Tracing metals from source to sink in Irish-type Zn-Pb(-Ba-Ag) deposits

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Abstract: The Irish Midlands Zn-Pb(-Ba-Ag) Orefield represents one of the best studied palaeo-hydrothermal systems worldwide. Despite this, the detailed origins of ore and trace metals and the controls of their variability in deposits across the Orefield, have not been considered in detail. In this contribution, I have used diverse data sources in an attempt to track the metals from their source and assess how they were fractionated at various stages along the reconstructed flow path. This includes: (1) circulation of fluids to depths of up to ~7 km in the Lower Palaeozoic wedge of arc-derived detritus that underlies the Orefield and through a primary 'reaction zone'; (2) fluid transit within the wedge and then up through the redox boundary represented by the Old Red Sandstone; and (3) fluid ingress into the receptive Lower Carboniferous host rocks in the ore deposits themselves, initially through focused feeder pipes and then spreading out upwards and especially laterally into the surrounding carbonate units. The results show that the Lower Palaeozoic package was a particularly fertile source from which metals were easily extracted and that this exerted a primary control on metal tenor in the overlying deposits. However, additional fractionation steps, including loss to and extraction of metals from, the Old Red Sandstone, and sequential deposition of metals during cooling, neutralisation and fluid mixing were also important. The presence beneath the Irish Midlands Basin of a weakly metamorphosed rock package formed from arc-derived detritus is considered to be a critical component of the mineral system.

Keywords: Irish Orefield, Zinc, Lead, Barium, Hydrothermal, Source Rocks, Metals

Introduction

The development of large hydrothermal systems in the Earth's crust is of considerable academic and economic interest. In recent decades, the geochemistry of seawater interaction with the oceanic crust and its control on global thermal and geochemical fluxes has advanced dramatically. In contrast, the effects of extensive seawater circulation within the continental crust are relatively poorly known. This is despite the importance of such systems at several stages of Earth history, when the incipient break-up of megacontinents heralded periods of intense hydrothermal activity and the formation of large, sediment-hosted ore deposits (Barley & Groves, 1992; Leach et al., 2005; Wilkinson, 2014).

Active faulting, subsidence and the deposition of thick sedimentary sequences in areas of continental crust undergoing extension are often synchronous with elevated heat flow, volcanism and metamorphism. In such environments, the coincidence of an anomalous thermal regime with enhanced crustal permeability may lead to the initiation of fluid flow with deep penetration of fluids from the surface to mid-crustal levels (Wickham & Taylor, 1985; McKibben *et al.,* 1987; Nesbitt &

Muehlenbachs, 1989; Ilchik & Barton, 1997). Despite evidence for such processes, and the observation of significant fluid flow at depth in deep drillholes (Kozlovsky, 1987; Kerr, 1994), the importance of deep circulation in modifying the thermal and rheological properties of the crust (e.g. Russell, 1978) and in ore deposit formation is still disputed.

Stratiform and stratabound, sediment-hosted ore deposits, such as the giant (2.37×10^8t) McArthur River deposit of the Australian Proterozoic (Large *et al.*, 1998), form many of the world's greatest economic concentrations of base metals. These deposits are principally located in relatively shallow sedimentary basins developed in rift zones and are the product of a range of processes ranging from hydrothermal exhalation through syn-diagenetic pore-filling and replacement and later epigenesis. In particular, studies of the Australian deposits (e.g., Williams, 1978; Cooke *et al.*, 2000; Large *et al.*, 2002; Magnall *et al.*, 2020a) and classic Canadian districts (e.g. Sangster & Savard 1998, and references therein; Gadd *et al.*, 2016, 2017; Magnall *et al*., 2020b) have provided a variety of constraints on the timing of mineralization relative to host rock deposition and lithification, the sources of mineralizing brines and sulphur, and the controls of metal transport and deposition.
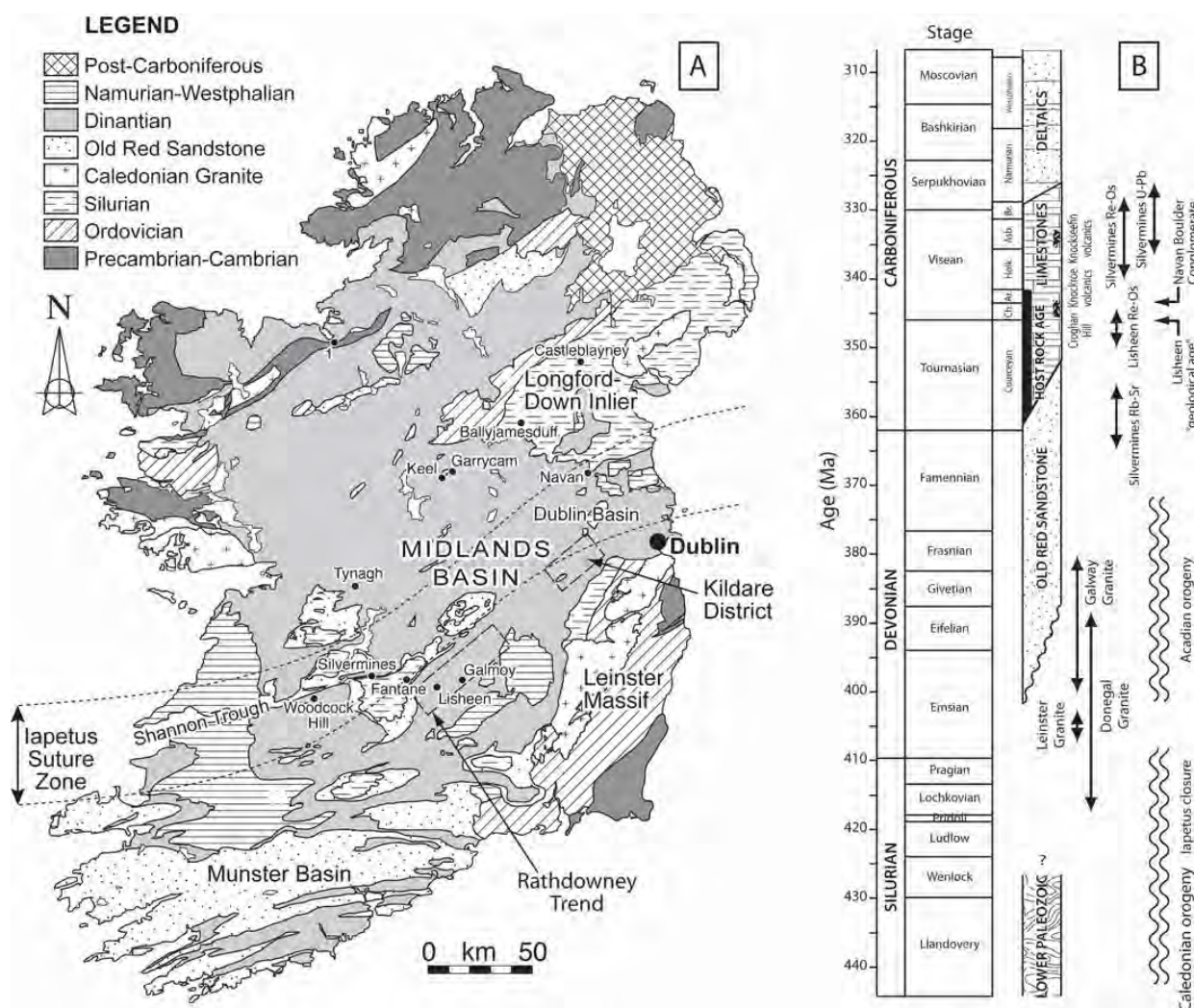
Figure 1: A). *Simplified geological map of Ireland (modified from Wilkinson, 2010) showing main rock units and locations referred to in the text.* **B).** *Stratigraphic column for the Irish Midlands showing Silurian to Upper Carboniferous units, host rock age range, geochronological and geological constraints on timing of mineralisation and key geological events. Ages of Carboniferous stage boundaries are from Davydov et al. (2010). Navan Boulder Conglomerate age is from Ashton et al. (1992); the Lisheen "geological age" is from Wilkinson et al. (2011); Re- Os ages are from Hnatyshin et al. (2015); Silvermines Rb-Sr age is from Schneider et al. (2007); Silvermines U-Pb (apatite) age is from Vafeas et al. (2023). Modified from Wilkinson & Hitzman (2015).*

The Carboniferous Zn-Pb(-Ba-Ag) deposits of the Irish Midlands Basin represent one of the world's largest known concentrations of base metals that formed in the shallow continental crust. Extensive research over six decades has led to a potentially unique understanding of how such systems operated; nonetheless, some aspects, particularly regarding the timing of mineralization have remained controversial. Research in the past two decades (Everett *et al.* 1999a, 1999b, 2003; Boyce *et al.*, 2003; Wilkinson *et al.*, 2005a; Wilkinson & Hitzman, 2015) supports early hypotheses (Russell, 1978, 1986) that deep circulation of modified seawater within the continental crust underlying the Midlands Basin was an important process in the genesis of the deposits and that ore formation occurred in the shallow subsurface. Evidence for fluid mixing, carbonate rock replacement, vein formation and cavity filling as important mineralizing processes, together with the key role of bacteriogenic reduction of seawater sulphate, are now well

documented (e.g., Boast *et al.* 1981; Hitzman & Beaty 1996; Anderson *et al.* 1998; Eyre 1998; Blakeman *et al.*, 2002; Wilkinson *et al.*, 2005b; Wilkinson & Hitzman, 2015; Torremans *et al.*, 2018). The orefield represents one of the few localities in the world where the relationships between different parts of an ore-forming system (potential source rocks, fluid conduits and deposits) are visible in the field and known from drill core and geophysical imaging. It therefore provides an excellent natural laboratory for a study of the geochemistry of a major crustal fluid flow system, the operation of shallow crustal ore-forming processes and their interface with the hydrosphere.

The focus of this contribution is on the origin and pathway of the principal ore metals – and some of the associated minor metals – from source rocks, from which the ore metals are thought to have been extracted, to ore deposit "sinks" and their surrounding dispersion halos. In between, parts of the transport
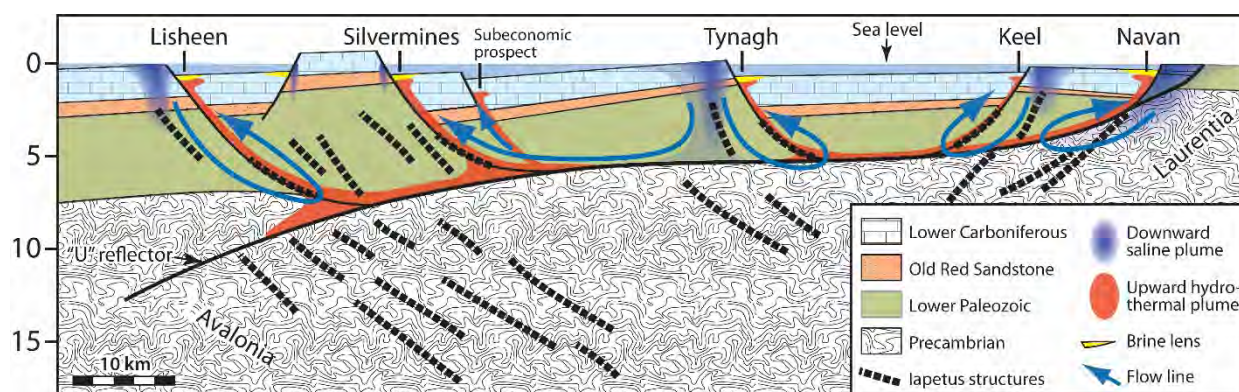
Figure 2: *Simplified cross section showing deep structure beneath the Midlands Basin, in part informed by seismic data and inferred hydrothermal flow system geometry.*

path where fractionation of metals in hydrothermal fluids may occur, either by precipitation or dissolution of key minerals, are also considered on both deposit and regional scales.

Background Geology and Review of Ore Genetic Model

The geological setting and mineralization of the Irish Orefield are extensively described in numerous previous publications (e.g., Hitzman & Large, 1986; Phillips & Sevastopulo, 1986; Andrew, 1993; Wilkinson, 2003; Wilkinson *et al.*, 2003, 2005a; Wilkinson & Hitzman 2015 and references therein). Here I present a brief summary of the key points.

