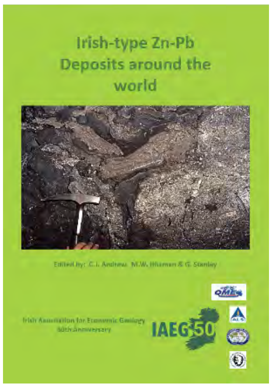

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Fraternal twins or distant cousins; comparing and contrasting the Red Dog district and Irish Midlands Orefield

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Fraternal twins or distant cousins; comparing and contrasting the Red Dog district and Irish Midlands Orefield

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Abstract: The Lower Carboniferous rocks in the Irish Orefield and Red Dog district are host to some of the highest value Zn deposits in the geological record. A comparison of different mineral system components (geodynamic setting, (basin) architecture, fluid flow drivers, and depositional mechanisms) between the two districts reveals there are perhaps more similarities than differences. These include the complex accretionary evolution of the underlying basement terranes, ore fluid chemistry, common age of the mineralization for some of the deposits (331 – 346Ma), timing of mineralization relative to host rock deposition (syndiagenetic), highly productive depositional environment, and contribution of bacteriogenic sulphur to the metal trap. Key differences correspond with the different host rocks (siliciclastic dominant vs. carbonate dominant) and diagenetic assemblages (barite vs. dolomite) in either district, rather than reflecting fundamentally different ore forming processes.

Keywords: Red Dog, Alaska, Irish Midlands, barite, geodynamic setting, comparisons

Introduction

Zinc ± Pb ± Ag ± barite deposits belong to the broad family of sediment hosted massive sulphide (SHMS) deposits. SHMS deposits are most commonly divided into clastic-dominant type (CD) and Mississippi-Valley type (MVT) deposits (Leach *et al.*, 2005). Irish-type deposits have been considered to be intermediate between the two, although with their own distinctive characteristics (Leach *et al.*, 2010; Wilkinson, 2013). The CD subtype includes deposits that have traditionally been referred to as sedimentary exhalative (SedEx; Carne & Cathro, 1982) or shale hosted massive sulphide (SHMS) deposits (e.g., Broadbent *et al.*, 1998), terms that are now avoided for different reasons. The SedEx terminology implies that sulphide minerals precipitated directly from seawater following the exhalation of hydrothermal fluids at the seafloor (Goodfellow *et al.*, 1993), although there is rarely robust evidence to show this. The SHMS terminology is also problematic, as shale is often misused to describe any fine-grained sedimentary rock, rather than a mudstone with a high phyllosilicate content (c.f. Aplin & Macquaker, 2011). Additionally, the abbreviation (*shale hosted*) is identical to the broader family of sediment hosted massive sulphide (SHMS) deposits.

World class Zn deposits broadly occur in two major time periods in Earth's history, in the Palaeo to Mesoproterozoic and the lower Palaeozoic (Leach *et al.*, 2010). Lower Carboniferous marine sedimentary rocks, however, are host to some of the most significant Zn-Pb deposits in the world (Fig. 1). For example, in the Irish Midlands, a succession of Lower Carboniferous carbonate rocks host more than 25 economic and sub-economic base metal deposits, which collectively contain more than 20 Mt Zn metal (Wilkinson & Hitzman, 2014). The deposits of the Irish Midlands are the most important

