X8 anion-exchange resin, using a protocol adapted from Yamakawa et al. (2009) and Dauphas et al. (2009a). The digestion and chemical separation procedure used is detailed in Table 1. The same method was applied for both sulfide and whole-rock samples. We found that another purification step, which would have added some additional blank (especially critical for Fe isotopic analyses; see below) was not necessary to obtain reliable isotopic data with acceptable uncertainties. Full recovery of Zn and Fe was determined semi-quantitatively by comparing voltages between unprocessed and processed standard materials, and found to be complete ($100 \pm 2\%$).

4.3. Mass spectrometric measurements

Zn, Fe and Pb isotopic measurements were carried out using a Thermo-Scientific Neptune MC-ICP-MS instrument, while S isotopic measurements were carried out by in-situ laser

ablation attached to a gas extraction line and a VG SIRA II isotope ratio gas mass spectrometer. Details of the methods are described below.

4.3.1. Zn isotopic analyses

A stable introduction system (SIS) consisting of double-pass Scott spray chamber with a self-aspirating concentric PFA nebulizer was used for Zn, Fe and Pb isotopic measurements. The low-resolution entrance slit was used in this study for Zn and Pb isotopic analyses. As both Cu-doping and standard-bracketing methods were tested as alternatives for optimum isotopic measurements (see below), the Faraday cups were aligned to measure ^{64}Zn (L2), ^{66}Zn (centre), ^{67}Zn (H1), ^{68}Zn (H2), ^{70}Zn (H4), ^{63}Cu (L3) and ^{65}Cu (L1) isotopes. One measurement consisted of 80 integrations of 4.2 s, comprising four blocks of 20 cycles each. On-peak baseline was performed before each block, and peak centring on ^{64}Zn was carried out at the start of the sample isotopic measurement. Standards and samples were measured in solution in ultra-pure 0.34M HNO_3 . Ultra-pure c. 0.5M HNO_3 was aspirated between each measurement for at least 1 minute. Ni skimmer and sample cones were used for both sample and standard measurements.

Zn isotopic ratios are expressed in standard delta notation in per mil units relative to the average value of the respective bracketing standards, as follows:

$$\delta^{66}\text{Zn}_{\text{IMC}} = [({}^{66}\text{Zn} / {}^{64}\text{Zn})_{\text{sample}} / ({}^{66}\text{Zn} / {}^{64}\text{Zn})_{\text{IMC}} - 1] * 1000$$

The Johnson Matthey Purotronic Zn metal (batch 12053; reference IMC Zn) was used both as in-house standard bracket and normalising standard. The widely used ‘Lyon’ Zn

standard JMC 3-0749L was not available at the time of analyses due to its exhaustion. Currently, no data exist on the isotopic difference between standards IMC 12053 and JMC 3-0749L. Mason et al. (2005) reported 0.09‰ isotopic differences between Purotronic IMC 27040 Zn (i.e. same metal wire but different batch number to our in-house standard) and JMC 3-0749L Zn. A similar fractionation factor is expected between IMC 12053 Zn and JMC 3-0749L Zn. Despite not being negligible, this would not affect the total range of $\delta^{66}\text{Zn}$ displayed by our data (0.55‰), though individual analyses may be shifted by c. 0.1‰ towards heavier Zn if normalised to the Lyon JMC Zn standard. However, the similar Zn isotopic range between our data and those reported in Wilkinson et al. (2005a), as well as acceptable values for the SRM 682 standard (see below), both suggest a very small to negligible effect. Our Zn isotope data can thus be directly compared with existing Zn isotope data reported from the Irish orefield (Wilkinson et al., 2005a).

A method of sample-standard bracketing was adopted (e.g. Bermin et al., 2006), with particular care in matching intensities between sample and standard. On average, three sample analyses were carried out, each being bracketed by two standard analyses. Cu doping coupled with standard-bracketing was also tested as an alternative for mass bias correction (Stenberg et al., 2004; Chen et al., 2009), but did not offer substantial improvements on data quality and time of analyses compared to the normal standard bracketing method. The extent of instrumental mass bias for Zn (assessed using repeated measurements of IMC Zn standard) in our Neptune instrument is indistinguishable from that theoretically predicted (Fig. 5).

Sample analyses were carried out at least twice (up to four times in some cases, see Table 2) in separate analytical sections. The reported results are an average of these repeats (average uncertainty of 0.03‰, SD). Sample uncertainties were also independently assessed

using the pooled standard deviation (as defined in John et al., 2007) on samples analysed a number of times (samples drilled from D1; see Table 2). The resulting uncertainty ($\pm 0.07\text{‰}$) is comparable to the instrumental reproducibility based on multiple analyses of standard IMC Zn ($\pm 0.03\text{‰}$; $n = 120$), and compares with uncertainties for both standard and sample analyses ($\pm 0.04\text{‰}$; see above).

The robustness of our method was assessed by repeating the entire procedure (including microdrilling, dissolution, chromatographic separation and spectrometry) on two sphalerite samples (D4-drill 6 and D3-drill 6; Table 2) drilled along the same growth bands. More sphalerite was drilled in both cases (at least twice as much) to also assess the validity of our blank correction for Fe (see below). For $\delta^{66}\text{Zn}$, identical results were obtained in the two cases (Table 2), giving us confidence in the reliability of our method, which can be applied to a variety of sample material. In all cases, the blank contributed less than 0.01% of the total sample signal and is thus insignificant, and, unlike Fe, does not require any blank correction procedure.

$\delta^{66}\text{Zn}$ (delta notation relative to IMC Zn) for synthetic standard SRM 682 and MASS-1 sulfide standard (Wilson et al., 2002) are $2.51 \pm 0.03\text{‰}$ (SD, $n = 6$) and $0.02 \pm 0.06\text{‰}$ (SD, $n = 4$), respectively. Our value for standard SRM 682 is within error of that reported in John et al. (2007) ($2.45 \pm 0.05\text{‰}$). The $\delta^{66}\text{Zn}$ value for MASS-1, which was digested following a procedure adapted from Wilson et al. (2002) using a combination of concentrated HF, HNO_3 , aqua regia and 6M HCl, is the first published analysis for this sulfide standard. One Zn isotopic analysis was obtained for standard NOD-P1 ($0.63 \pm 0.07\text{‰}$, SD) using substantially more material than for Fe, which is a major chemical constituent of this standard (8.3%) compared to Zn (1600 ppm). Our $\delta^{66}\text{Zn}$ value is within

error of that reported in Chapman et al. (2006) ($0.78 \pm 0.09\%$). This result supports our Fe isotopic data for this standard, for which a $\delta^{56}\text{Fe}$ difference of more than 0.2‰ between the published value of Dideriksen et al. (2006) and our results was obtained (see below).