The Irish Zn-Pb(-Ba) deposits are hosted by a Lower Carboniferous marine transgressive sequence of limestones, marls, and shales (Philcox, 1984) that conformably overlies clastic red beds (Old Red Sandstone) of Devonian-Carboniferous age (Fig. 1). The Lower Carboniferous rocks were deposited during a period of active down-warping and block faulting associated with crustal extension (Andrew, 1993) along the Laurussian passive margin. Locally important submarine eruptions of mildly alkaline basalts, trachytes and more primitive ankaramites occurred during basin development, particularly in the Limerick area on the edge of the Shannon Trough (Fig. 1; Strogen, 1988; Somerville *et al.*, 1992), consistent with mild extension during this time. Although age constraints are limited, the deposits are thought to have formed between ~359-342 Ma (e.g., Hnatyshin *et al.*, 2015), at least partly overlapping with Visean volcanism (Wilkinson & Hitzman, 2015). A younger U-Pb age on apatite of 331 ±5.6 Ma has been obtained recently from Silvermines (Vafeas *et al.*, 2023).

The deposits are mainly located in the hangingwall of extensional faults that form complex, *en echelon* geometries, with relay ramps playing an important control on flow localisation (Torremans *et al.*, 2018; Kyne *et al.*, 2019). In many cases, synsedimentary movement on these faults can be demonstrated (e.g. Fusciardi *et al.*, 2003), although the timing of mineralization with respect to such movement has been disputed. Mineralization is mineralogically fairly simple, dominated by sphalerite, galena and pyrite with variable marcasite, and sulphosalts that are generally texturally late. Coeval gangue minerals comprise variably ferroan calcite, dolomite, ferroan dolomite and

barite, with minor quartz. Rare, but sometimes locally concentrated Cu and Ni minerals, particularly bornite, chalcopyrite and niccolite, have been observed (Hitzman *et al.*, 2002; Fusciardi *et al.*, 2003; Wilkinson *et al.*, 2005b). Ore textures are complex, with multiple generations of carbonate replacement, veining and relatively minor open space filling. Some examples of laterally extensive, finely-laminated pyrite(-sphalerite-galena), plus the barite orebody mined at Silvermines, have been interpreted to represent an exhalative or near-surface expression of the hydrothermal systems. This is supported by the discovery of a tubeworm fossil in the Magcobar open pit at Silvermines (Boyce *et al.*, 2003) and the large budget of bacteriogenically derived sulphur in the ores (Fallick *et al.*, 2001; Wilkinson *et al.*, 2003).

Conformably underlying the host sequence are clastic terrestrial red beds of the Old Red Sandstone (ORS) Formation (Fig. 1). These have been interpreted as a potential aquifer for mineralizing fluids and source of metals (e.g., Hitzman & Beaty, 1986) but lead isotope studies have shown that only a minor component of ore lead can have been derived from these rocks (Everett *et al.*, 2003). Unconformably beneath the ORS lies a 2-6 km-thick (Jacob *et al.*, 1985; Lowe & Jacob, 1989;) wedge of late Cambrian to Silurian age rocks. These were originally laid down as continental arc-derived, quartz-rich feldspathic greywackes, minor volcanics, chert and shale in the Iapetus Ocean (e.g., Bruck *et al.*, 1979; Morris, 1983, 1987; Murphy, 1987; Hutton & Murphy, 1987) and were metamorphosed to zeolite to prehnite-pumpellyite grade in the Caledonian Orogeny (Oliver, 1978, 1988). Lead isotope studies of ore deposit galena, Lower Palaeozoic-hosted, galena-bearing veins (O'Keeffe, 1986; Dixon et al., 1990) and Lower Palaeozoic basement rocks (LeHuray *et al.*, 1987; O'Keeffe, 1986; Dixon *et al.*, 1990; Everett *et al.*, 2003) show that there is an excellent match between the predicted composition of Lower Palaeozoic rock-derived Pb and ore Pb at the time of mineralization. The systematic geographic pattern of less radiogenic Pb in the northwest and more radiogenic in the southeast is mimicked in both datasets, implying a dominantly vertical flow system and is interpreted as reflecting mixing of Laurentian (NW) and Avalonian (SE) Ordovician Pb sources across the Iapetus Ocean basin.

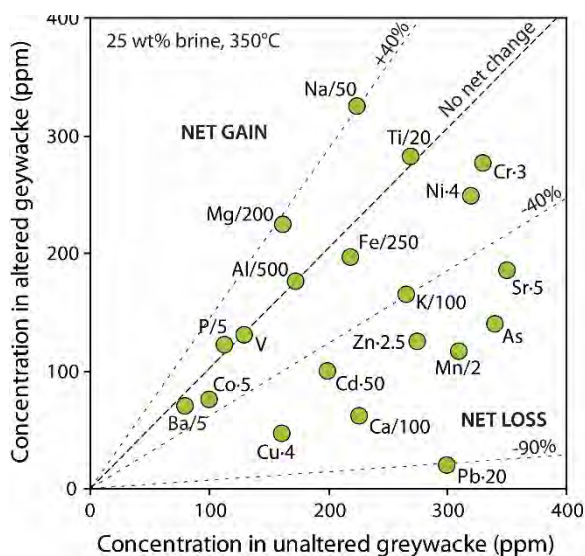The main mineralizing solutions, referred to hereafter as

Figure 3: *Isocon plot comparing composition of Lower Palaeozoic greywacke before and after interaction with brine at 350ºC, 500 bar (data from Bischoff et al., 1981). Immobility line (isocon) is defined by Al, but Ti, V and P are essentially immobile as well. Significant gain of Mg and Na in the rock is recorded during the experiment, balanced by variable loss to the brine of a range of alkali, alkali earth and transition metals.*

'principal orefluids', are known from fluid inclusion studies to be derived from partly evaporated seawater (Everett *et al.* 1999a, 1999b; Gleeson *et al.*, 1999; Banks *et al.*, 2002; Wilkinson *et al.*, 2005a) that was heated locally to at least 280ºC (Wilkinson, 2010) by deep crustal circulation via Caledonian faults and fractures (Everett *et al.*, 1999a) within the Lower Palaeozoic wedge (Fig. 2). Deeper circulation is inferred in some places (Walshaw *et al.*, 2006; Wilkinson & Hitzman, 2015), based on Sr and Nd isotopic data. These fluids are thought to have circulated back upwards in thermohaline convection cells and mixed with low temperature brines that were reservoired within shallow parts of the Carboniferous basinal sequence (Fig. 2). Where such brines were enriched in bacteriogenic sulphur, extensive mineralization developed. In some cases, cooling ± wallrock reaction of the principal orefluid alone may have led to sulphide deposition, utilising minor 'hydrothermal' sulphur that was co-transported with metals in the deep fluid, but such occurrences are typically subeconomic (Fig. 2). The depth at which fluid mixing and mineralization occurred (linked to arguments about timing) has long been controversial but the belief advanced here and detailed in a number of previous publications is that this happened at depths of near seafloor to a few hundred of metres subseafloor (see arguments in Wilkinson 2003; Wilkinson *et al.*, 2003, 2011 and summarised in Wilkinson & Hitzman, 2015).

Primary Source of Metals, Mineralogical Residence and Extraction Processes in a Deep Reaction Zone

As noted above, there is strong isotopic evidence that Pb was largely derived from Lower Palaeozoic rocks. This, combined with C, O and Sr isotope tracers (e.g., Everett, 1999; Wilkinson

et al., 2005a), which suggest that the principal orefluid had equilibrated with these rocks, provides a convincing case for a Lower Palaeozoic source of multiple ore-forming components. This idea has been tested in a number of published and unpublished experimental studies, which provide insight into the availability of metals in these rocks and how they may have been solubilised.

Bischoff Hydrothermal Greywacke Experiments

In a classic paper, Bischoff *et al.* (1981) explored the interaction of hydrothermal fluids with Irish greywacke samples, using both seawater and saline brine compositions, at temperatures of 200 and 350ºC. These showed that ore metals, and other minor metals such as Mn, As, Zn, Cd, Ni and Co, could be readily extracted from Irish greywackes, but only at significant levels in the brine (~25 wt% solids) and at high temperature (Fig. 3). The brine results show that, of the components enriched in the deposits, Pb is the most efficiently extracted from greywacke (Fig. 4), with more than 90% of the original 15 ppm taken into solution. This indicates that Pb resides in mineralogical sites that are accessible to fluids in samples crushed to <150 μm and in mineral(s) that are soluble in brine at 350ºC. Copper is the next most efficiently removed (~75%), followed by Ca, Mn, As, Zn, Cd and Sr (all >50% mobilised). Although this efficiency pattern highlights particularly labile metals, the absolute amounts taken into solution are also in part controlled by absolute abundances in the rock. Looking at things this way, Ca, K and Fe are by far the most abundant elements taken into solution (Fig. 4), followed by significant Mn. Of the ore metals, Zn is the most enriched in the brine by mass, with ~60 ppm of the original 110 ppm in the rock being extracted. This is followed by Ba, Sr, Cu, Cr, Ni, Pb and As (all >10 ppm of the original amount removed). Because of the greater efficiency of removal of Pb relative to Zn and Ba, Zn/Pb and Ba/Pb ratios in the brine (4.29, 3.57 respectively) that are inferred from the change in rock composition (the brine compositions measured are unreliable for chalcophile metals such as Pb because of a problem with alloying with the gold capsules used) are lower than in the original rock (7.33, 26.7 respectively; Table 1). Thus, putative ore fluids might be expected to be more Pb-rich than the source rock due to this extraction-related fractionation behaviour.

Cold Acid Leach Greywacke Experiments

Three Lower Palaeozoic greywacke samples were selected for analysis: 01-0108 (Castleblayney, Co. Monaghan), 01-0110 (Ballyjamesduff, Co. Cavan) and WKH-1 (Woodcock Hill, Co. Clare). See Everett (1999) for more sampling details. 0.25g of each powdered rock was leached at room temperature in 6N HCl at a ratio of 1.00g:10ml for a period of two hours in sealed polystyrene test tubes (see Crowther, 2007). The test tubes were agitated throughout the leaching time, to ensure that rock material remained in suspension. After the experiment, each test tube was centrifuged to remove residual material from suspension and the supernatant liquid was poured into separate PTFE test tubes and evaporated to dryness. Leachate fractions were remobilised in 10 ml 2% HNO$_3$ and analysed by ICP-AES at Imperial College London using standard procedures. Results are summarised in Supplementary Material.

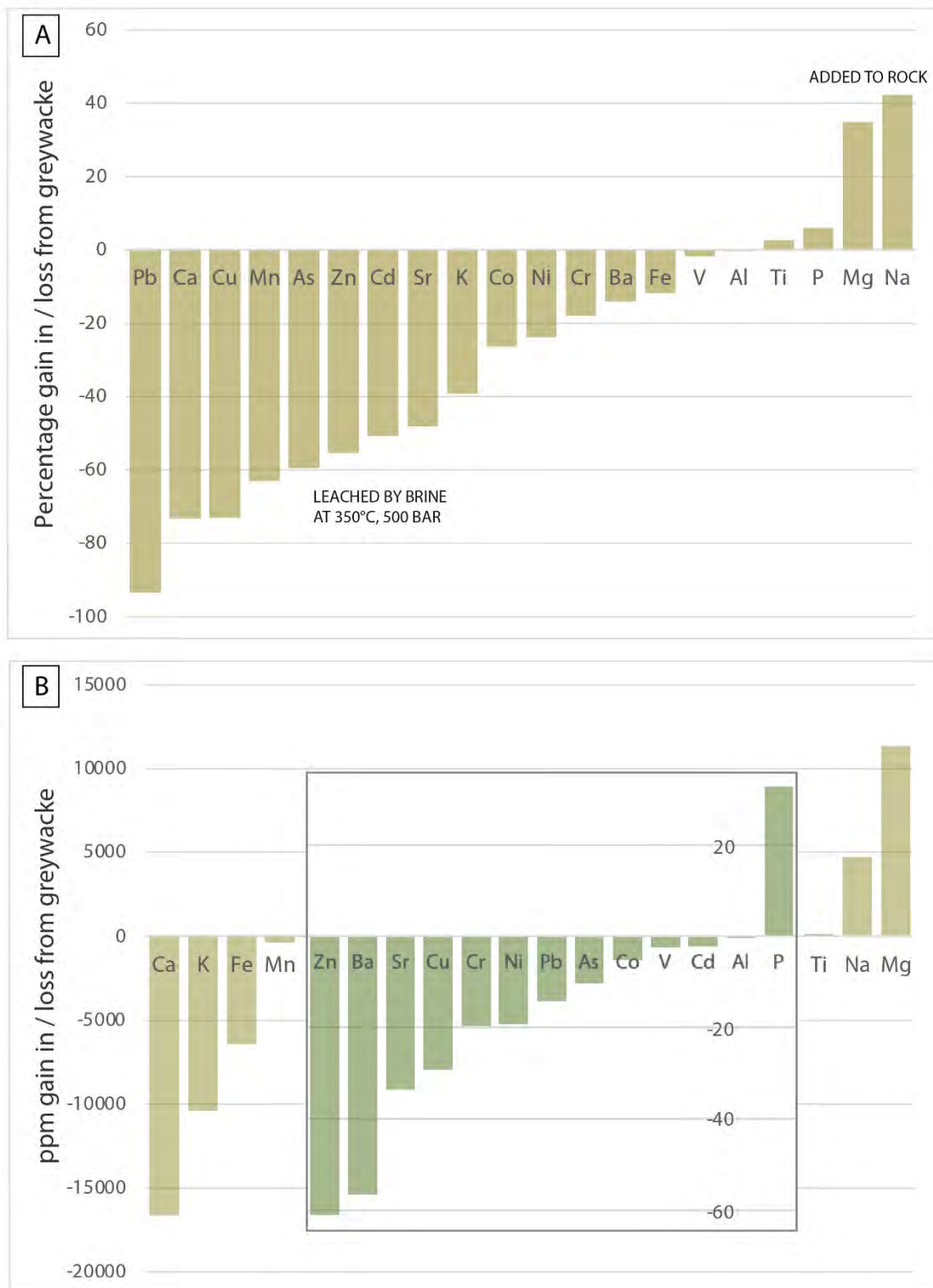Simple acid leaching experiments such as this are designed to