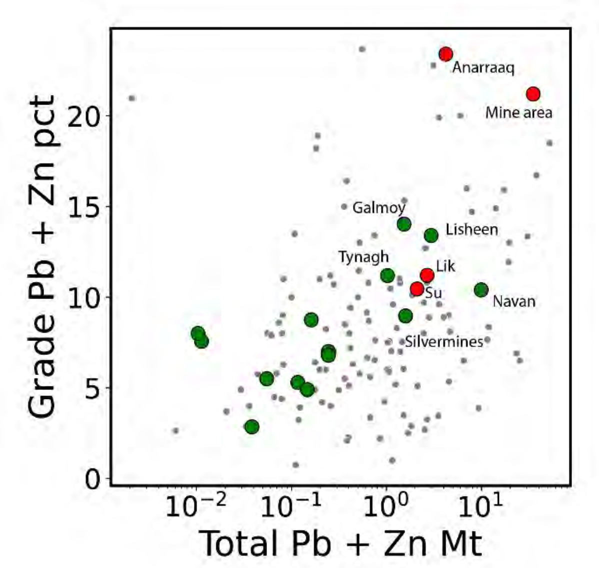

Figure 1. *Total Pb and Zn (Mt) vs. grade Pb and Zn (%) for clastic dominant (CD-type) deposits (modified from USGS data compilation; Taylor et al., 2009). The major Irish-type deposits are green, and the 5 economic discoveries are labelled. The deposits in the Red Dog district are red.*