4.3.2. Fe isotopic analyses

Fe isotopic analyses were carried out at medium resolution, which allowed the identification of a plateau free of argide interferences (Weyer and Schwieters, 2003; Schoenberg and von Blanckenburg, 2005). The Faraday cups were aligned to measure ^{53}Cr (L4), ^{54}Fe (L1), ^{56}Fe (centre), ^{57}Fe (H1), ^{58}Fe (H2), and ^{60}Ni (H4) isotopes. One measurement consisted of one block of 30 cycles of 8.2 s each. The ion intensity of ^{53}Cr was measured to monitor possible interferences of ^{54}Cr on ^{54}Fe (Dauphas et al., 2009a). The ^{54}Cr correction procedure assumed a natural isotopic abundance for Cr. The calculated contribution of ^{54}Cr is $<0.01\%$ of the total ^{54}Fe , which is negligible and requires no correction. Ni skimmer and sample cones were used for both sample and standard measurements. X-skimmer cones were also tested towards the end of this study, which increased substantially (up to four times) the ^{56}Fe sensitivity compared to the normal Ni skimmer cones. This allowed us to repeat some Fe isotopic analyses (samples drilled from 21644A), though we note that very careful tuning was necessary to obtain reasonable errors for individual analyses, which were thus more time consuming.

Fe isotopic ratios are expressed in standard delta notation in per mil units relative to the average value of the respective bracketing standards, as follows:

$$\delta^{56}\text{Fe} = [({}^{56}\text{Fe} / {}^{54}\text{Fe})_{\text{sample}} / ({}^{56}\text{Fe} / {}^{54}\text{Fe})_{\text{IRMM14}} - 1] * 1000$$

As recommended by Dauphas et al. (2009a), a method of sample-standard bracketing was adopted for Fe isotopic analyses, with particular care taken in matching standard and sample intensities (Fe intensities matched within less than 5% in all measurements). On average, five sample analyses were carried out, each being bracketed by two standard analyses. Following published Fe isotopic studies, the metal standard IRMM-14 was used as the bracketing standard. Repeated measurements of this standard indicate that the instrumental mass bias follows the mass dependent isotopic fractionation ($\delta^{56}\text{Fe} \sim 0.67 \times \delta^{57}\text{Fe}$) predicted by theory (Fig. 5). The wide spread of log 57/54 Fe and log 56/54 Fe ratios for the same standard (Fig. 5) reflect different instrumental mass bias observed across multiple days and analytical sessions, but the slope in all cases follows mass dependent fractionation.

Generally, the uncertainty for individual $\delta^{56}\text{Fe}$ sample analyses is marginally worse than for Zn, which is likely to be related to some mass bias instability due to the presence of matrix elements eluted with Fe. Another column purification step could have been used (Dauphas et al., 2009a; Yamakawa et al., 2009), but this has deliberately been omitted to minimize the blank, especially for samples containing as little as 5-10 μg Fe. The possible influence of matrix element on the accuracy of Fe isotopic data has been tested in Schoenberg and von Blanckenburg (2006) and Dauphas et al. (2009a) using Fe solution doped with various metals. Both studies indicate that the presence of residual matrix elements after chemistry does not have an impact on the accuracy of the Fe isotopic data, as long as their concentration are kept at a low level (element/Fe < 2; Dauphas et al., 2009a). We have systematically checked for the presence of residual matrix elements, and we found that these account for less than 5-10% of the total amount of Fe present for analysis.

Following our purification procedure, we found that most of the matrix elements in sphalerite samples were eliminated after repeated washing with 6M HCl prior to elution of Fe using 0.4M HCl. A minimum of 2.5 mls of sample solution was necessary for a single measurement; when a limited amount of Fe was available, only one analysis was carried out (Table 1). In any case, the reported errors (after replicate analyses) are in the range of those reported elsewhere. The large error obtained in some cases (up to 0.3‰; Table 2) is nevertheless small relative to the large range of $\delta^{56}\text{Fe}$ obtained in this study.

The Fe blank contribution (average of 300 mV), which includes sample digestion, chemistry and mass spectrometric procedures, generally accounts for between 2% and 5% of the sample signal, and less than 1-2% where larger samples ($> 10 \mu\text{g Fe}$) were processed. A blank contribution of $>2\%$ (maximum of 5.9%; Table 2), despite extensive cleaning of the resin, relates to very small sample sizes for a relatively low Fe content in sphalerite ($< 0.5 \text{ wt\%}$; Gagnevin and Menuge, unpublished data). Measurement of the isotopic composition of the blank was thus attempted in two instances. Despite not being accurate (only two blocks of data were obtained in each case using 1 ml of solution), a highly fractionated Fe isotopic composition was systematically obtained ($\delta^{56}\text{Fe} = -7.4 \pm 0.7\text{‰}$ and $-9.7 \pm 0.4\text{‰}$, average of -8.6‰). A blank correction was thus applied (Table 2) to all $\delta^{56}\text{Fe}$ sample analyses using this mean, highly fractionated $\delta^{56}\text{Fe}$ blank value of -8.6‰ . This blank correction results in an average decrease of about 0.2‰ ($\pm 0.14\text{‰}$) from the measured $\delta^{56}\text{Fe}$ value. This blank correction can be considered reasonably accurate, since larger microdrilled samples (D4-drill 6 and D3-drill 6) yielded identical values to smaller samples of the same material where a more substantial blank correction was applied (Table 2). Consequently, the blank correction is not considered in the overall uncertainty of individual Fe isotopic measurements, as reported in Fig. 6 and Table 2. Similar $\delta^{56}\text{Fe}$ values

in replicates with contrasted amounts of Fe imply that full Fe recovery was achieved during chromatographic separation. Finally, we note that the extent of isotopic variation before and after the blank correction is within the range of the instrumental reproducibility assessed from repeated analyses of IRMM-14 standard (0.14‰; n = 180) in more than half of the cases, further emphasizing that this correction does not have a significant impact on the final, blank-corrected values. The correlation between $\delta^{56}\text{Fe}$ and $\delta^{66}\text{Zn}$ (see Fig. 6) can thus be considered as valid and reasonably accurate.

When sufficient solution was available (in eleven cases), samples were run twice in separate analytical sessions. In such cases, the reported results are an average of these repeats. When Fe isotopic analyses were carried out only once (due to a limited amount of available solution), the reported uncertainty corresponds to the pooled standard deviation from the eight replicate analyses ($\pm 0.13\text{‰}$). We note that this uncertainty is similar to the external instrumental reproducibility based on multiple analyses of standard IRMM-14 over a period of eight months ($\pm 0.14\text{‰}$; n = 180).

$\delta^{56}\text{Fe}$ (delta notation relative to IRMM-14 standard) for the basalt standard BCR-2 and Mn-nodule standard NOD-P1 are $0.03 \pm 0.07\text{‰}$ (SD, n = 8) and $-0.67 \pm 0.02\text{‰}$ (SD, n = 7), respectively. Our $\delta^{56}\text{Fe}$ average value for BCR-2 is within the 0.02-0.05‰ range of published values (Dauphas et al., 2004; 2007; 2009a; Dideriksen et al., 2006). However, our $\delta^{56}\text{Fe}$ value for the NOD-P1 standard is significantly lighter than previously reported ($\delta^{56}\text{Fe} = -0.4\text{‰}$; Dideriksen et al., 2006). We suggest that this discrepancy may be related to a different digestion method for this Mn-nodule standard. Our digestion procedure involves a combination of HCl, HNO₃ and HF, leaving no observed undigested residue. This contrasts with the Dideriksen et al. (2006) study where only 6M HCl was used for

standard digestion, with reportedly incomplete digestion, which may have led to a different result through incomplete release of Fe. We thus consider the value reported in Dideriken et al. (2006) as being less reliable.