Figure 4: *Quantification of gains and losses in the Bischoff et al. (1981) experiments based on change in Lower Palaeozoic greywacke composition during the experiment (derived from the data plotted in Fig. 3). A. Percentage changes in element concentrations relative to initial composition, listed in order from maximum relative loss (Pb) to maximum relative gain (Na). B. Absolute changes in element concentrations listed in order from maximum absolute loss (Ca) to maximum absolute gain (Mg). Trace elements with small gains or losses are shown in the inset on an expanded scale.*
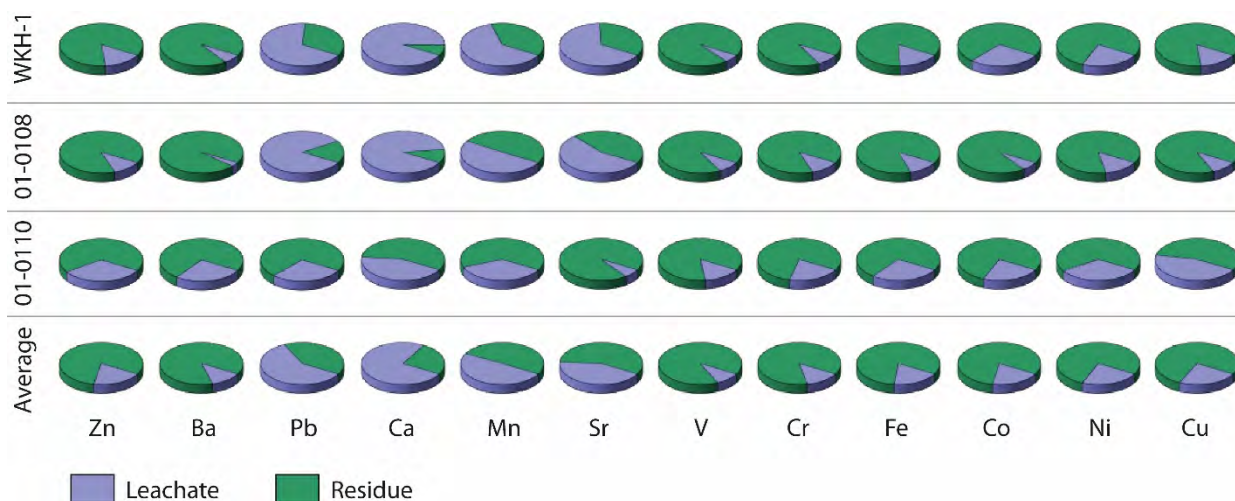
Figure 5: *Pie charts illustrating relative proportion (by mass) of a range of elements solubilised by a cold acid leach, relative to the proportion retained in the residue for three Lower Palaeozoic greywacke samples.*

investigate the mobility of elements during fluid-rock interaction, focusing on those bound in relatively soluble minerals or labile sites such as in carbonates, sulphides, oxides and adsorbed on clays or other mineral surfaces. Considering the proportion of metals in the bulk rock that are extracted (Fig. 5) shows that similar behaviour to the Bischoff *et al.* (1981) experiments is evidenced: (1) Pb is much more efficiently extracted than either Zn or Ba; (2) significant amounts of Ca, Mn and Sr are leached, assumed to be due to dissolution of carbonate; and (3) siderophile metals and Cu are extracted in similar proportions to Zn, possibly indicating a similar residence. One difference is the much greater absolute extraction of Pb over Zn, with an average Zn/Pb ratio in the leachates of 0.91 (Table 1), compared with 11.25 in the Bischoff *et al.* (1981) 350ºC brine experiment. This is interpreted to be partly due to the alloying and loss of Pb mentioned earlier, plus the fact that the greywackes used in the cold acid leach experiments had lower bulk Zn content (58-61 ppm) and slightly higher Pb (11-23 ppm). It is also likely that the hydrothermal experiments also mobilised metals from phases not broken down in the cold acid leach experiments (e.g., certain silicates) as well as allowing precipitation of new phases that incorporated elements from the starting fluid. This led to a net gain by the rock of Mg and Na, changes that would be expected in a real crustal flow system. A last noteworthy point is that some variability between samples is evident: for example, a significantly greater fraction (and total amount) of Ba, Zn and other siderophiles were mobilised from 01-0110, but significantly less Pb, Ca and Sr (Fig. 5).

Comparison with 'Principal Orefluid' Compositions

Quartz-carbonate veins observed in exposed inliers of Lower Palaeozoic rocks in the Irish Midlands contain fluid inclusions with properties similar to those of the 'principal orefluid' – the

hydrothermal end-member observed in the ore deposits (Samson & Russell, 1987; Everett *et al.*, 1999a; Wilkinson, 2010). Coupled with isotopic evidence, this has been used to suggest that these veins represent the fluid conduits exploited by

mineralizing fluids in transit through the Lower Palaeozoic wedge (Everett *et al.,* 1999a, 1999b; Wilkinson *et al.*, 2005a). Everett *et al.* (1999a) and Wilkinson et al. (2005a) reported major, minor and trace element data from fluid inclusions in feeder vein samples. The patterns of Mg depletion and Ba, Mn, Fe, Cu, Zn, Pb, Co, Ni enrichment in these fluids (Fig. 6), relative to a putative evaporated seawater precursor (Everett *et al.,* 1999b; Gleeson et al., 1999; Banks *et al.*, 2002; Wilkinson, 2010), are broadly consistent with the greywacke-fluid interaction experimental findings. In particular, the results indicate that 'proto-orefluids' that had passed through the Lower Palaeozoic wedge were significantly enriched in Pb, Co, Fe, Mn > Zn, Ba, Cu, Ni, Li > Sr relative to the proposed evaporated seawater precursor and confirm the particularly high leachability of Pb from these rocks. It is perhaps noteworthy that Mn, Pb and Co are 'scavenged' elements in seawater, i.e., they are not biolimited and accumulate by adsorption on sediment particles, especially oxyhydroxides. This means they can be enriched above normal crustal concentrations in marine sediments but also could be substantively located in adsorbed sites that would be amenable to desorption during hydrothermal fluid interaction.

Consideration of metal ratios (Table 1) shows that seawater-derived hydrothermal fluids that interact with basaltic crust are relatively enriched in Zn, with Zn/Pb ratios from vents in the East Pacific Rise and Lau Basin of >45 and, in some cases, several hundred. By contrast, fluids that have interacted with clastic rocks (e.g., Salton Sea, oilfield brines) exhibit a narrow range of ~4-5 – possibly reflecting buffering by sphalerite-galena – although this range also matches that of global average shale and footwall rocks in the Irish Midlands (Table 1). Two vents from the Guaymas Basin also have low Zn/Pb ratios; Pb enrichment here is accounted for by the fact that these fluids have interacted with an organic- and carbonate-rich sediment cover as confirmed by Pb and Sr isotope data (Von Damm, 1990).

The available fluid inclusion compositional data from Ireland (Table 1 – overleaf) shows that most feeder vein fluids linked

Sample Type	Zn/Pb (mass)	Ba/Pb (mass)	Reference
Fluids			
Seawater	316	9280	Von Damm (1990)
Rainbow vent fluid	341		Douville et al. (2002)
21 N OBS vent fluid	109	>17.2	Von Damm (1990)
21 N NGS vent fluid	69.0	>57.9	Von Damm (1990)
21 N SW vent fluid	145	>34.2	Von Damm (1990)
Lau Basin, VL-1	63.1	>8.57	Fouquet et al. (1993)
Lau Basin, VL-2	233	>5.26	Fouquet et al. (1993)
Lau Basin, VL-3	243	>10.0	Fouquet et al. (1993)
Red Sea Atlantis II Deep Brine	28.8		Brooks et al. (1969)
11-13 N EPR vent fluid 1-13	238		Von Damm (1990)
11-13 N EPR vent fluid 2-13	58.5		Von Damm (1990)
11-13 N EPR vent fluid 3-13	45.1		Von Damm (1990)
11-13 N EPR vent fluid 4-11	663		Von Damm (1990)
11-13 N EPR vent fluid 5-11	85.3		Von Damm (1990)
11-13 N EPR vent fluid 6-11	1540		Von Damm (1990)
Guaymas 1	5.00	>30.0	Von Damm (1990)
Guaymas 2	1.87	>43.6	Von Damm (1990)
Guaymas 3	19.4	>15.2	Von Damm (1990)
Guaymas 4	26.1	>155	Von Damm (1990)
Axial Volcano, Inferno	118		Von Damm (1990)
Salton Sea brines (average)	5.33	2.04	McKibben et al. (1987)
Formation brines∮	4.40	0.97	Kharaka et al. (1987)
Zambian copper belt, pre-kinematic fluid inclusions§	1.31	2.97	Davey et al. (2020)
Tri-State MVT quartz-hosted fluid inclusions	4.33	28.2	Stoffell et al. (2008)
Irish orefield fluids			
LP feeder vein average (Decrepitation ICP-AES)	0.48	25.5	Everett (1999), Wilkinson et al. (2005)
LP feeder vein average, regional samples (LA-ICP-MS)*	1.28	4.6†	Wilkinson et al. (2007), Collins (unpub)
LP feeder vein, Fantane Quarry (LA-ICP-MS)	<1.01	62.8	Wilkinson et al. (2009)
Silvermines orefluid (LA-ICP-MS; excluding 3 outliers)	n.d.	24.4	Wilkinson et al. (2009)
Feeder veins, Navan and Keel (LA- ICP-MS)	54.8	86.1	Wilkinson et al. (2007)
Rocks			
Average shale	4.75	29	Turekian & Wedepohl (1961)
Irish orefield rocks			
ORS (bleached/altered; n=12)	0.44	77.6	Everett (unpub)
ORS (n=35)	1.30	31.8	Everett (unpub)
ORS (n=4)	3.56	43.8	Wilkinson (unpub)
Lower Paleozoic greywacke (n=1)	7.33	26.7	Bischoff et al. (1981)
Lower Paleozoic greywacke (n=3)	3.13	27.1	Crowther (2007)
Irish orefield fluid-rock interaction experiments			
Cold acid leach of Irish greywacke (n=3)	0.91	6.34	Crowther (2007)
Cold acid leach of bleached/altered ORS (n=12)	0.57	187	Everett (unpub)
Cold acid leach of ORS (excluding four outliers, n=35)	2.11	82.6	Everett (unpub)
Cold acid leach of ORS (n=3)	4.97	87.7	Crowther (2007)
Seawater after greywacke interaction (200°C)	17.0	120	Bischoff et al. (1981)
Seawater after greywacke interaction (350°C)∞	30.0	42.0	Bischoff et al. (1981)
Brine after greywacke interaction (200°C)	46.3	44.7	Bischoff et al. (1981)
Brine after greywacke interaction (350°C)∞	11.2	5.06	Bischoff et al. (1981)
Extracted from greywacke by brine (net change during alteration)	4.29	3.57	Bischoff et al. (1981)
Ore Deposits			
Navan	4.33		Ashton et al. (2018)
Tara Deep	4.72		Ashton et al. (2018)
Lisheen	5.88		Fusciardi et al. (2003)
Lisheen	5.93		Torremans et al. (2018)
Lisheen Island Pod	12.5		Doran et al. (2022)
Galmoy	15.6		Production 1997-2000; Lowther et al. (2003)
Galmoy	4.96		Production 1997-2006; mineralsireland.ie
Silvermines	2.73		Taylor & Andrew (1978), Taylor (1984)
Average MVT ore¶	3.00		Leach et al. (2005)
Average SedEx ore¶	2.46		Leach et al. (2005)