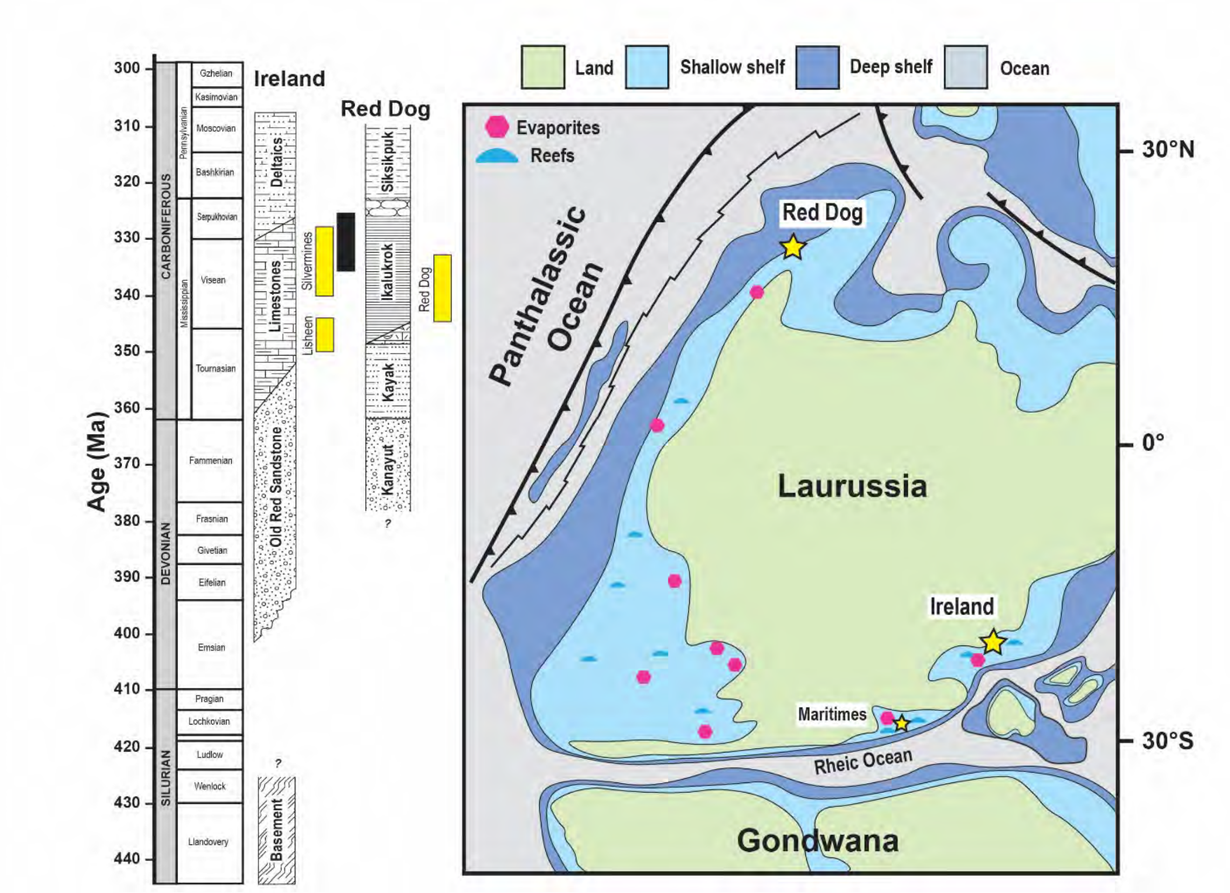

Figure 2. *A chronostratigraphic chart for the Irish ore field and Red Dog district, annotated with Re-Os ages for the mineralization at Lisheen, Silvermines and Red Dog (yellow bars). The right-hand side shows the palaeogeography during the Early Mississippian, with the Irish Orefield located on the southeastern margin of Laurussia and the Red Dog district on the northern margin (modified from Cocks & Torsvik, 2011).*

source of Zn in Europe, and also contain a suite of potential by-product critical metals (Ag, Ba, Ni, Co, Cu, Ge, Ga and Sb). In northwestern Alaska, multiple world-class deposits make up the Red Dog district, which contains defined reserves of approximately 33Mt of Zn (Blevings *et al*., 2013). In addition, there are also a number of barite deposits in the Red Dog district, including an estimated 1 Gt of barite in the Anarraaq deposit (Kelley *et al*., 2004a).

The composition of the host rock and timing of sulphide mineralization with respect to host rock deposition are two of the most important classification criteria when subdividing SHMS deposits. In terms of host rock composition, Mississippi-Valley type deposits are epigenetic, post-date host rock deposition by 10s to 100s my and are hosted by platform carbonate rocks; CD-type deposits can be hosted by stratigraphic packages containing different lithologies (including carbonates), but which have a predominantly siliciclastic composition, can have syn-sedimentary components, but more often are syn-diagenetic (Leach *et al*., 2010). Irish-type deposits are likewise hosted in non-argillaceous carbonates, in stratigraphic successions that may be a mixture of carbonate and siliciclastic rocks.

In recent years, studies on SHMS deposits have harnessed new geochronological and in situ techniques, which have enabled more detailed investigations of ore-forming processes. These datasets are also being incorporated into more holistic mineral systems models, which describe how different aspects of basin evolution align to produce in ore forming systems (e.g. Rodríguez *et al*., 2021; Lawley *et al*., 2022). This includes identifying the critical processes that are necessary to form an ore deposit (e.g., geodynamic setting, (basin) architecture, fluid flow drivers, and depositional mechanisms).

Recent Re-Os and apatite dating on deposits in the Red Dog district (Morelli *et al.*, 2004; Reynolds *et al., 2021)* and on the Silvermines and Lisheen deposits in the Irish Midlands (Hnatyshin *et al*., 2015a; Vafeas *et al*., 2023) have shown that both of these systems are broadly coeval, suggesting there was a relatively short period of geological time with exceptional Zn endowment in the Lower Carboniferous. Here, we compare and contrast mineral system components of the Red Dog district and Irish Orefield, which are both associated with the margins along the Laurentian craton (Fig. 2) and discuss the similarities and differences in these mineral systems.

Review of mineral system components

Tectonic setting

The Laurentian craton comprises several older terranes, including a core of 6 or 7 fragments of Archaean crust, which were assembled between 2.0 to 1.8Ga and became part of the Rodinian supercontinent around 1 Ga (Bleeker, 2002). Following the break-up of Rodinia in the Neoproterozoic, Laurentia became an independent continent with the Iapetus Ocean on the eastern and southern margins and the Panthalassic Ocean on the northern and western margins (Torsvik, 2003). During the mid-Silurian Caledonide Orogeny, the collision of Avalonia-Baltica on the eastern margin of Laurentia resulted in the closure of the Iapetus Ocean and formation of Laurussia (Cocks & Torsvik, 2011).