4.3.3. Pb isotopic analyses

A method of standard bracketing coupled with Tl-doping on standard SRM981 was adopted for Pb isotopic analyses. The final Pb isotopic ratios are the result of six sample analyses and four standard analyses; mass bias was corrected following the exponential law (White et al., 2000). The average $^{206}\text{Pb}/^{204}\text{Pb}$ value for standard SRM981 (16.929 ± 0.004 ; SD, $n = 20$) is well within the accepted range for both TIMS and MC-ICPMS measurements (see compilation on GeoReM; Jochum et al., 2005). Linear mass bias behaviour was assumed between each bracketing standard analysis.

4.3.4. S isotopic analyses

In-situ sulfur isotopic analyses were carried out using a Spectron Lasers 902Q CW Nd-YAG laser attached to a gas extraction line and a VG SIRA II gas mass spectrometer, using the method described in Wagner et al (2002). Zn-Fe-Pb and S isotopic analyses were performed on separate thin-section material. The correlation between these analyses (as illustrated in Figs 6 and 7) was achieved on petrographic grounds (mainly on colour) and/or by measuring the distance in relation to the layered-structure between the laser and microdrilled trenches. Barite contamination was not noted during laser S analyses, and due to the translucence of barite in the wavelength of the Nd-YAG laser, combustion of this mineral is unlikely (Alonso-Azcárate et al., 1999); such contamination would result in

higher $\delta^{34}\text{S}$ results since Navan barite typically has a $\delta^{34}\text{S} > 20\text{‰}$ (Anderson et al, 1998). However, the persistently light $\delta^{34}\text{S}$ signature of sphalerite in the two samples with microscopically detectable barite suggests negligible contribution of barite to the sulfur budget. There would also be a relatively limited contribution of S from any minor sulfate molecules compared to the abundant sulfides. Nevertheless, these data can be regarded as maximum values for the sphalerite analysed.

RESULTS

Our sphalerite data (Table 2) show a large and statistically highly significant correlation of $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ ($R^2 = 0.78$; Fig. 6a). A total isotopic range of 0.55‰ and 2‰ has been measured for $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$, respectively, in sphalerite microsamples (Fig. 6a). Significantly, the range of $\delta^{66}\text{Zn}$ (0.33‰) and $\delta^{56}\text{Fe}$ (0.95‰) across 3 mm of sphalerite colloform texture growth banding (sample D1; Fig. 6b) is large compared to the range exhibited by most terrestrial igneous rocks (+0.2 to +0.3‰ for $\delta^{66}\text{Zn}$ and -0.3 to +0.5 for $\delta^{56}\text{Fe}$; Wilkinson et al., 2005a; Schoenberg and von Blanckenburg, 2006; Dauphas et al., 2009b). In this sample, both $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ evolve from lighter to heavier isotopic values with sphalerite growth (Fig. 6b).

In-situ S isotopic analyses of sphalerite display a substantial range, from $\delta^{34}\text{S} = -13.2\text{‰}$ (sample D5) to +14.6‰ (sample D4) (total of 28‰; Fig. 7). $\delta^{34}\text{S}$ variations between successive sphalerite layers also display substantial variability (Table 2). In the case of sphalerite D1, the increase in $\delta^{56}\text{Fe}$ and $\delta^{66}\text{Zn}$ is mimicked by a modest decrease in $\delta^{34}\text{S}$ (from -6.2‰ to -8.8‰; Fig. 6b).

5. DISCUSSION

6.1. Evidence for Fe and Zn kinetic isotope fractionation

Several processes may be considered to account for the correlation between $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$, including: 1) variations in redox conditions, 2) mixing between fluids (Wilkinson et al., 2005a), potentially derived from several basement components, or 3) kinetic fractionation either during sphalerite precipitation (Wilkinson et al., 2005a; John et al., 2008; Kelley et al., 2009) or high temperature fluid-rock reaction. Redox processes are unlikely to have been important during Fe precipitation in sphalerite in the Navan ore deposit. Iron has two oxidation states and undergoes extensive redox cycling (Beard et al., 2003; Johnson et al., 2008) whereas Zn does not, and redox processes are therefore expected to fractionate the isotopes of Fe differently to those of Zn, thus ruling out hypothesis 1. Moreover, Fe(III) is readily reduced to Fe(II) in the presence of sulfide (Rickard and Morse, 2005). Given the formation environment of much of the ore at Navan, it seems unlikely that extensive redox cycling of Fe would be developed. Fluid mixing (hypothesis 2), is highly unlikely to account for such large variations in $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ given the homogenous $^{206}\text{Pb}/^{204}\text{Pb}$ signature in sphalerite (mean $^{206}\text{Pb}/^{204}\text{Pb} = 18.197 \pm 0.003$, Table 2; statistically indistinguishable from the Pb isotope composition of Pb concentrates at Navan: 18.19 ± 0.03 ; Fallick et al. 2001), as well as the homogenous $\delta^{56}\text{Fe}$ signature measured in both Zn concentrates and basement rocks. Perhaps more significant, is the fact that the surface reservoir would be highly unlikely to be the dominant reservoir in the case of the metals, and, if present, has been predicted to be isotopically heavy ($\delta^{66}\text{Zn} > 0.5\%$ Wilkinson et al 2005a). Both our data at Navan and Wilkinson et al. (2005a) have established that basement derived Zn has a $\delta^{66}\text{Zn}$ value of around -0.05 to 0.2‰. Any

minor carbonate-hosted Zn component mixing would increase $\delta^{66}\text{Zn}$ values beyond this range (Wilkinson et al, 2005a). From Fig. 6, this is certainly not the case. Indeed, the bulk of the ore (represented by the Zn concentrates) has $\delta^{66}\text{Zn}$ indistinguishable from the basement values. Some variation in $\delta^{66}\text{Zn}$ may, however, be explained by source heterogeneity (see below).

We propose that the ranges of Zn and Fe isotope signatures reported in this study are caused primarily by kinetic isotopic fractionation. This fractionation may have occurred during high temperature fluid-rock reaction and primary leaching of metals from the source rocks, but we consider this hypothesis unlikely for a number of reasons. Firstly, the range of Zn, and more so Fe, isotope compositions is much greater in the sphalerite samples than in the potential source rocks (Fig. 6a). Secondly, any such inheritance will have been greatly reduced by mixing of fluids from different source rocks prior to sphalerite crystallization. This is demonstrated by the lack of Pb isotope variation in sphalerite, contrasting with the inevitably large range in such ratios, at the time of mineralization, amongst the diverse Lower Palaeozoic volcanic and sedimentary source rocks. Indeed the remarkable homogeneity of Pb isotope signatures within a given Irish deposit is well established (Dixon et al., 1990; Everett et al., 2003), and especially so for Navan (Fallick et al, 2001). For these reasons it is unlikely that the incoming metal-bearing fluids varied by more than 0.2‰ in $\delta^{66}\text{Zn}$.