Table 1. *Summary of metal ratios in rocks, fluids and ores*
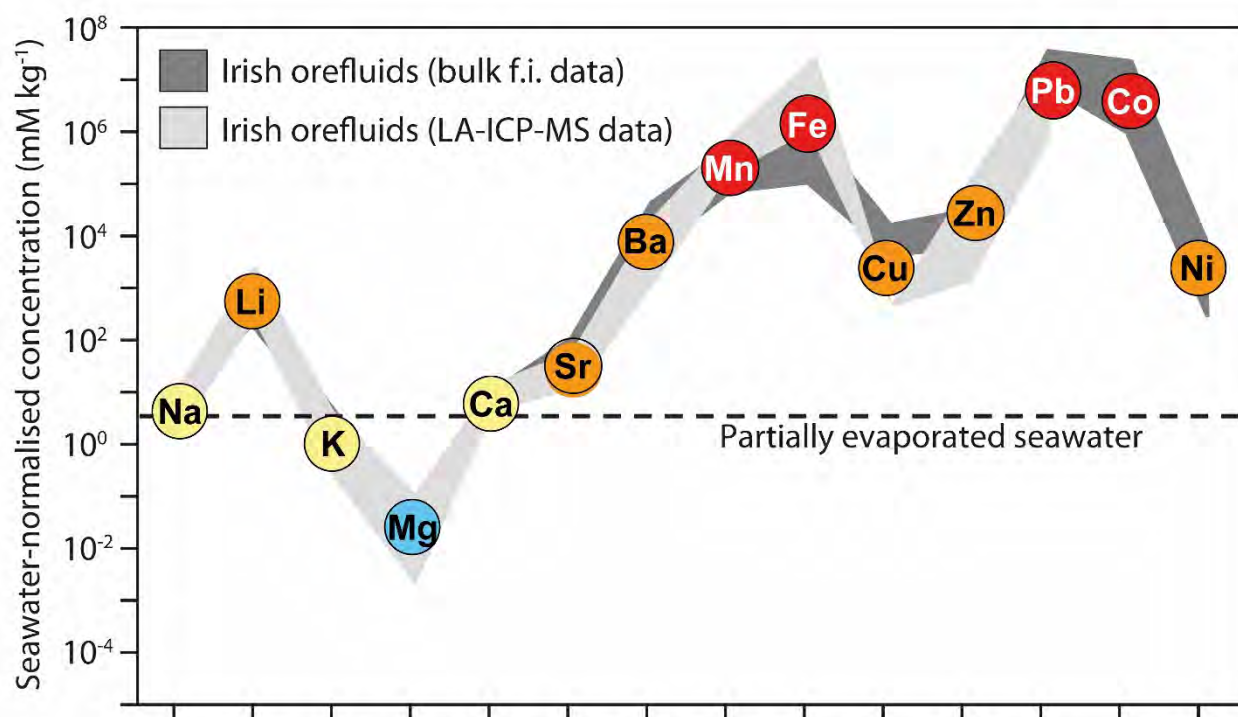
Figure 6: *Irish 'principal orefluid' compositions determined by bulk decrepitation ICP-AES and individual fluid inclusion LA-ICP-MS analysis (data from Everett et al., 1999a; Wilkinson et al., 2005a; Wilkinson et al., 2007) normalised to a nominal partially evaporated seawater precursor, as inferred from fluid inclusion halogen analyses (Gleeson et al., 1999; Banks et al., 2002). The plot shows that Mn, Fe, Pb and Co (red) are highly enriched (>105 times initial concentration) during seawater interaction with the (presumed) Lower Palaeozoic wedge. Li, Sr, Ba, Cu, Zn and Ni are moderately enriched (10 to 104 times) and Mg is strongly depleted from the starting fluid.*

to the Carboniferous mineralizing system have Zn/Pb ratios of ~0.5-3, so appear to be relatively Pb enriched. This range is a good match for the cold acid leach experiments on greywacke (Zn/Pb ~0.9) and is not dissimilar to the brine value inferred from the Bischoff *et al.* (1981) experiments based on the rock composition before and after hydrothermal interaction (~4.3). These values are also similar to brine inclusions measured from the Zambian Copper Belt (~1.3; Davey *et al.*, 2020). These results lead to the conclusion that relatively low Zn/Pb ratios are a natural product of saline fluid interaction with clastic rocks, especially those containing Pb-bearing phases such as K-feldspar and plagioclase. A link between systems containing clastic aquifers and elevated Pb in ores (vs. carbonate aquifers) has long been recognised in MVT deposits (Sverjensky, 1986).

An exception to this general pattern is the feeder vein fluid data acquired from Keel and Navan in the northern Midlands (Wilkinson *et al.*, 2007) which suggests much higher average Zn/Pb ratios in fluids of ~55. This might reflect fractionation of metals prior to arrival of fluids at the sampled veins (e.g., by preferential galena precipitation). Alternatively, there is the potential involvement of a greater component of volcanic source rocks north of the Iapetus suture zone, as observed beneath the Navan deposit (Ashton *et al.*, 2015) that would likely lead to higher Zn/Pb, more in line with fluids in basalt-interacted systems (Table 1).

Considering Ba/Pb ratios, basalt-interacted hydrothermal

fluids have elevated values >5, though more typically >30 (Table 1). Conversely, clastic-interacted fluids appear to exhibit lower ratios of <3 (Salton Sea, oilfield brines, Zambian copper belt brines). This appears to support the inference that Pb is generally enriched in fluids interacting with clastic source rocks, particularly feldspathic ones. However, the existing Irish 'principal orefluid' fluid inclusion datasets mostly yield Ba/Pb ratios of >24 (Table 1), with the northern Midlands samples from Navan and Keel having an even higher average ratio of 86. These values are not dissimilar to those of the bulk greywacke in Ireland and average crustal shale so, although high Ba/Pb implies significant mobility of Ba in the Irish system, this probably has more to do with unusually efficient extraction of Ba (in a similar proportion to Pb). It is hypothesized that this is due to the relatively reduced nature of the Lower Palaeozoic wedge which would favour Ba mobility by suppressing fluid sulphate content; high SO_4^{2-} would limit Ba transport due to saturation with barite (e.g., see Cooke *et al.*, 2000). Even higher Ba/Pb values for the northern Midlands fluids could be interpreted again as reflecting a greater volcanic component in the source rock sequence north of the Iapetus Suture.

Mineralogical Controls of Metal Release

It is evident that arc detritus of the Lower Palaeozoic sequence was a fertile source of base metals (and Ba) for mineralization in the Irish Orefield. Three questions that follow are: (1) which minerals are the principal host for the ore and associated metals; (2) what conditions might have been required for metal
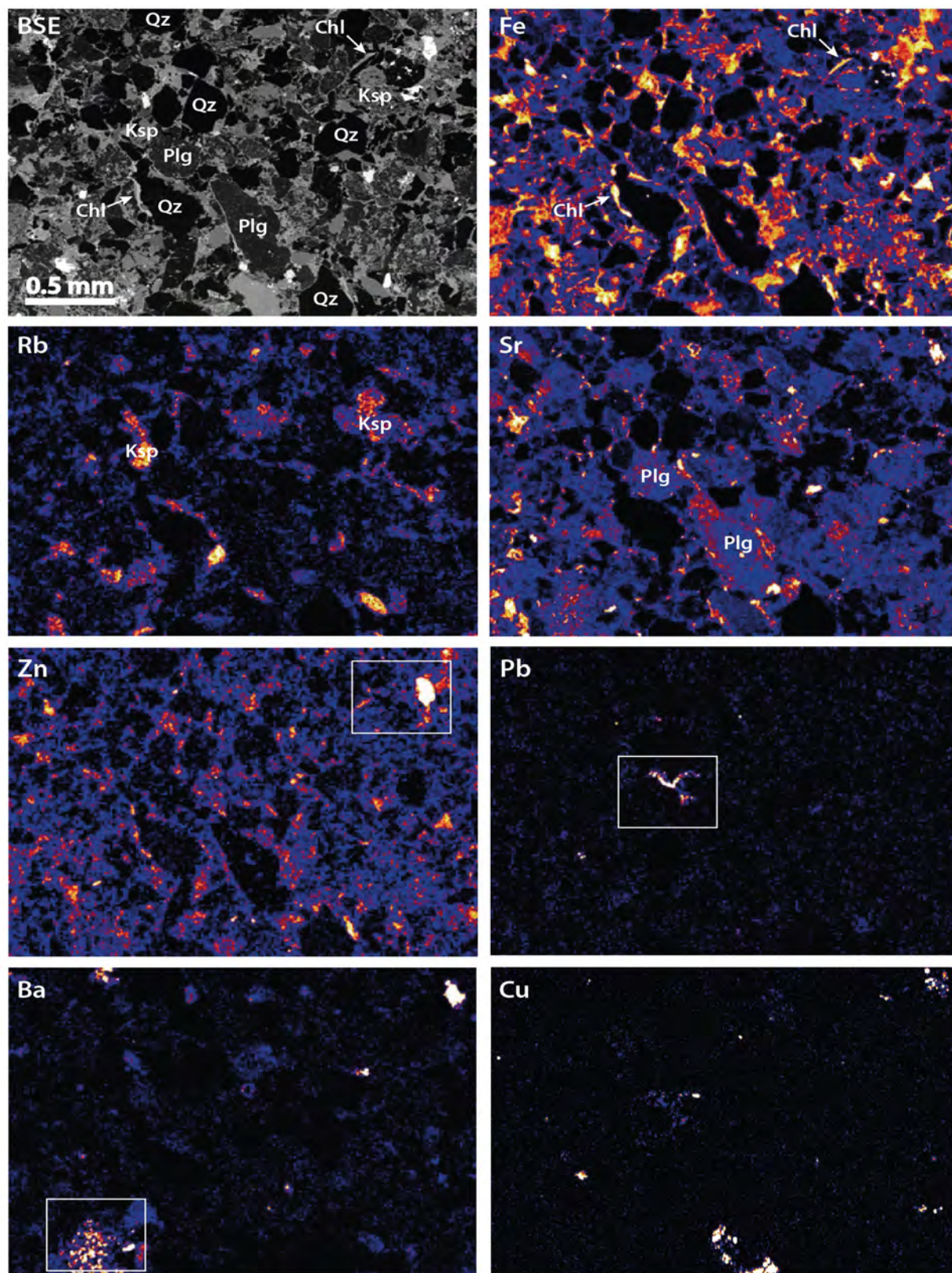
Figure 7:   Scanning electron microscope backscattered electron and particle-induced X-Ray emission (PIXE) element maps of greywacke sample 01-0110, acquired at the nuclear microprobe facility, University of Melbourne. Some of the images were previously reported by Wilkinson et al. (2009). The Fe map primarily highlights chlorite grains wrapping detrital grains and in the matrix; Rb highlights detrital alkali feldspar and Sr detrital plagioclase. Pb, Ba and Cu maps show that these elements are primarily hosted by low abundance phases containing high concentrations of metals. Boxes indicate areas shown in higher magnification in Figure 8. Qz = quartz, Chl = chlorite, Ksp = K-feldspar, Plg = plagioclase/albite.
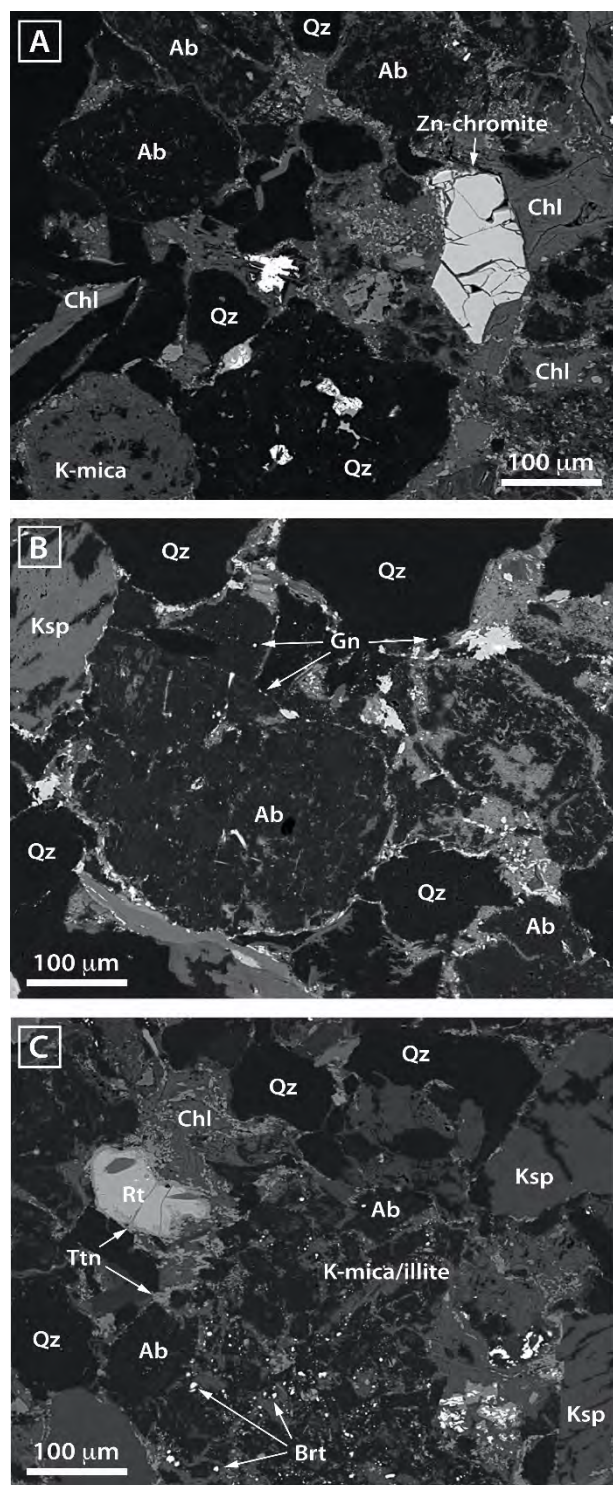
Figure 8: High magnification scanning electron microscope backscattered electron and particle induced X-Ray emission (PIXE) element maps of parts of the greywacke sample 01-0110 shown in Figure 7. A. Area focusing on deportment of Zn, which principally occurs in chlorite (Chl) and Zn-chromite. Qz = quartz, Ab = albite. B. Area focusing on deportment of Pb which occurs as minute grains of galena (Gn) in the matrix and within secondary albite. Ksp = K-feldspar. C. Area focusing on the deportment of Ba, which occurs primarily in minute barite grains (Brt) in an area of altered alkali feldspar. Rt = rutile, Ttn = titanite.