The Caledonian orogenic cycle includes the Grampian Orogeny (Early Middle Ordovician, 475-460Ma) and the Acadian Orogeny (Early Devonian, ~400Ma). The Grampian Orogeny resulted from a collision between the Laurentian continental margin and an oceanic arc terrane; continued subduction of the Iapetus Ocean floor led to the approach of the Avalonian continent towards the deformed and metamorphosed Laurentian margin and accreted terrane. The opposing shorelines became juxtaposed along the Iapetus Suture in the Late Silurian, and the final stage of this collision during the Early Devonian resulted in the Acadian Orogeny. The development of a N-dipping subduction zone and associated back-arc extension during the Late Devonian-Early Carboniferous led to the formation of interconnected basins, which host the deposits of the Irish Orefield (Davies *et al*., 2012; Smit *et al*., 2018).

The Red Dog district is located at the western end of the Brooks Range Mountains, which is a 950km long fold and thrust belt in the northern half of Alaska (Young, 2004; Blevings *et al*., 2013). The Arctic Alaska terrane is a composite of pre-Mississippian subterranes that were accreted in the Mid to Late Devonian (Colpron & Nelson, 2009). The Middle Devonian to Mississippian was a period of syn-rift to post-rift tectonic transition (Anderson & Meisling, 2021), with Late Devonian (Frasnian) to Early Carboniferous (Late Early Mississippian) Endicott and Lisburne Groups forming a basal clastic succession (>4000m thick) that transitioned to a passive margin carbonate platform (Moore & Nilsen, 1984; Cocks & Torsvik, 2011).

The Irish Orefield and Red Dog district have both been affected by tectonic inversion. In the Irish Orefield, Late Carboniferous Variscan deformation resulted in basin inversion and the development of open folding and reverse faulting (Coller, 1984; Wartho *et al*., 2006); these structures are variably orientated, as a result of inheritance from earlier structures and local stress fields (Woodcock, 2012).

A younger stage of Palaeocene and Oligocene compression is then linked to north-south Alpine-Pyrenean compression (Cooper *et al.*, 2012). In the Red Dog district, Late Jurassic to Cretaceous convergence of the Arctic Alaska terrane of Devonian to Jurassic passive margin sedimentary rocks (Moore *et al*., 1986; Moore *et al.*, 1994) with oceanic Angayuchan terrane (Young, 2004).

Stratigraphy

Red Dog district

The 200 by 600 km Kuna Basin contains clastic sedimentary rocks that were deposited during a mid-Devonian to Mississippian period of extension and minor igneous activity (Young, 2004). The basement rocks underlying the Kuna Basin are unexposed in the Red Dog district but are assumed to consist of Proterozoic to early Palaeozoic metasedimentary and minor metavolcanic rocks similar to local exposures in the southern Brooks Range (Dumoulin *et al*., 2002). Regionally, the basement rocks are overlain by the Baird Group, which is an Early Ordovician to Middle Devonian marble unit (Moore *et al*., 1986; Young, 2004). The overlying Endicott Group comprises a succession of Upper Devonian to Lower Mississippian fluvial-deltaic sandstones, nonmarine conglomerates, and marine shales, and are the oldest exposed rocks in the Red Dog district (Tailleur, 1970; Moore *et al.*, 1986). There are various subdivisions of the Endicott Group, with the Kayak Shale representing the start of a major marine transgression that resulted in deposition of the Lisburne Group (Dumoulin *et al*., 2014).

The Lisburne Group contains carbonate-rich shelf facies rocks (Utukok and Kogruk Formations) and broadly coeval deeper-marine siliciclastic rocks of the Kuna Formation (Dumoulin et al., 2004). The Kuna Formation, which hosts the deposits, comprises black shale, siliceous mudstone, chert, barite, limestone, dolostone, lithic turbidite and calcareous shale (Slack *et al*., 2004). High concentrations of total organic carbon, together with phosphorites and abundant radiolarians, indicate high levels of biological productivity during deposition of the Kuna Formation (Dumoulin *et al*., 2014). The presence of trace fossils in the host rocks of the Mine Area deposits indicate sediment deposition in an oxygenated middle to outer shelf environment (Reynolds *et al*., 2015). However, more broadly bulk geochemical data also more reducing conditions may have been prevalent (Dumoulin *et al*., 2014; Slack *et al*., 2015). Mineralized rocks are stratabound within the Ikalukrok unit, which is an informal subdivision of the uppermost part of the Kuna Formation and is also host to barite and phosphorites (Dumoulin *et al*., 2004; Johnson *et al.*, 2004; Reynolds *et al.*, 2021).