Therefore, we propose that kinetic fractionation occurred as a result of rapid sphalerite precipitation at the site of mineral precipitation in the throat of the ore system, resulting in light $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$. This is in agreement with experimental studies of Zn isotope fractionation (Archer et al. 2004), which demonstrate a fractionation of ~0.36‰ in $\delta^{66}\text{Zn}$

when ZnS is precipitated rapidly from solution by addition of sulfide, in line with the maximum 0.55‰ fractionation obtained in our study. Also consistent is the inference that Zn isotope fractionation is intimately associated with changes in temperature at the site of precipitation (John et al., 2008). In the case of Fe, the lack of experimental data on the extent of Fe isotope fractionation in sphalerite crystallized in low temperature environments makes this model more speculative. However, precipitation experiments on Fe sulfides suggest that, in the absence of redox processes, crystallised Fe is isotopically lighter than coexisting aqueous Fe(II) solution and tends to isotopically re-equilibrate with time to heavier compositions (Butler et al., 2005; Guilbaud et al., 2010), in line with our proposed interpretation. Therefore, experimental data predominantly supports this model of kinetic fractionation during precipitation (Archer et al., 2004; Butler et al., 2005; Guilbaud et al., 2010). However, these experiments were performed at low temperatures (< 40°C) and in the case of Fe, involving minerals (e.g. mackinawite), which would not be stable at the temperature conditions prevalent during ore deposition at Navan. Moreover, the extent of fractionation reported in these experiments on Fe did not exceed 1‰, which contrasts with the 2‰ total $\delta^{56}\text{Fe}$ variation reported in our study. Notwithstanding these differences, we propose that ^{54}Fe may be preferentially kinetically fractionated into sphalerite in ore-forming, *low to medium* temperature, hydrothermal systems, but we acknowledge that further experimentation in this area is necessary to fully validate this hypothesis.

Kinetic isotopic fractionation has been suggested to account for Zn isotopic variability in the Irish ore field (Wilkinson et al., 2005a), but this model was based on reconnaissance samples with limited intra-deposit analyses. Kinetic fractionation was also suggested to explain variations in $\delta^{66}\text{Zn}$ between orebodies of the Red Dog district, Alaska (Kelley et al., 2009), based upon several deposits within the district as well as bulk sphalerite separates. Our study investigates layered sphalerite growth bands at the hand specimen scale from a

single deposit, and used several isotopic systems, set against a framework of knowledge of the bulk system and putative sources, thus providing the most robust evidence to date for kinetic isotopic fractionation during sphalerite precipitation. Rather than being of closed system, Rayleigh-type (Wilkinson et al., 2005a; Kelley et al., 2009), the fractionation recorded in Navan is more likely to be associated with various precipitation regimes during mineral formation involving different surface reactions and diffusional mechanisms (e.g., DePaolo, 2011), possibly in response to different fluid mixing rates in a system open to repeated fluid influx. Large variations in $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ observed within only a few millimetres of sphalerite growth (Fig. 6b), with no obvious textural discontinuity (see Fig. 3b) and without significant variations in $\delta^{34}\text{S}$ (see below), indicate that the fractionation process is likely to have occurred at very short length and time scales, in line with experimental data (Butler et al., 2005; Archer et al., 2004).

Black et al. (2011) noted the need to investigate the magnitude of isotopic fractionation between structures where zinc is directly bound to sulfur, such as aqueous bisulfide complexes, and ZnS minerals. Our data directly contribute to this on-going effort. The fact that more than half of our isotopic data on sphalerite extend to lighter $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ values than the Zn concentrates, considered as equivalent to the bulk mineralising fluid, indicate that most of Zn and Fe fractionation is linked to the sphalerite precipitation process, and that any other type of fractionation (i.e. between species dissolved in the ore fluid; Matthews et al., 2001; Hill and Schauble, 2008; Black et al., 2011; Fujii et al., 2011) will likely be subordinate in magnitude.

6.2. Bearing of S isotopic data on fractionation processes

It is well documented that Irish-type ores were deposited by mixing of a deep-seated, basement-derived hydrothermal fluid with cool surface brines derived from seawater evaporation (Banks et al., 2002). The surface brine contained abundant bacteriogenic H_2S , with lighter sulfur ($\delta^{34}\text{S} < -5\text{‰}$) and the hydrothermal fluid delivered a subordinate ($\sim 10\%$) amount of heavier sulfur ($\delta^{34}\text{S}$ generally $> 0\text{‰}$) (Anderson et al., 1998; Wilkinson et al., 2005b; Blakeman et al., 2002; Barrie et al., 2009a). In this study, sphalerite dominated by the hydrothermal S isotope signature is exclusively related to light $\delta^{66}\text{Zn}$ ($< -0.15\text{‰}$; Fig. 7), with $\delta^{56}\text{Fe}$ lighter than -1.2‰ (Table 2). This strongly suggests that light Fe and Zn isotopes are associated with early precipitation of sphalerite from the hydrothermal system. In contrast, bacteriogenic sphalerite $\delta^{34}\text{S}$ values almost exclusively correlate with $\delta^{66}\text{Zn}$ signatures heavier than -0.15‰ (Fig. 7). These results indicate that Zn fractionation occurred in response to fluid mixing. The effect of S isotope kinetic fractionation, if any, would be subordinate and cannot explain the 28‰ variations obtained in this and other Navan studies (e.g., Blakeman et al. 2002; Anderson et al, 1998; Fallick et al. 2001). It has been demonstrated that sulfur isotope fractionation related to the precipitation of metal sulfides is small compared to that created by bacterial reduction (Bottcher et al, 1998), leaving no possibility that the large fractionations seen in ore sulfides results from fractionation of the hydrothermal source.

6.3. Large scale $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ variations

Concentrate data provide estimates of average Fe and Zn isotope variation for the deposit. They show that the heavier Fe and Zn isotope values ($> -1.2\text{‰}$ and $> -0.15\text{‰}$ respectively) dominate the ore deposit (Fig. 6a), and that the lighter isotopic values found associated with hydrothermal sulfide are a minor component of the deposit. Using similar concentrates,

Fallick et al. (2001) showed that bacteriogenic sulfide dominates (~90%) the deposit. In terms of mass balance, the sphalerite with lighter Zn and Fe isotope values formed early but is a minor component of the reservoir, and should not be regarded as typical of the inflowing hydrothermal fluid. Instead, the heavier values of $\delta^{56}\text{Fe}$ and $\delta^{66}\text{Zn}$ in sphalerite, similar to ore concentrates and basement rocks (Fig. 6, 7), are more representative of the hydrothermal fluid composition, while the light $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ values are the fractionated derivative of the parent hydrothermal fluid through early sulfide precipitation. This is a new insight into hydrothermal systematics of Zn and Fe isotopes. That the sphalerite values extend above the range of concentrate values is explained by the need for mass balance. The data from a variety of basement whole rocks ($\delta^{66}\text{Zn} = -0.02$ to $+0.23\text{‰}$), also echo the values obtained in the concentrates ($\delta^{66}\text{Zn} = -0.08$ to $+0.08\text{‰}$; Fig. 6a, 7). The latter also indicate that, in this giant system, in-flowing metals do not have entirely homogeneous $\delta^{66}\text{Zn}$. Our $\delta^{66}\text{Zn}$ data on basement rocks suggest that mixing between a light, basement-derived, $\delta^{66}\text{Zn}$ value and heavy ($>1.3\text{‰}$), carbonate-derived, $\delta^{66}\text{Zn}$ value, such as suggested in Wilkinson et al. (2005a), is unlikely at Navan. However, the average 0.12‰ $\delta^{66}\text{Zn}$ of the basement measured in Wilkinson et al. (2005a) is in line with our data ($0.11 \pm 0.10\text{‰}$; $n = 6$), and further corroborates that the basement is isotopically not homogenous, nor homogenised in the hydrothermal system. We also note that data from the Lisheen deposit presented by Wilkinson et al. (2005a), also indicates a similar occurrence of relatively low $\delta^{66}\text{Zn}$ with hydrothermal sulfide $\delta^{34}\text{S}$.