release; and (3) given the somewhat higher Zn/Pb of the measured greywacke samples from Ireland (Table 1) compared with 'principal orefluids', what controls the fractionation of Pb from Zn during metal liberation?

Based on their hydrothermal experiments, Bischoff *et al.* (1981) concluded that Ca and Mn were primarily released by dissolution of dolomite. This is consistent with the high percentage extraction of Ca, Mn (and Sr) observed in the cold acid leachates (Fig. 5) but the difference between Ca and the less abundant Mn and Sr in these experiments and the fact that Mn and Sr do not fall on a common line with Ca through the origin in the Bischoff *et al.* (1981) data for the rock before and after reaction (Fig. 3) might imply that Mn and Sr are partly derived from a less soluble, non-carbonate phase. Alternatively, preferential reprecipitation of Mn (and potentially Fe) in oxyhydroxides or clays in the experiments could also account for the difference in behaviour. Iron and K were interpreted to be derived from illite breakdown; other potential sources of Fe such as sulphides and oxyhydroxides were ignored. The base metals were inferred to come from an unidentified 'common matrix' (Bischoff *et al.*, 1981).

A more detailed investigation of the mineralogy and residence of metals in Lower Palaeozoic greywackes was reported by Wilkinson *et al.* (2009). Particle-induced X-ray emission (PIXE) analyses of the same three greywacke samples used in the cold acid leach experiments yielded an estimated bulk composition of ~60 ppm Zn, ~20 ppm Pb, consistent with the average of the bulk rock analyses for these samples (74 ppm Zn, 23 ppm Pb). Images generated by PIXE mapping and using SEM backscattered electron imaging (Figs. 7, 8) show that Fe and Zn are hosted by chlorite (average 18 wt% Fe, 215 ppm Zn), but also occur in illite and other fine-grained phases in the greywacke matrix. Zinc also occurs at very high concentrations in Zn-chromite grains (Fig. 7), but these are rare in the samples studied. The chalcophile metals, including Pb, were found in trace sulphides (Fig. 8). Pb also occurs at low concentrations in K-silicates. Barium was primarily found in the form of barite (Fig. 8) and at low concentrations in K-silicates. These conclusions on the mineralogical residence of the main ore metals are partly consistent with the inferences of Bischoff *et al.* (1981).

Combining estimates of modal mineralogy with estimated concentrations of major, minor and trace metals in the minerals allows the residence (or deportment) of key elements to be quantified. The results for 01-0108 (Fig. 9) show that siderophile metals are primarily hosted by chlorite with a significant concentration of Ni and Mn in the (primarily illitic) matrix. The chalcophile metals – Cu, Pb and As – are primarily hosted by matrix-hosted sulphides, with compositional evidence pointing to pyrite, arsenopyrite and trace galena. At least 50% of the Ba is hosted by barite which occurs as fine-grained disseminations in the matrix (Fig. 8), possibly associated with breakdown of barian K-feldspar and often enclosed by secondary albite, implying a pre-metamorphic (weathering or diagenetic) origin. Sample 01-0110 shows a broadly similar pattern for Zn and the other siderophile elements but has slightly more Zn and less Ni in the matrix. Cu, Pb and As are still substantively present in sulphides but a significantly greater proportion are hosted by chlorite and the matrix. 01-0110 has more leachable Zn than 01-0108 (Fig. 5) which could be accounted for by the higher
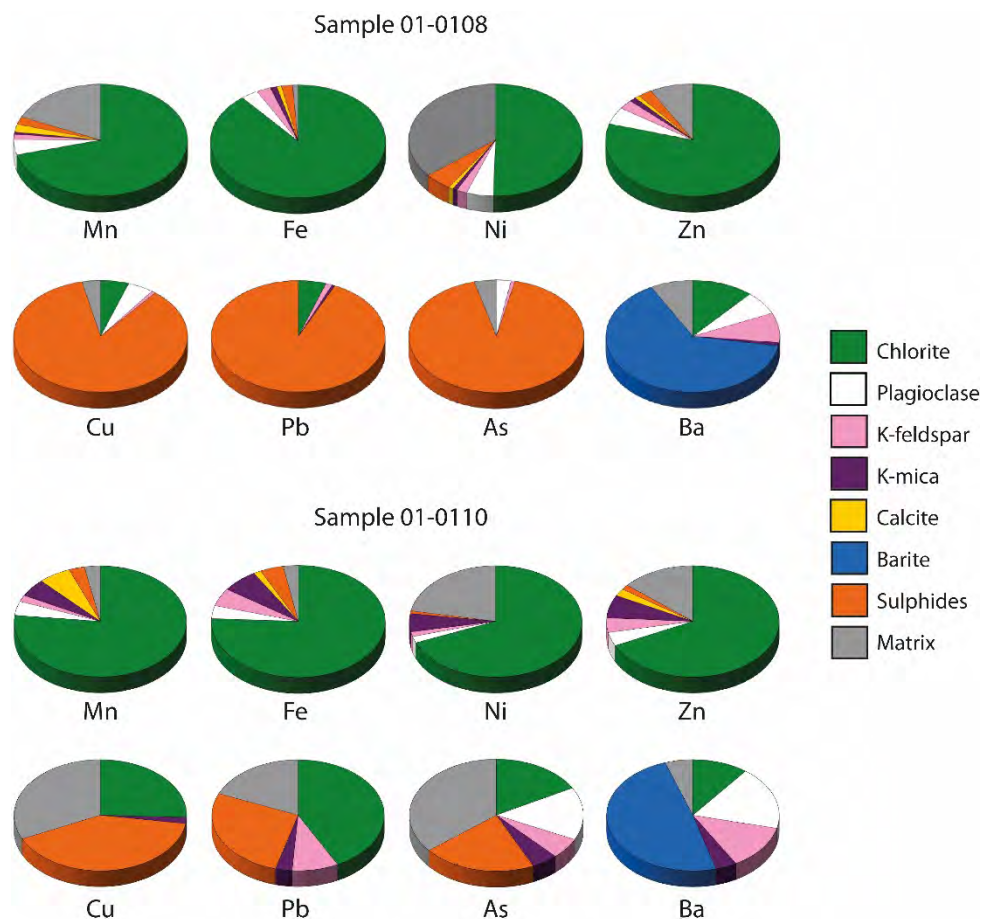
Figure 9: *Pie charts illustrating mineralogical deportment of metals in two Lower Palaeozoic greywacke samples, calculated by combining estimates of modal mineralogy, mineral density and estimates of average element concentrations in each phase, either derived from stoichiometric values (e.g. barite, galena) or from PIXE measurements. The matrix is assigned an average density of 2.7 g cm-3. Some adjustments were made to ensure results could be reconciled with bulk rock compositional data. This introduces some uncertainties but will not affect the general patterns of residence observed.*

proportion of Zn in the matrix. 01-0110 also has a greater proportion of leachable Ba (Fig. 5) which is most likely due to the greater amount of barite in the sample, despite the more diverse deportment (Fig. 9). Conversely, 01-0108 has significantly more leachable Pb than 01-0110 and differs primarily from 01-0110 in that much more of the Pb is hosted by trace sulphides rather than in primary silicates like K-feldspar (Fig. 9).

These observations suggest that the greywacke matrix is an important source of labile Zn (as inferred by Bischoff *et al.* (1981), but that for significant extraction of more of the bulk rock Zn the hydrothermal fluids would need to be capable of breaking down chlorite. The presence of significant Ni in labile sites can account for the local enrichment of Ni in some of the deposits (e.g., Lisheen). The predominance of barite as the primary host of Ba indicates that reduced hydrothermal fluids are required for mobilisation. Heterogeneity in the K-feldspar content of the greywackes and the extent of weathering/burial diagenesis and/or the redox state of the fluids would influence regional variations in the Ba content of proto-orefluids. Trace sulphides, especially galena, in the greywacke matrix appear to be key for Pb mobility and the textural position of these grains can account for the relative enrichment of Pb in the

fluid-rock experiments and in the measured fluid compositions. It follows that for hydrothermal fluids to extract ore metals from these rocks they must be capable, in the main "reaction zones" (Fig. 2), of: (1) dissolving barite (so relatively reduced); (2) dissolving sulphides (so relatively low pH and/or high temperature and low in total reduced sulphur); and (3) capable of leaching the greywacke matrix (producing low Zn/Pb fluids) or destroying or leaching metals from chlorite (producing higher Zn/Pb fluids), possibly via biotitisation or sericitisation.

Fractionation of metals during upward flow

Lower Palaeozoic transit

The observation of sulphides in feeder veins, principally pyrite, but with galena, sphalerite and chalcopyrite present locally (Everett, 1999; Everett *et al.*, 1999a), indicates that some loss of metals occurred from fluids during transit through the Lower Palaeozoic wedge. Regionally, the historic mining of mainly Pb from veins of this kind, especially within the Longford Down inlier (Fig. 1; Morris, 1984; O'Keeffe, 1986), suggests that Pb depletion could be one of the principal effects.
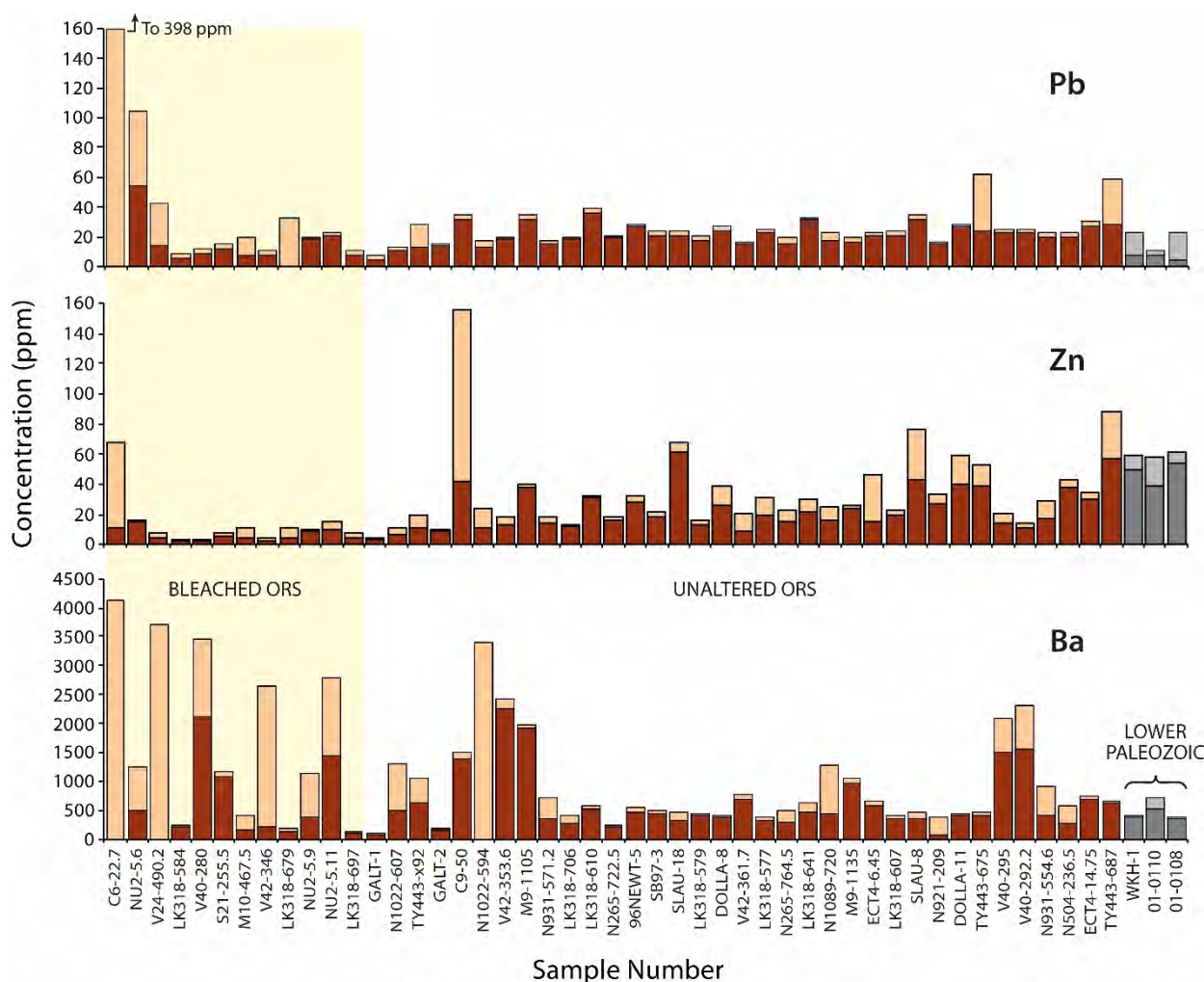
Figure 10: *Histograms showing distribution of Pb, Zn and Ba between cold acid leachates and residues in a variety of ORS samples, both hydrothermally altered (left side) and apparently unaltered (right). Results for three Lower Palaeozoic grey-wackes are included for comparative purposes (data reported in Fig. 5). The total height of each bar represents the bulk rock concentration of each element.*