Irish Midlands

The Carboniferous basins are underlain by a basement of Silurian graywackes, siltstones, shales, and volcanic rocks that were deformed and variably metamorphosed during the Caledonian orogeny. The terrigenous clastic Old Red Sandstone (Devonian-Carboniferous) sits unconformably on the basement, within basins associated with NE striking faults (Woodcock, 2012; Friend *et al.* 2000). The Old Red Sandstone is overlain conformably by a marine transgressive sequence of Lower Carboniferous carbonate-rich shales, siliciclastic sedimentary rocks, and argillaceous bioclastic limestone (Philcox, 1984).

Mineralized rocks are stratabound within two Lower Carboniferous (Tournaisian and Viséan) stratigraphic units, characterized by different carbonate facies that depend on the location in the Irish Orefield. In north central Ireland, the Navan Group is characterized by near-shore shallow marine facies, comprising high energy oolitic and bioclastic grainstones and minor sandstones (Wilkinson, 2003). In southern Ireland, the Waulsortian Limestone is characterized by deeper water facies from a ramp environment (>100s meters depth), comprising biomicrite mounds surrounded by argillaceous bioclastic limestones (Hitzman & Large, 1986; Wilkinson, 2003). The Waulsortian is overlain by the Lough Gur Formation, which is mainly cherty bioclastic mudstones. In the Limerick area, the Lough Gur is interbedded with the Knockroe Volcanics, which are composed of fine-grained tuffs and basaltic lava flows (Late Chadian to Early Arundian; Timmerman, 2004).

Paragenesis and geochronology of the mineralized rocks

Red Dog district

The deposits in the Red Dog district include the Mine Area deposits (Main, Aqqaluk, Paalaaq, Qanaqiyaq), Anarraaq and Su-Lik. Early studies on the Red Dog deposits favoured genetic models involving SedEx processes (e.g., Lange *et al*., 1985; Moore *et al.*, 1986), although the complex textures differ from classic stratiform deposits considered to form via exhalative processes (Kelley and Jennings, 2004). Paragenetic studies have since favoured syn-diagenetic models involving sub-seafloor replacement, with the earliest stages of mineralization potentially occurring within unconsolidated sediments (e.g. Kelley *et al.*, 2004b). The paragenesis described by Kelley *et al*. (2004b) for the Mine area deposits comprises; (1) early deposition of barite, brown sphalerite, pyrite, and minor galena, (2) hydrothermal recrystallization of barite and deposition of yellow brown sphalerite, (3) precipitation of barite and red brown sphalerite in crosscutting veins (4) late-stage tan sphalerite in post ore breccias. The volumetrically most important are stages 2 and 3 (Leach et al. 2004), which are also geochemically similar (Kelley *et al.* 2004b). At Annarraq, the ore lenses are thought to have replaced barite and carbonate units in the Ikalukrok unit (Kelley *et al*., 2004a). Recently, widespread barite replacement textures and the infill of large cavities by quartz and sulphide have been described, consistent with open space filling (Reynolds *et al.*, 2021).

Overall, some of the textural evidence is consistent with diagenetic formation of barite and pyrite immediately below the seafloor. For example, mudstone samples preserve disruption of laminae by barite, indicating formation in unconsolidated sediment, and sulphides preserve colloform and dendritic textures that are similar to modern seafloor massive sulphide deposits (Kelley *et al.* 2004b). There is also ample evidence that when the bulk of the mineralization was emplaced the host rock was mostly lithified; the massive sulphide ore (stage 2) also has a fragmented or clastic appearance, which could indicate brecciation (Kelley *et al*., 2004b). The timing of cementation was likely influenced by lithological variability and diagenetic processes that may have been accelerated during the onset of hydrothermal activity.