The small range of Zn and Fe isotopes in sphalerite microsamples with bacteriogenic sulfide dominance (samples D2 and D5; Fig. 7) is comparable to the range of Zn isotopes for concentrate and basement samples (Fig. 6a). We note that samples D2 and D5 display layering at a scale greater than 1 cm, with intergrowth of various sulfide phases along the

layering structure (see Fig. 2b, e), and in this respect they differ from the other three samples. These two samples reflect the bulk system, suggesting that little or no fractionation of Zn and Fe isotopes took place after initial hydrothermal influx, which suggests either a very limited rate of input of hydrothermal fluids during sphalerite precipitation, and/or much slower sphalerite growth rates, allowing isotopic re-equilibration within the fluid from which sphalerite was deposited. It is also possible that the temperature was lower following the initial precipitation, as the hydrothermal fluid mixed with the surface brine, which may also have diminished the extent of kinetic fractionation.

6.4. Model and implications

Based upon our Zn, Fe and S isotopic data, published fluid inclusion evidence (Wilkinson 2010, and references therein) and Zn isotopic inferences based on active hydrothermal fluids (John et al., 2008), it is proposed that sphalerite that precipitated early from an influx of hydrothermal fluid had lighter $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ due to kinetic isotope fractionation, a hydrothermal S signature ($\delta^{34}\text{S} > 0\text{‰}$; Fig. 7), and precipitated at relatively high temperature ($\sim 150\text{--}170^\circ\text{C}$) and relatively low salinity ($\sim 12\text{--}16$ wt% NaCl equivalent). Although genetically significant, this was quantitatively a minor component of the Zn, Fe and S budgets at Navan. Subsequent sphalerite, precipitated at lower temperature ($< 150^\circ\text{C}$) and higher salinities ($\sim 20\text{--}25$ wt% NaCl equivalent), had variably heavier $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ with a more bacteriogenic S signature ($\delta^{34}\text{S} < -5\text{‰}$; Figs 6, 7) due to substantial mixing with bacteriogenic sulfide in a cooler H_2S rich brine. Following this model, it is proposed that samples D3 and D4 represent sphalerites precipitated rapidly upon hydrothermal input in the throat of the ore system, with mixing between the two fluids, and fractionation of Zn and Fe isotopes (Fig. 6a, 7). Conversely, samples D1 and D2 represent sphalerites with

dominant bacteriogenic S, which is the dominant signature in the whole deposit. It is thus concluded that a fine interplay between fluid mixing, rapid crystallization, kinetic reactions, probably enhanced by basement variability, was responsible for the Zn-Fe-S isotope systematics of Navan sphalerite. Due to this complexity, we re-emphasise that a simple model of closed Rayleigh-type Fe and Zn isotopic fractionation is not tenable.

Our model, based upon a combination of different isotopic systems, has several important implications for understanding ore genesis and for mineral exploration strategy:

1) The Zn and Fe isotopic compositions of samples inferred to have formed in the hydrothermal throat of the Navan ore system are not representative of the bulk system.

2) The influx of deep hydrothermal fluids, whose sulfur budget was comparably minor compared to shallow bacteriogenic fluids (Fallick et al., 2001), was a fundamental trigger to sphalerite mineralisation.

3) Fe isotopes in sphalerite may be kinetically fractionated in relatively low temperature hydrothermal environments, a process previously not observed.

4) The high variability of Zn and Fe isotopic compositions encountered within a very narrow area of the giant Navan ore deposit (even at the hand sample scale) suggests that the use of Zn and Fe isotopes as potential tracers of fluid migration pathways in Navan, and possibly in other Irish-type deposits is unlikely to be feasible, unless combined with a variety of sampling and targeting strategies both at the macro and micro-scales.

5) Isotopically heavy Zn and Fe may be detectable as a geochemical halo in rocks equilibrated with the exhaust fluid remaining after precipitation of a large hydrothermal orebody, raising the possibilities of quantifying orebody sulfide crystallization and of remotely detecting orebodies.

666 6) Finally, this study helps to clarify the mechanism of Zn and Fe isotope fractionations in
667 nature. As such, it has implications beyond ore deposit genesis, e.g. impacts of vent-related
668 Zn and Fe in oceanographic studies or understanding the Zn isotope compositions of
669 natural backgrounds in geobiological and pollution studies.

671 **Acknowledgments**

672
673 We acknowledge funding of this research by Research Frontiers Award 08/RFP/GEO1397
674 from Science Foundation Ireland to JFM. AJB is funded by NERC support of the Isotope
675 Community Support Facility at SUERC. SUERC is funded by NERC and the Consortium
676 of Scottish Universities. We thank Boliden Tara Mines Limited for permission to collect
677 samples and to publish these results, Michael Murphy and Dr Shane Tyrrell for technical
678 supports. We are grateful for the comments of three anonymous reviewers, which helped to
679 improve and clarify this paper. This is the first publication from the National Centre for
680 Isotope Geochemistry (NCIG), a joint venture of UCD, Trinity College Dublin and
681 University College Cork, funded mainly by Science Foundation Ireland.

FIGURE CAPTIONS

Fig. 1: Sketch map (adapted from Ashton et al., 2003) projection of the top surface of the Navan orebody representing the different units within the orebody, main structural features (faults) and the location of the sampling areas. Sampling was concentrated in a similar structural setting to the Blakeman et al. (2002) study.

Fig. 2: Images of the thin sections of samples investigated in this study. Note the complexity of the textures, all varying from one sample to the other, despite common mineralogy. The sphalerite colloform texture has been the focus of this study (sampling areas highlighted in white dashed boxes). The growth direction was determined on careful petrographic grounds as established by Barrie et al. (2009a). Growth can reasonably be assumed to be perpendicular to layering towards convex direction (as indicated by arrows). Scale bar = 5 mm. D1 = 21643B; D2 = 21642E; D3 = 21642C; D4 = 21644A; D5 = NO1663-NV3.

Fig. 3: Photomicrographs of the layered texture in samples D4 (21644A), D1 (21643B) and D3 (21642C). Arrows indicate the direction of growth.