However, from the available fluid data (Table 1) it is not easy to assess whether such fractionation was significant. It is concluded here that only limited fractionation is likely, given that the measured feeder veins are likely to have formed in the upper parts of the Lower Palaeozoic wedge and that such fractionation processes are likely to have already initiated, yet the metal ratios observed in fluid inclusions are broadly consistent with expected source rock extraction patterns.

Old Red Sandstone Transit

After passing through the Lower Palaeozoic sequence, proto-orefluids would have traversed the Old Red Sandstone (Figs. 1, 2). The effects of this transit would likely vary significantly from south to north across Ireland because of the thinning of the unit from 5-6 km in the Munster Basin (Williams *et al.*, 1989) to typically <100 m in central Ireland (Emo & Grennan, 1982), and <50 m at Navan. The best studied area is at Silvermines (Fig. 1; Mallon, 1997; Everett, 1999) where the ORS is well exposed in the footwall of the main normal fault systems and has been intersected in numerous drillcores. This area is of

particular interest because of the extensive vein systems developed within it that were mined in antiquity. Field evidence at Silvermines (e.g., Mallon, 1997) and Pb isotope data (Everett *et al.*, 1999a) indicate that flow within the ORS was mainly structurally controlled and involved limited extraction of Pb, with significant lateral flow through the unit unlikely.

Cold acid leach ORS experiments and residue analysis:

Samples of both apparently unaltered (red) and altered (variably bleached) ORS were collected across the Irish Midlands by Everett (1999). These were leached using the same HCl acid leach procedure described above as part of the Everett et al. (2003) study of Pb isotopes. In addition, bulk samples of ~0.25 g were digested in PTFE tubes containing HF, HNO_3 and $HClO_4$ in a ratio of 3:2:1. Samples were heated for 3 hours at 90ºC and 3 hours at 140ºC before being evaporated to dryness. Once dry, samples were remobilised in 10 ml 2% HNO_3 prior to analysis at Imperial College London by ICP-AES (see Everett, 1999, for further details).
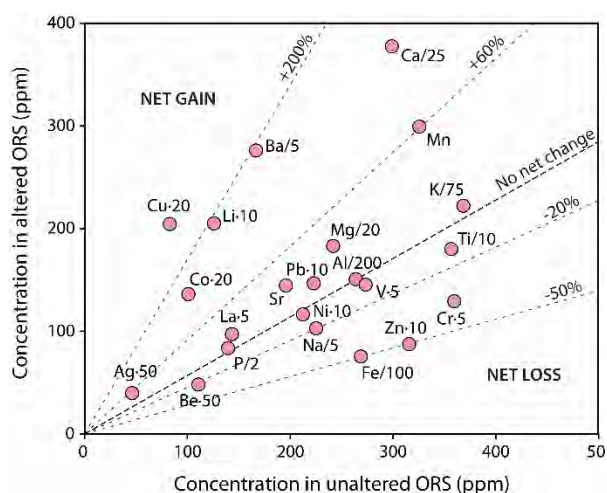
Figure 11: Isocon plot for the ORS, showing the linearly-scaled average composition of 12 altered samples plotted against the average composition of 15 unaltered samples. Some outlying results were excluded in the calculation of averages (see text for details). Immobility is assumed for Al which defines the isocon, but P is also an essentially immobile element; the isocon has a slope of 0.57 indicating bulk mass gain. Modified after Wilkinson (2014).

Consideration of the results for Pb (Fig. 10) shows that high concentrations in the ORS are limited to three altered samples in which a large proportion of the total Pb is leachable (likely in the form of added hydrothermal galena). In unaltered samples, the average Pb content is ~26 ppm with only a low acid leachable fraction (average ~17%). Thus, the ORS has similar bulk Pb content to Lower Palaeozoic greywackes, but the leachable fraction is much lower.

Results for Zn (Fig. 10) clearly show that altered ORS is generally depleted in Zn. Unaltered samples contain on average ~35 ppm Zn and typically about a quarter of this is leachable in cold acid experiments. The results indicate that the bulk Zn content of the ORS is lower than for Lower Palaeozoic greywackes but the leachable fraction (at least in a cold acid attack) in ppm terms is about the same (Fig. 10).

Barium results are more variable but Ba-rich altered samples have a very high proportion of acid soluble Ba (probably added hydrothermal barite). Unaltered samples contain an average ~860 ppm Ba of which about a quarter on average is leachable. Comparison with the Lower Palaeozoic greywacke results shows that, at least locally, the ORS contains significantly more leachable Ba and could conceivably source Ba to mineralizing fluids.

Chemical mass transfer analysis of fresh and altered ORS:

Whole rock data from 12 samples of bleached ORS were averaged (samples shown in Figure 9) and compared with the average composition of 15 red sandstone samples, selected to represent a "least altered" precursor. The Zn concentration in one altered sample and Pb data from three altered samples that were anomalously high (due to significant sulphide overprint)

were excluded from the averages. A conventional mass transfer analysis approach (Gresens, 1969; Grant, 1986) was used, with Al used as the immobile reference, to calculate net changes in element concentrations during the natural alteration process. The isocon slope defined by Al immobility (Fig. 11) has a slope of 0.57 indicating bulk mass gain during alteration; petrographic analysis of altered rocks shows that calcite, dolomite, quartz, chlorite and illite were all precipitated during hydrothermal interaction (Hitzman *et al.*, 2002; Everett et al., 2003) and can account for the bulk mass gain and associated immobile element dilution.

Calculated net gains and losses for a range of elements, in both mass percentage of the initial concentration and in absolute ppm amounts are illustrated in Figure 11. In terms of major changes, the primary effects are the loss of Fe (due to removal of Fe oxide grain coatings during bleaching), addition of Ca, Mg, Mn and Sr (calcite-dolomite precipitation; see Everett *et al.*, 2003) and addition of K (muscovite precipitation). In terms of efficiency of extraction, Zn, Fe and Cr are the most mobile, with around 50% of the original Zn and Fe being removed during alteration. The ORS is therefore a source of Zn and Fe (and potentially trace Cr) for the overlying deposits.

However, a lot of elements show net addition during alteration, indicating that the ORS also acted as a trap: in percentage gain terms, Cu is the most added, followed by Ba, Li, Co and Ca (all >100% gained). The enrichment of Cu (~330% gain) and Ba (~190% gain) in the ORS is not surprising given the observation of extensive vein-hosted chalcopyrite and barite in the Shallee zone at Silvermines (Rhoden, 1959; Taylor & Andrew, 1978; Mallon, 1997), which was economically worked for Cu in the 17th and 18th Centuries (Grennan & Andrew, 2019). The occurrence of argentiferous galena veins at Shallee, discovered in ~1770, is indicative of the trapping of substantive amounts of Pb (and Ag) in the ORS although the percent gains recorded here (Fig. 12) in unveined, primarily unmineralized samples, are small (~15% gain, equivalent to ~3 ppm). The ~50% gain in Ag (equivalent to an average of about 0.5 ppm addition) is consistent with the occurrence of Ag mineralization that was reputedly worked at Silvermines from 1289 (Grennan & Andrew, 2019). The enrichment in Ba may be partly due to the development of barian muscovite (Mallon, 1997) which is also a likely host for elevated Li (~190% gain). Co addition (~140% gain) is attributed to incorporation in hydrothermal pyrite and/or chlorite.

Although extensive trapping of Cu, Pb and other metals is noted in the ORS at Silvermines, the extent of this process appears to vary between deposits, with only limited sulphide development (chalcopyrite, galena) observed in the upper parts of the ORS intersected at Lisheen (Everett *et al.,* 2003). Bleaching of the ORS at Navan is restricted to <3 m wide zones around faults (Mallon, 1997; Everett *et al.*, 2003) which contain significant chlorite, calcite, dolomite and quartz but only trace sulphides (pyrite, chalcopyrite, sphalerite and galena). This could reflect a number of factors, such as the temperature and oxidation state of proto-orefluids, with the possibility of more reduced and higher temperature fluids in the south leading to greater degrees of reaction with the ORS and thus more metal fractionation.
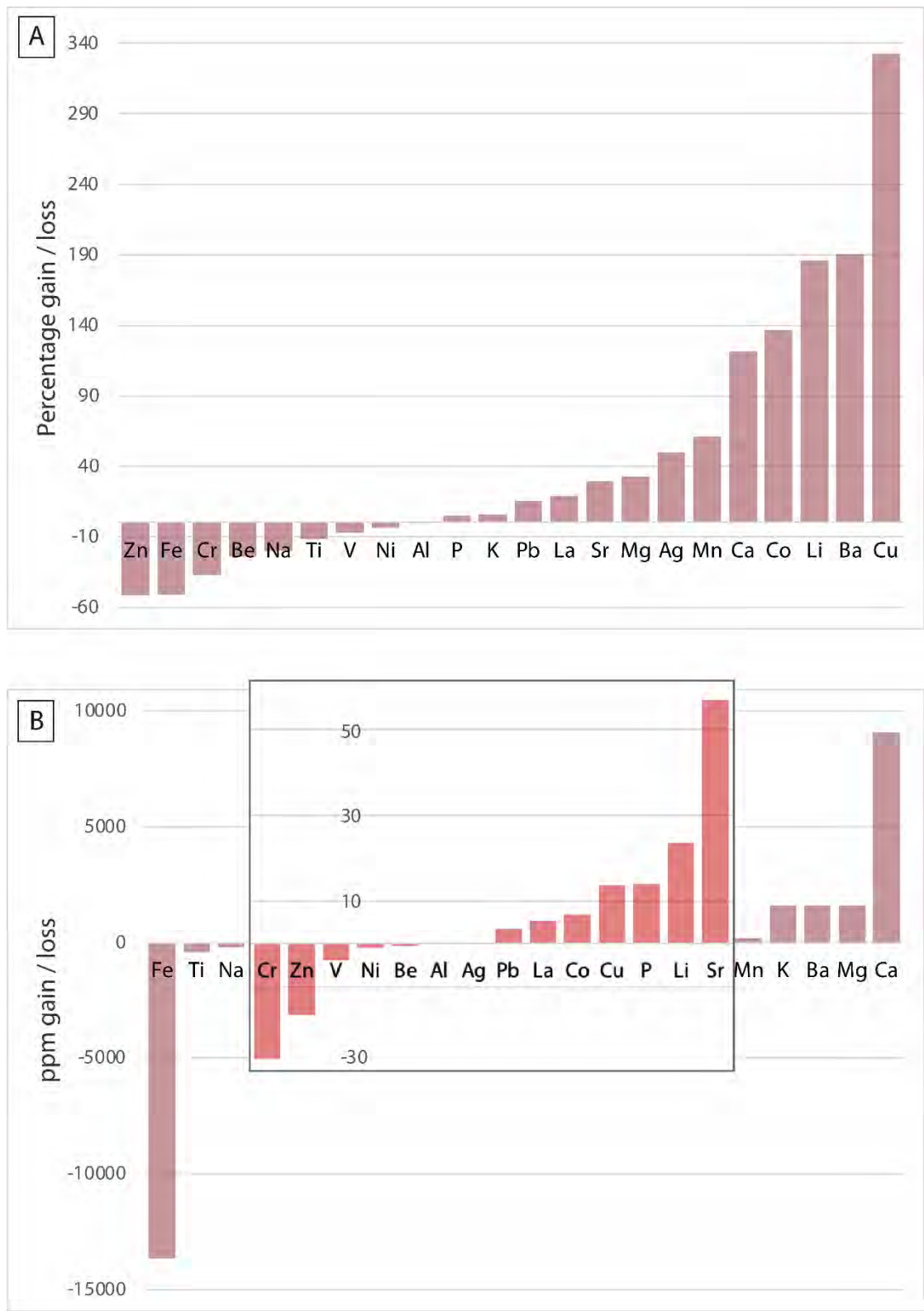
Figure 12: *Quantification of gains and losses in the ORS during natural alteration by hydrothermal fluids based on the mass transfer data shown in Figure 11. A. Average percentage changes in element concentrations in altered rocks relative to the average unaltered precursor, listed in order from maximum relative loss (Zn) to maximum relative gain (Cu). B. Absolute changes in element concentrations listed in order from maximum absolute loss (Fe) to maximum absolute gain (Ca). Trace elements with small gains or losses are shown in the inset on an expanded scale.*