Fig. 4: Details of the colloform zone microdrilled in sample D1 (21643B). The New-Wave microdrilling device allowed following individual, convoluted, growth zones (identified by color).

Fig. 5 (a) Zn isotopic analyses on both Cu-doped and undoped standard solution for standard IMC Zn (n = 152; data collected over a period of eight months), which has been

used as bracketing standard for Zn isotopic analyses. Both Cu-doped and undoped standard solution plot along a linear trend, whose slope is almost identical to that predicted theoretically for mass bias behaviour of Zn (Bermin et al., 2006). (b) Fe isotopic analyses of undoped standard solution (using the same 2 ppm solution) for standard IRMM-14 (n = 4; data collected over a period of two months). These plot along a linear trend, whose slope is comparable to the theoretical slope (e.g. Arnold et al., 2004). Note that only a subset of standard analyses is reported here; all the other standard analyses, which were used as standard brackets during sample analyses, plot along a sub-parallel mass bias line (e.g. Arnold et al., 2004).

Fig. 6: a) Correlation between $\delta^{56}\text{Fe}_{\text{IRMM-14}}$ and $\delta^{66}\text{Zn}_{\text{IMC}}$ for all five sphalerite samples and the mine concentrates. The Fe isotopic data have been blank-corrected (see text for details). The sphalerite Zn and Fe isotope data exhibit a well-defined correlation ($R^2 = 0.79$). Our $\delta^{66}\text{Zn}$ data (from -0.32‰ to 0.23‰) overlaps with that reported in Wilkinson et al. (2005a) for the Irish midlands orefield (-0.17‰ to 0.34‰, omitting two heavy $\delta^{66}\text{Zn}$ values of 0.64‰ and 1.33‰). The grey box represents the isotopic range of the basement samples. b) Small scale Fe and Zn isotopic variations between successive layers in sphalerite from sample D1. S isotope data are also presented in boxes above or below each $\delta^{66}\text{Zn}$ data point.

Fig. 7: Correlation between $\delta^{66}\text{Zn}_{\text{IMC}}$ and $\delta^{34}\text{S}_{\text{CDT}}$ (symbols as in Fig. 6a). Boxes show compositions of sphalerite where hydrothermal and bacteriogenic fluids are proposed to dominate. Black box: range of $\delta^{66}\text{Zn}_{\text{IMC}}$ for the basement samples. See text for details.

REFERENCES

- Alonso-Azcárate J., Boyce A.J., Bottrell S., MacAulay C., Rodas M., Fallick A.E. and Mas J.R. (1999) Development and use of in situ laser S isotope analyses for pyrite-anhydrite geothermometry: An example from the pyrite deposits of the Cameros Basin, NE Spain. *Geochimica et Cosmochimica Acta* **63**, 509-513.
- Anderson I.K., Andrew C.J., Ashton J.H., Boyce A.J., Caulfield J.B.D. and Fallick A.E. (1989) Preliminary sulphur isotope data of diagenetic and vein sulphides in the Lower Palaeozoic strata of Ireland and southern Scotland: implications for Zn+Pb+Ba mineralization. *Journal of the Geological Society of London* **146**, 715-720.
- Anderson I. K., Ashton J. H., Boyce A. J., Fallick A. E. and Russell M. J. (1998) Ore depositional processes in the Navan Zn-Pb deposit, Ireland. *Economic Geology and the Bulletin of the Society of Economic Geologists* **93**(5), 535-563.
- Archer C., Vance D. and Butler I. (2004) Abiotic Zn isotope fractionations associated with ZnS precipitation. *Geochimica et Cosmochimica Acta* **68**(11), A325.
- Arnold G. L., Weyer S. and Anbar A. D. (2004) Fe isotope variations in natural materials measured using high mass resolution multiple collector ICPMS. *Analytical Chemistry* **76**(2), 322-327.
- Ashton J. H., Downing D. T. and Finlay S. (1986) The geology of the Navan Zn-Pb orebody. In *Geology and genesis of mineral deposits in Ireland* (ed. C. J. Andrew et al.), pp. 243-280. Irish Association for Economic Geology.
- Ashton J. H., Holdstock M. P., Geraghty J. F., O'Keeffe W. G., Martinez N., Peace W. and Philcox M. E. (2003) The Navan Orebody — discovery and geology of the South West Extension. In *Europe's Major Base Metal Deposits* (ed. J. H. Ashton et al.), pp. 405–436. Irish Association for Economic Geology.
- Banks D. A., Boyce A. J. and Samson I. M. (2002) Constraints on the origins of fluids forming Irish Zn-Pb-Ba deposits: Evidence from the composition of fluid inclusions. *Economic Geology and the Bulletin of the Society of Economic Geologists* **97**(3), 471-480.
- Barrie C. D., Boyce A. J., Boyle A. P., Williams P. J., Blake K., Wilkinson J. J., Lowther M., McDermott P. and Prior D. J. (2009a) On the growth of colloform textures: a case study of sphalerite from the Galmoy ore body, Ireland. *Journal of the Geological Society* **166**, 563-582.
- Barrie C. D., Boyle A. P., Boyce A. J., Ashton J. H. and Prior D. J. (2009b) Chaos and Ordering in layered sulfides: Growth, mechanics or inheritance?, Micro-Analysis, Processes and Time (MAPT): *Biennial Meeting of the Mineralogical Society of Great Britain and Ireland, Edinburgh*, p. 156.
- Beard B. L., Johnson C. M., Skulan J. L., Nealson K. H., Cox L. and Sun H. (2003) Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chemical Geology* **195**(1-4), 87-117.

- Bermin J., Vance D., Archer C., and Statham P. J. (2006) The determination of the isotopic composition of Cu and Zn in seawater. *Chemical Geology* **226**(3-4), 280-297.
- Bischoff J. L., Radtke A. S., and Rosenbauer R.J. (1981) Hydrothermal alteration of graywacke by brine and seawater: roles of alteration and chloride complexing on metal solubilization at 200°C and 350°C. *Economic Geology and the Bulletin of the Society of Economic Geologists* **76**(3), 659–676.
- Black J. R., Kavner A., and Schauble E. A. (2011) Calculation of equilibrium stable isotope partition function ratios for aqueous zinc complexes and metallic zinc. *Geochimica et Cosmochimica Acta* **75**(3), 769-783.
- Blakeman R. J., Ashton J. H., Boyce A. J., Fallick A. E. and Russell M. J. (2002) Timing of interplay between hydrothermal and surface fluids in the Navan Zn + Pb orebody, Ireland: Evidence from metal distribution trends, mineral textures, and $\delta^{34}\text{S}$ analyses. *Economic Geology and the Bulletin of the Society of Economic Geologists* **97**(1), 73-91.
- Bottcher M. E., Smock A. M. and Cypionka H. (1998) Sulfur isotope fractionation during experimental precipitation of iron (II) and manganese (II) sulfide at room temperature. *Chemical Geology* **146**(3-4), 127-134.
- Boyce A.J., Coleman M.L. and Russell M.J. (1983) Formation of fossil hydrothermal chimneys and mounds from Silvermines, Ireland. *Nature* **306**, 545-550.
- Braithwaite C. J. R. and Rizzi G. (1997) The geometry and petrogenesis of hydrothermal dolomites at Navan, Ireland. *Sedimentology* **44**(3), 421-440.
- Busigny V. and Dauphas N. (2007) Tracing paleofluid circulations using iron isotopes: A study of hematite and goethite concretions from the Navajo Sandstone (Utah, USA). *Earth and Planetary Science Letters* **254**(3-4), 272-287.
- Butler I. B., Archer C., Vance D., Oldroyd A. and Rickard D. (2005) Fe isotope fractionation on FeS formation in ambient aqueous solution. *Earth and Planetary Science Letters* **236**(1-2), 430-442.
- Chapman J. B., Mason T. F. D., Weiss D. J., Coles B. J. and Wilkinson J. J. (2006) Chemical separation and isotopic variations of Cu and Zn from five geological reference materials. *Geostandards and Geoanalytical Research* **30**(1), 5-16.
- Chen J. B., Louvat P., Gaillardet J. and Birck J. L. (2009) Direct separation of Zn from dilute aqueous solutions for isotope composition determination using multi-collector ICP-MS. *Chemical Geology* **259**(3-4), 120-130.
- Dauphas N., Janney P. E., Mendybaev R. A., Wadhwa M., Richter F. M., Davis A. M., van Zuilen M., Hines R. and Foley C. N. (2004) Chromatographic separation and multicollection-ICPMS analysis of iron. Investigating mass-dependent and -independent isotope effects. *Analytical Chemistry* **76**(19), 5855-5863.
- Dauphas N. and Rouxel O. (2006) Mass spectrometry and natural variations of iron isotopes. *Mass Spectrometry Reviews* **25**(4), 515-550.

- Dauphas N., Cates N. L., Mojzsis S. J. and Busigny V. (2007) Identification of chemical sedimentary protoliths using iron isotopes in the >3750 Ma Nuvvuagittuq supracrustal belt, Canada. *Earth and Planetary Science Letters* **254**(3-4), 358-376.
- Dauphas N., Pourmand A. and Teng F. Z. (2009a) Routine isotopic analysis of iron by HR-MC-ICPMS: How precise and how accurate? *Chemical Geology* **267**(3-4), 175-184.
- Dauphas N., Craddock P. R., Asimow P. D., Bennett V. C., Nutman A. P. and Ohnenstetter D. (2009b) Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth and Planetary Science Letters* **288**(1-2), 255-267.
- Dekov V. M., Cuadros J., Kamenov G. D., Weiss D., Arnold T., Basak C. and Rochette P. (2010) Metalliferous sediments from the HMS Challenger voyage (1872-1876). *Geochimica et Cosmochimica Acta* **74**(17), 5019-5038.
- DePaolo D. J. (2011) Surface kinetic model for isotopic and trace element fractionation during precipitation of calcite from aqueous solutions. *Geochimica et Cosmochimica Acta* **75**(4), 1039-1056.
- Dideriksen K., Baker J. A. and Stipp S. L. S. (2006) Iron isotopes in natural carbonate minerals determined by MC-ICP-MS with a Fe-58-Fe-54 double spike. *Geochimica et Cosmochimica Acta* **70**(1), 118-132.
- Dixon P. R., Lehuray A. P. and Rye D. M. (1990) Basement Geology and Tectonic Evolution of Ireland as Deduced from Pb Isotopes. *Journal of the Geological Society* **147**, 121-132.
- Everett C. E., Rye D. M. and Ellam R. M. (2003) Source or sink? An assessment of the role of the old red sandstone in the genesis of the Irish Zn-Pb deposits. *Economic Geology and the Bulletin of the Society of Economic Geologists* **98**(1), 31-50.
- Fallick A. E., Ashton J. H., Boyce A. J., Ellam B. M. and Russell M. J. (2001) Bacteria were responsible for the magnitude of the world-class hydrothermal base metal sulfide orebody at Navan Ireland. *Economic Geology and the Bulletin of the Society of Economic Geologists* **96**(4), 885-890.
- Fujii T., Moynier F., Pons M. L., and Albarede F. (2011) The origin of Zn isotope fractionation in sulfides. *Geochimica et Cosmochimica Acta* **75**(23), 7632-7643.
- Guilbaud R., Butler I. B., Ellam R. M. and Rickard D. (2010) Fe isotope exchange between Fe(II)(aq) and nanoparticulate mackinawite (FeSm) during nanoparticle growth. *Earth and Planetary Science Letters* **300**(1-2), 174-183.
- Guilbaud R., Butler I. B. and Ellam R. M. (2011) Abiotic Pyrite Formation Produces a Large Fe Isotope Fractionation. *Science* **332**(6037), 1548-1551.
- Hill P. S. and Schauble E. A. (2008) Modeling the effects of bond environment on equilibrium iron isotope fractionation in ferric aquo-chloro complexes. *Geochimica et Cosmochimica Acta* **72**(8), 1939-1958.

- Hitzman M. W. (1995) Mineralization in the Irish Zn-Pb-(Ba-Ag) orefield. In: Anderson, K., Ashton, J., Earls, G., Hitzman, M. and Tear, S. (eds), Irish Carbonate-Hosted Pb-Zn Deposits, *Society of Economic Geologists*, Guidebook Series **21**, 25-61.
- Jochum K. P., Nohl L., Herwig K., Lammel E., Toll B. and Hofmann A. W. (2005) GeoReM: A new geochemical database for reference materials and isotopic standards. *Geostandards and Geoanalytical Research* **29**(3), 333-338.
- John S. G., Park J. G., Zhan Z. T. and Boyle E. A. (2007) The isotopic composition of some common forms of anthropogenic zinc. *Chemical Geology* **245**(1-2), 61-69.
- John S. G., Rouxel O. J., Craddock P. R., Engwall A. M. and Boyle E. A. (2008) Zinc stable isotopes in seafloor hydrothermal vent fluids and chimneys. *Earth and Planetary Science Letters* **269**(1-2), 17-28.
- Johnson C. M., Beard B. L. and Roden E. E. (2008) The iron isotope fingerprints of redox and biogeochemical cycling in the modern and ancient Earth. *Annual Review of Earth and Planetary Sciences* **36**, 457-493.
- Kelley K. D., Wilkinson J. J., Chapman J. B., Crowther H. L. and Weiss D. J. (2009) Zinc Isotopes in Sphalerite from Base Metal Deposits in the Red Dog District, Northern Alaska. *Economic Geology* **104**(6), 767-773.
- Leach D. L. and Sangster D. F. (1993) Mississippi Valley-type lead-zinc deposits. In: Kirkham, R.V. et al. (eds) Mineral Deposit Modeling. *Geological Association of Canada Special Paper* **40**, 289-314.
- LeHuray A.P., Caulfield J.B.D., Rye D.M. and Dixon P.R. (1987) Basement controls on sediment hosted Zn-Pb deposits. A Pb isotope study of Carboniferous mineralisation in central Ireland. *Economic Geology and the Bulletin of the Society of Economic Geologists* **82**(7), 1695-1709.
- Markl G., von Blanckenburg F. and Wagner T. (2006) Iron isotope fractionation during hydrothermal ore deposition and alteration. *Geochimica et Cosmochimica Acta* **70**(12), 3011-3030.
- Mason T. F. D., Weiss D. J., Chapman J. B., Wilkinson J. J., Tessalina S. G., Spiro B., Horstwood M. S. A., Spratt J. and Coles B. J. (2005) Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia. *Chemical Geology* **221**(3-4), 170-187.
- Matthews A., Zhu X. K., and O'Nions K. (2001) Kinetic iron stable isotope fractionation between iron (-II) and (-III) complexes in solution. *Earth and Planetary Science Letters* **192**(1), 81-92.
- Matthews A., Morgans-Bell H. S., Emmanuel S., Jenkyns H. C., Erel Y. and Halicz L. (2004) Controls on iron-isotope fractionation in organic-rich sediments (Kimmeridge Clay, Upper Jurassic, southern England). *Geochimica et Cosmochimica Acta* **68**(14), 3107-3123.