Metal Zonation in the Ore Deposits

In comparison to the data presented here from footwall sources of information, metal distribution and controls within the deposits themselves are relatively well studied, in large part due to the wealth of company assay data available. Classic papers by Taylor & Andrew (1978) and Taylor (1984), which highlighted patterns of Pb and Zn distribution at Silvermines, were followed in more recent times by detailed maps, based on tens of thousands of drillcore assays, of Zn, Pb and Fe at Navan (Ashton *et al.*, 2015, and references therein), and of Zn, Fe Pb, Ni and Ag distributions at Galmoy (Lowther *et al.*, 2003) and Lisheen (Fusciardi *et al.*, 2003; Torremans *et al.*, 2018).

Silvermines

At Silvermines, which is a more Pb-rich deposit compared with the others that have been developed (Table 1), Taylor (1984) recorded Zn/Pb ratios of <0.1 in narrow zones ~100-200 m long close to the B-fault that localised mineralization in the B-zone (Fig. 13). These were interpreted to be feeder zones where mineralizing fluids were focused. Ratios increased to over 0.5 into the hangingwall B-zone ore, over a distance of around 250 m. These values contrast with the 2.6 average for ore extracted from the B-zone during the life of the mine (Taylor, 1984) and the 2.73 for the entire deposit (Table 1), implying that the more distal ore zones were increasingly Zn-rich. The best depiction of vertical and lateral metal zonation at Silvermines is given by Torremans *et al.* (2018), with a cross-section of the G-zone clearly showing consistently low Zn/Pb (<2) in the main G-fault and then sharp increases to values ~10, mostly within the first 100 m into the hangingwall.

Overall, the Silvermines system contained more Pb than the other mined deposits, as well as up to 1.13 oz/short ton (35 ppm) Ag (Taylor, 1984). The Ag/Pb ratio of the B-zone ore of 0.0013 (the same as the Ag/Pb ratio of the ore resource reported at Lisheen in 1996; Shearley *et al.*, 1996) is significantly lower than the 0.024 of the Lower Palaeozoic rocks and 0.042 of unaltered ORS considered in this paper. Given that Ag was not detected in the cold acid leachates of Lower Palaeozoic samples reported here, it is suggested that Ag was not efficiently extracted from the primary source rocks. However, the chemical mass transfer analysis of altered ORS (Fig. 11) shows that some Ag is likely to have been preferentially trapped in the unit rather than sourced from it, with an elevated Ag/Pb of ~0.05 in altered ORS. Thus, loss of Ag from orefluids prior to arrival at the Lower Carboniferous host rocks is also a possible explanation for apparently low Ag contents in the ores. Median Ag/Pb of ores in SedEx deposits in general is 0.0020 (derived from Leach *et al.*, 2005) so 'missing' Ag (relative to common source rock contents) may be a common phenomenon.

Lisheen

Fusciardi *et al.* (2003) presented the first detailed metal zoning maps at Lisheen and identified a general trend of increasing Zn/Pb away from the main controlling fault structures (Fig. 13), with Pb showing similar behaviour to Cu, Ni (Fig. 13) and Ag in being concentrated at several points close to these structures. These zones had previously been interpreted as feeders (Eyre, 1998) and this is supported by sulphur isotope data

(Wilkinson *et al.*, 2005b). Torremans *et al.* (2018), building on the earlier work, confirmed that Cu, Ni, Co, Cd, and Ag are enriched proximal to distinct points along the major normal faults (Fig. 13). Petrogenetic observations have shown that this pattern is related to the predominance of chalcopyrite, bornite, tetrahedrite-tennantite, Pb sulphosalts, galena, niccolite and pararammelsbergite in these fault-proximal locations (Redmond, 1997; Eyre, 1998; Fusciardi *et al.,* 2003; Wilkinson *et al.*, 2005b). In their mass transfer study of dolomite alteration, Wilkinson *et al.* (2011) observed similar patterns of metal addition near the main faults at Lisheen, but also recorded net gains of Cd, Li, Na, K, Be, Ba and P that were assumed to be contributed by the 'principal orefluids'. Nickel was considered to be the best indicator of the location of major feeder zones.

Galmoy

At Galmoy, Lowther *et al.* (2003) documented zones of high combined Zn+Pb proximal to the G-fault in the G-zone and in the centre of the CW orebody along the 'NW fissure', interpreted to represent the main points of fluid ingress into the deposits (Fig. 13). Zn/Pb ratios in the G-zone are in the range 2-30, but the majority are in the range 2-7 (mined average for Galmoy as a whole = 4.96; Table 1). Zones of high Pb correspond to high Ag (e.g., G-zone northeast, up to 430 ppm) and low Zn/Pb ratios of 2-7, consistent with these areas representing the location of high temperature feeder zones. High Ag zones correspond to the occurrence of 'ruby silver' (?pyrargyrite). The CW zone, which is regarded as a satellite orebody further from the main controlling fault array (Lowther *et al.*, 2003), is very Zn-rich, with much of the ore having a Zn/Pb ratio above 12, and it is also very low in Ag. The high Zn/Pb ratio that characterised the initial 3 years of production (Table 1) reflects the fact that the CW orebody was developed first. The more Zn-rich nature of the orebodies at Galmoy, especially the CW zone, may be linked to the generally lower temperatures of mineralization documented in fluid inclusion studies (Eyre, 1998; Wilkinson, 2010). Unlike Silvermines and Lisheen, Zn/Pb ratios appear to decrease towards the lower grade orebody margins (Fig. 13).

Navan

At Navan, the Zn/Pb ratio decreases downwards in the successive ore lenses, reaching a maximum at the base of the ore zones (Ashton *et al.*, 2015), consistent with the temperature dependence of galena and sphalerite solubility in sulphide-saturated fluids that favours galena precipitation at higher temperatures. Fe shows the opposite behaviour, tending to be enriched at higher stratigraphic positions (Andrew & Ashton, 1995). In general, zones of maximum Zn+Pb, inferred to represent zones of focused fluid input, correspond to intermediate Zn/Pb ratios of 4-5, as in the 5-lens of the main ore zone and in the SWEX 3-U lens (Fig. 13). Although Zn/Pb ratios tend to increase away from potential feeders in the SWEX, in the Main zone Zn/Pb trends are complex and actually decrease towards the west. This relatively Pb-rich area is loosely coincident with the position of an extensive zone of cross-stratal dolomitization interpreted to be related to downward flowing low temperature brines (Ashton *et al.*, 2015). Modelling of fluid mixing at Navan (Yardley, unpublished) showed that mixing small amounts of the 'principal orefluid' into large amounts of brine
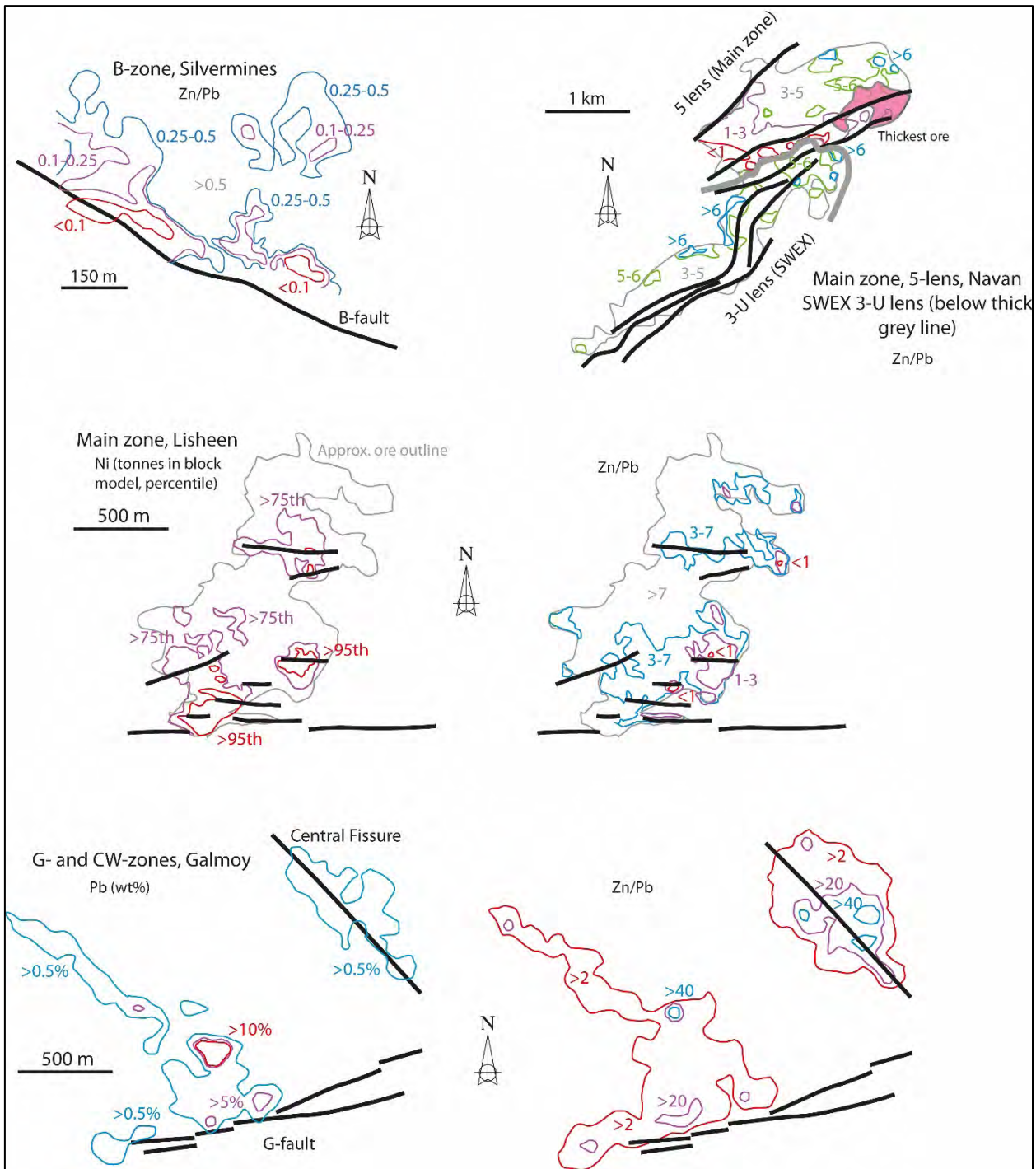
Figure 13: *Simplified maps of metal distribution and zoning patterns in the main Irish ore deposits. Data from Fusciardi et al. (2003), Torremans et al. (2018), Ashton et al. (2015) and Lowther et al. (2003).*

would favour galena precipitation over sphalerite, all else be-ing equal. Interestingly, Marks *et al.* (2014) reported a broad halo of low grade, galena-dominant sulphide mineralization up to 2.5 km from the main deposit that was characterised by Zn/Pb ratios of <1, which could be similarly controlled.

Summary

Thus, the metal zonation patterns in the different deposits are generally comparable, with high Pb, Ni, Cu and Ag in proximal

locations and increasing Zn/Pb ratios upwards. Lateral varia-tions in Zn/Pb are inconsistent, with the higher temperature systems at Silvermines and Lisheen (Wilkinson, 2010) show-ing increasing Zn-Pb laterally but with Galmoy and Navan ex-hibiting the opposite pattern. Fe has not been considered in de-tail here but is generally displaced from high Pb and/or Zn zones, commonly occurring as a paragenetically early 'cap' above the main mineralization and laterally offset into the hangingwall away from major fault feeders. Such patterns in
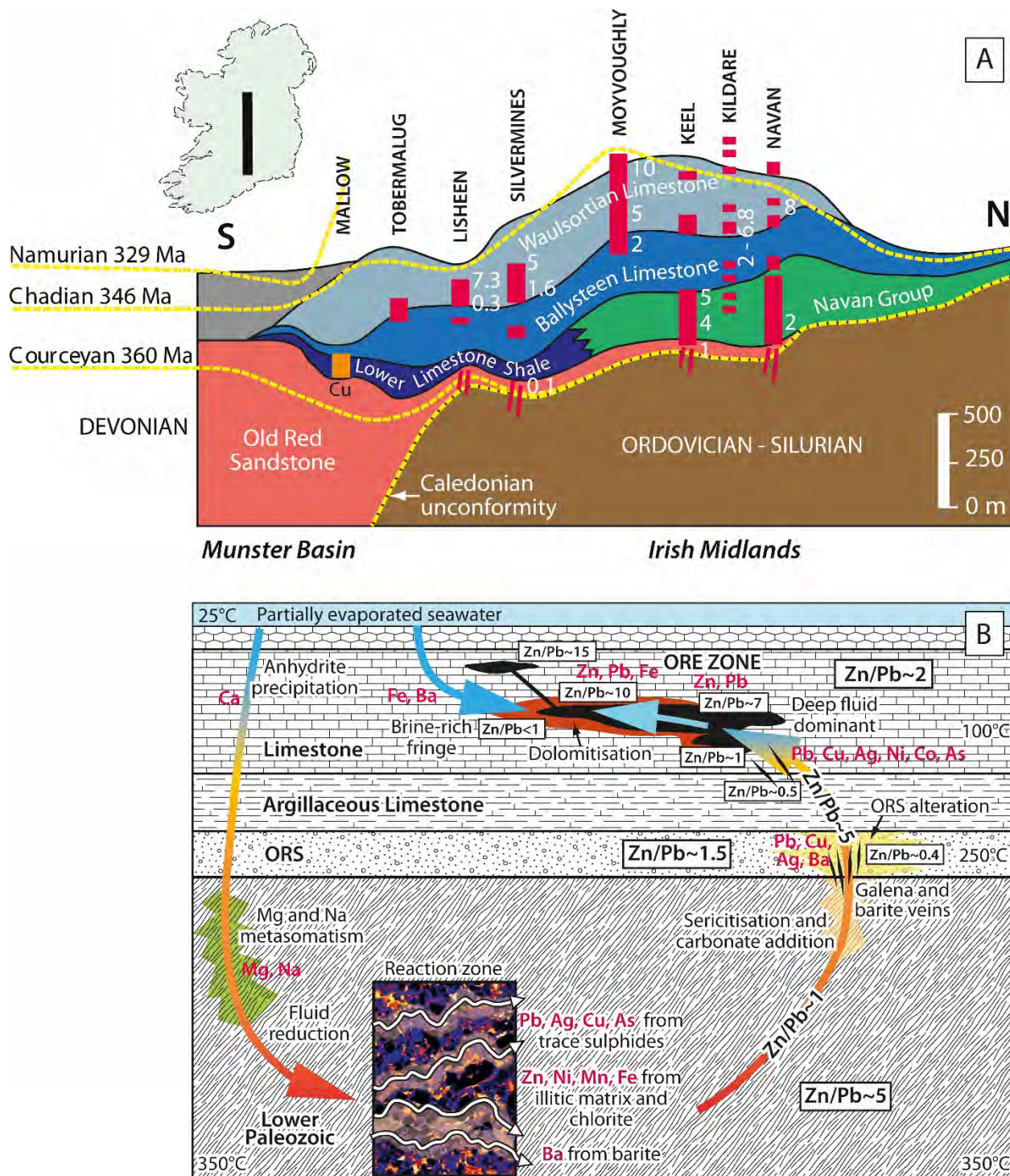
Figure 14: *A). Regional and deposit-scale variation in Zn/Pb ratios. Based on Johnston (1999) from the stratigraphic cross-section of Andrew (1993), with additional data from cross-sections in Torremans et al. 2018). B). Model for metal fractionation processes along the source rock extraction-transport-trap pathway.*

Zn, Pb and Fe are not unusual in sediment-hosted Zn-Pb deposits (Robb, 2004; Wilkinson, 2014). Ireland is a little more unusual, perhaps, in having notable enrichment of Ni, Co, Cu and Ag in the most proximal positions, thought to reflect the involvement of some relatively high temperature fluids (temperatures >300 to 350ºC are typically required to start to mobilise significant Cu; Von Damm, 1990), at the point where

extensive Mg metasomatism and acidity generation takes place in seawater-interacted systems (Bischoff & Dickson, 1975; Bischoff *et al.*, 1981).

From a regional perspective, Johnston (1999) highlighted the fact that Zn/Pb ratios of mineralization appear to increase northwards across the Midlands at a given stratigraphic level,

as well as upwards through the ore zones. At ORS level, these ratios vary from ~0.1 in the south to ~2 in the north; at base Waulsortian level the range is 1.6 to 8 (Fig. 14), increasing to 10 towards the top of the Waulsortian.

Metal Fractionation from Source to Sink

The lines of evidence considered here paint a quite detailed picture of how, in the Irish palaeo-hydrothermal system, metals were fractionated on their pathway – starting with extraction from source rocks, transport in fluids, potential losses and gains *en route* in the footwall and final stages of fractionation during deposition in the orebodies (Fig. 14). The key message of extraction from the Lower Palaeozoic source rocks is that they were a fertile source of multiple ore and trace metals, including some characteristic ones (Cu, Ni, Co) that ended up in the deposits in proximal ore zones. The greater mobility of Pb from these source rocks, due to its deportment in trace sulphides in matrix sites (and ultimately probably derived from weathering/diagenesis of feldspars), than Zn (which substantively resides in chlorite) led to the generation of 'principal orefluids' with relatively low Zn/Pb ratios. However, regional heterogeneity in the make-up of the Lower Palaeozoic wedge likely led to significant local variability in fluids compositions as suggested by fluid inclusion analyses (Wilkinson *et al.*, 2007). In particular, higher Zn/Pb fluid ratios are apparent in the northern Midlands which might reflect a greater volcanic source component. Such higher fluid values are also consistent with the generally higher Zn/Pb ratios in ores recorded further north. Increases in fluid Zn/Pb ratios during fluid passage through the several km of the Lower Palaeozoic wedge could have occurred through preferential precipitation of galena over sphalerite, as expressed by the development of Pb-rich veins as described and mined historically in the Longford Down Massif. Higher temperature circulation, as has been suggested for the domain on the SE side of the Iapetus suture zone (Wilkinson, 2010) could also be partly responsible for generating fluids with lower Zn/Pb ratios and containing higher concentrations of Cu and Ni. Finally, significant local enrichment of fluids in Ba has been noted in the areas where significant barite accumulations developed (Silvermines, Garrycam; Fig. 1; Wilkinson *et al.*, 2007), most likely related to unusually efficient extraction or a locally enriched source.

It is clear that the ORS represented a major redox boundary in the Irish palaeo-hydrothermal flow system, with relatively reduced, greywacke-equilibrated fluids being highly reactive with the oxidised red beds as they migrated up faults through the unit. A degree of fluid cooling would also be a driver for precipitation reactions occurring at this level. The most significant chemical change was one of Fe (haematite) loss from the rocks (Fig. 12) leading to the characteristic bleaching observed in the field. The corollary of this process was the addition of significant amounts of Fe to the fluids which no doubt contributed to Fe oxide and/or sulphide mineralization in the overlying Lower Carboniferous. The Fe gain was balanced by loss of K, Ba, Mg and Ca from the fluids, forming carbonates, barite and illite-muscovite in the altered ORS. Trace elements trapped in the ORS at this point, in decreasing order of absolute amount, include Sr (carbonates, barite), Li (illite-muscovite) and Co (chlorite, pyrite). Copper, Pb and Ag also appear to have precipitated within the ORS; this would have led to

depletion of Cu and Ag in the orefluids and a further increased Zn/Pb ratio.

Significant amounts of Zn and Cr (most likely present adsorbed on oxide grain coatings) were also liberated from the ORS at this stage: an estimate of the volume of altered ORS at Silvermines combined with the average concentration of Zn released suggests that <2 to 8% of the mined zinc resource there could have been derived from this source, though the proportion would be less if all the subeconomic mineralization was included. The fate of Cr, likely derived from both the Lower Palaeozoic wedge (Figs. 4, 5) and from the ORS (Figs. 9, 11), in the deposits is uncertain. However, acid dissolution and residue analysis of black matrix breccia (ore host rock) samples from Lisheen and Galmoy indicate that Cr is elevated in the residue fraction of dolomitic matrix samples, so is most likely incorporated into minor hydrothermal illite and/or muscovite (Wilkinson *et al.,* 2011). There could be a well-developed zonation in bulk rock Cr around fluid conduits, similar to that observed for Ni, yet to be identified.

The extent of the controls of the ORS on fluid chemistry will have varied regionally, depending on the intensity of the fault-fracture networks developed within it and on the thickness of the unit. As it generally thins northward, it could be assumed that the likely effects noted above would also decrease northwards; thus, it is highly unlikely that the ORS sourced any significant amounts of Zn to the Navan deposit. Decreasing levels of exchange between transiting fluids and the ORS in the north would mean that metal ratios and trace element contents would more closely reflect the Lower Palaeozoic source. Unusually high Zn/Pb ratios in fluids would therefore be most likely attributable to a volcanic source component rather than due to loss of Pb in the ORS.

Finally, on entering the deposits, the combined effects of further decreasing temperatures, pH increase due to interaction with carbonate host rocks and, most significantly, mixing with low temperature, H_2S-rich brines (Samson & Russell, 1987; Wilkinson, 2010; Wilkinson *et al.*, 2005a; Wilkinson & Hitzman, 2015) led to sulphide precipitation and moderately predictable metal zoning patterns. Pb, Cu, Ni and Ag in particular were precipitated in sulphides at depth and in the more feeder-fault proximal positions (e.g., Russell, 1986) most likely because of a steeper decrease in sulphide solubility with decreasing temperature. Pb- (and Cu- Ni- Ag-) depleted fluids then spread out through the permeable host rocks, progressively mixing with brines and precipitating higher Zn/Pb mineralization. In extreme cases, where fluids were able to migrate some distance from the main feeders, Zn/Pb ratios could attain much higher values (above 10) – such as in the Island zone at Lisheen and the CW zone at Galmoy. Occasional anomalies, such as the low Zn/Pb zone that appears to be distal to feeder zones at Navan as well as in the much wider dispersion halo, and the outward zonation to lower Zn/Pb at Galmoy, could be due to non-linear solubility relationships during fluid mixing, favouring galena precipitation from brine-dominant mixtures. Regional variations in input fluid compositions are thought likely to modify the absolute metal ratios observed in the ores, if not the gross zoning patterns – for example, the more Pb-rich nature of mineralization at Silvermines.

Conclusions

The Irish Midlands Zn-Pb(-Ba-Ag) Orefield represents one of the best studied palaeo-hydrothermal systems worldwide. Although the ores are considered relatively simple mineralogically, the origins of the metals and the controls on the variability of metal ratios across the Orefield, and within individual deposits, have not been considered in detail. In this contribution, I have used diverse data sources in an attempt to track the metals and how they were fractionated at various stages along the reconstructed flow path, during: (1) circulation of fluids to depths of up to ~7 km in the Lower Palaeozoic wedge of arc-derived detritus that underlies the Orefield and through the primary 'reaction zone'; (2) their transit through the wedge and then up through the redox boundary represented by the Old Red Sandstone; and (3) fluid ingress into the receptive Lower Carboniferous host rocks in the ore deposits themselves, initially through focused feeder pipes and then spreading out upwards and especially laterally into the surrounding carbonate units. Many factors play into the development of this enormous mineralizing system, which is arguably one of the most well-endowed Zn districts on Earth. However, the significance of the underlying thick wedge of only very weakly metamorphosed and highly fractured Lower Palaeozoic rocks, containing a wealth of labile metals derived from the precursor Ordovician arcs, is emphasized (with an appropriate nod to Russell, 1978, for first pointing this out) as a key contributor to the remarkable metal endowment seen in Ireland.

Acknowledgements

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