- Mills H., Halliday A. N., Ashton J. H., Anderson I. K. and Russell M. J. (1987) Origin of a Giant Orebody at Navan, Ireland. *Nature* **327**(6119), 223-226.
- Peace W. M. and Wallace M. W. (2000) Timing of mineralization at the Navan Zn-Pb deposit: A post-Arundian age for Irish mineralization. *Geology* **28**(8), 711-714.
- Philcox M. E. (1984) Lower Carboniferous Lithostratigraphy of the Irish Midlands. *Special Publication, Irish Association for Economic Geology, Dublin*, 89 pp.
- Phillips W. E. A. (2001) Caledonian Deformation. In: Holland, C.H. (ed.) *The Geology of Ireland*. Academic Press, 179-199.
- Rickard D. and Morse J. W. (2005) Acid Volatile Sulphide (AVS). *Marine Chemistry* **97**, 141-197.
- Roedder E. (1968) Noncolloidal Origin of Colloform Textures in Sphalerite Ores. *Economic Geology and the Bulletin of the Society of Economic Geologists* **63**(5), 451-471.
- Rouxel O., Dobbek N., Ludden J. and Fouquet Y. (2003) Iron isotope fractionation during oceanic crust alteration. *Chemical Geology* **202**(1-2), 155-182.
- Rouxel O., Fouquet Y. and Ludden J. N. (2004) Subsurface processes at the Lucky Strike hydrothermal field, Mid-Atlantic Ridge: Evidence from sulfur, selenium, and iron isotopes. *Geochimica et Cosmochimica Acta* **68**(10), 2295-2311.
- Schoenberg R. and von Blanckenburg F. (2005) An assessment of the accuracy of stable Fe isotope ratio measurements on samples with organic and inorganic matrices by high-resolution multicollector ICP-MS. *International Journal of Mass Spectrometry* **242**(2-3), 257-272.
- Schoenberg R. and von Blanckenburg F. (2006) Modes of planetary-scale Fe isotope fractionation. *Earth and Planetary Science Letters* **252**(3-4), 342-359.
- Singer D. A. (1995) World class base and precious metal deposits—a quantitative analysis. *Economic Geology and the Bulletin of the Society of Economic Geologists* **90**(1), 88–104.
- Sivry Y., Riotte J., Sonke J. E., Audry S., Schafer J., Viers J., Blanc G., Freydier R. and Dupre B. (2008) Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters The Riou Mort-Lot River system. *Chemical Geology* **255**(3-4), 295-304.
- Stenberg A., Andren H., Malinovsky D., Engstrom E., Rodushkin I. and Baxter D. C. (2004) Isotopic variations of Zn in biological materials. *Analytical Chemistry* **76**(14), 3971-3978.
- Strogen P., Somerville I.D., Pickard N.A.H., Jones G.Ll. and Fleming, M. (1996) Controls on ramp, platform and basinal sedimentation in the Dinantian of the Dublin Basin and Shannon Trough, Ireland. In: Strogen, P., Somerville, I.D. and Jones, G.Ll. (eds) Recent advances in Lower Carboniferous Geology. *Geological Society Special Publication* **107**, 263-279.

- Symons D. T. A., Smethurst M. T. and Ashton J. H. (2002) Paleomagnetism of the Navan Zn-Pb deposit, Ireland. *Economic Geology and the Bulletin of the Society of Economic Geologists* **97**(5), 997-1012.
- Vaughan, A. (1991) The Lower Paleozoic geology of the Iapetus Suture zone in eastern Ireland. *Unpublished PhD thesis*, Trinity College Dublin, 237 p.
- Wagner T., Boyce A. J. and Fallick A. E. (2002) Laser combustion analysis of delta S-34 of sulfosalt minerals: Determination of the fractionation systematics and some crystal-chemical considerations. *Geochimica et Cosmochimica Acta* **66**(16), 2855-2863.
- Walshaw R. D., Menuge J. F. and Tyrrell S. (2006) Metal sources of the Navan carbonate-hosted base metal deposit, Ireland: Nd and Sr isotope evidence for deep hydrothermal convection. *Mineralium Deposita* **41**(8), 803-819.
- Weyer S. and Schwieters J. (2003) High precision Fe isotope measurements with high mass resolution MC-ICPMS. *International Journal of Mass Spectrometry* **226**(3), 355-368.
- White W. M., Albarede F. and Telouk P. (2000) High-precision analysis of Pb isotope ratios by multiple-collector ICP-MS. *Chemical Geology* **167**, 257-270.
- Williams B. and Brown C. (1986) A model for the genesis of Zn-Pb deposits in Ireland. In: Andrews, C.J. et al. (eds) *Geology and genesis of mineral deposits in Ireland. Irish Association for Economic Geology, Dublin*, 579-590.
- Wilkinson J. J. (2010) A Review of Fluid Inclusion Constraints on Mineralization in the Irish Ore Field and Implications for the Genesis of Sediment-Hosted Zn-Pb Deposits. *Economic Geology* **105**(2), 417-442.
- Wilkinson J. J., Weiss D. J., Mason T. F. D. and Coles B. J. (2005a) Zinc isotope variation in hydrothermal systems: Preliminary evidence from the Irish Midlands ore field. *Economic Geology* **100**(3), 583-590.
- Wilkinson J. J., Eyre S. L. and Boyce A. J. (2005b) Ore-forming processes in Irish-type carbonate-hosted Zn-Pb deposits: Evidence from mineralogy, chemistry, and isotopic composition of sulfides at the Lisheen mine. *Economic Geology* **100**(1), 63-86.
- Wilson S. A., Ridley W. I. and Koenig A. E. (2002) Development of sulfide calibration standards for the laser ablation inductively-coupled plasma mass spectrometry technique. *Journal of Analytical Atomic Spectrometry* **17**(4), 406-409.
- Yamakawa A., Yamashita K., Makishima A. and Nakamura E. (2009) Chemical Separation and Mass Spectrometry of Cr, Fe, Ni, Zn, and Cu in Terrestrial and Extraterrestrial Materials Using Thermal Ionization Mass Spectrometry. *Analytical Chemistry* **81**(23), 9787-9794.

Fig. 1

Sample D1 (21463B)

1031

Fig. 4

1032

Fig. 5

Fig. 6