These paragenetic studies are supported by Re-Os geochronology. A 10-point isochron on massive (stage 2) and vein (stage 3) pyrite from the Main deposit gives an age of 338.3 ± 5.8Ma, which defines the main ore stage (Morelli *et al*., 2004). At Anarraaq, recent Re-Os geochronology on the Ikalukrok mudstone (339.1 ± 8.3Ma), diagenetic pyrite (333.0 ± 7.4Ma), and hydrothermal pyrite (334.4 ± 5.3Ma) are all within uncertainty of each other and the age from the Main deposit (Reynolds *et al*., 2021). These ages overlap within uncertainty the biostratigraphic age (338 – 322Ma; Dumoulin et al., 2004). In contrast, attempts to date sphalerite that is intergrown with pyrite in the massive ore yielded imprecise ages with a high degree of scatter, indicating Re-Os systematics of sphalerite may be unreliable (Morelli *et al*., 2004).

Irish Midlands

The orebodies are stratabound (typically < 30m thick) in the Navan Group and Waulsortian Limestone Formation (Wilkinson and Hitzman, 2014). In some deposits (e.g., Lisheen, Silvermines, Galmoy) there is also a breccia unit close to the base of the Waulsortian. The sulphide mineralization is primarily sphalerite, galena, pyrite and marcasite, with minor chalcopyrite, tennantite and other sulfosalts (Wilkinson *et al*., 2005).

Geological interpretations at different localities suggest mineralization occurred within a few meters to hundreds of meters beneath palaeo-seafloor (Wilkinson *et al*., 2003, 2005) to >800 m (Reed and Wallace, 2001). The host rocks have all been affected by extensive calcite cementation and dolomitization during early diagenesis, i.e. upon sediment deposition and within tens of meters of seafloor (Lee & Wilkinson, 2002; Wilkinson, 2003). There are multiple generations of calcite that pre-date dolomite, which could indicate a major time gap (Hitzman, 1995), and sulphides that postdate pressure solution textures have been used to constrain mineralization to depths greater than 800m Reed & Wallace (2001). However, there are intraformational breccias containing clasts of dolomitized rock bound in un-dolomitized matrix, which indicate dolomitization must have formed relatively early; furthermore, caution has been recommended over the interpretation of solution seam formation, as they may form relatively early in active hydrodynamic basin environments (Wilkinson, 2003).

In terms of geochronological constraints, attempts to date mineralization at Silvermines involved Rb-Sr sphalerite (360 +/- 5Ma; Schneider *et al*., 2007) and a younger palaeomagnetic age (269 +/- 4 Ma; Symons *et al.*, 2002). More recent Re-Os geochronology on ore stage pyrite provides the most accurate age constraints (Hnatyshin *et al.*, 2015b); massive pyrite from the early main ore stage at Lisheen yields a Re-Os isochron age of 346 ± 3.0Ma, and massive pyrite from the ore stage at Silvermines produces a younger age of 334.0 ± 6.1Ma. Both Re-Os ages indicate sulphide mineralization within 15Ma of host rock deposition, which means a likely depth of no more than 200m beneath the palaeo-seafloor (Wilkinson *et al*., 2011). This has been further supported by recent U-Pb geochronology (331 ± 5.6Ma) of coarse-grained apatite from hydrothermal dolostone breccia at the Silvermines deposit (Vafeas *et al*., 2023).

Igneous activity (Os^i and He isotopes)

Red Dog district

There are some intermediate to mafic igneous rocks (sills and dikes), felsic flows and tuffs that are associated with Early to Late Mississippian extension (Moore *et al*., 1986; Young,

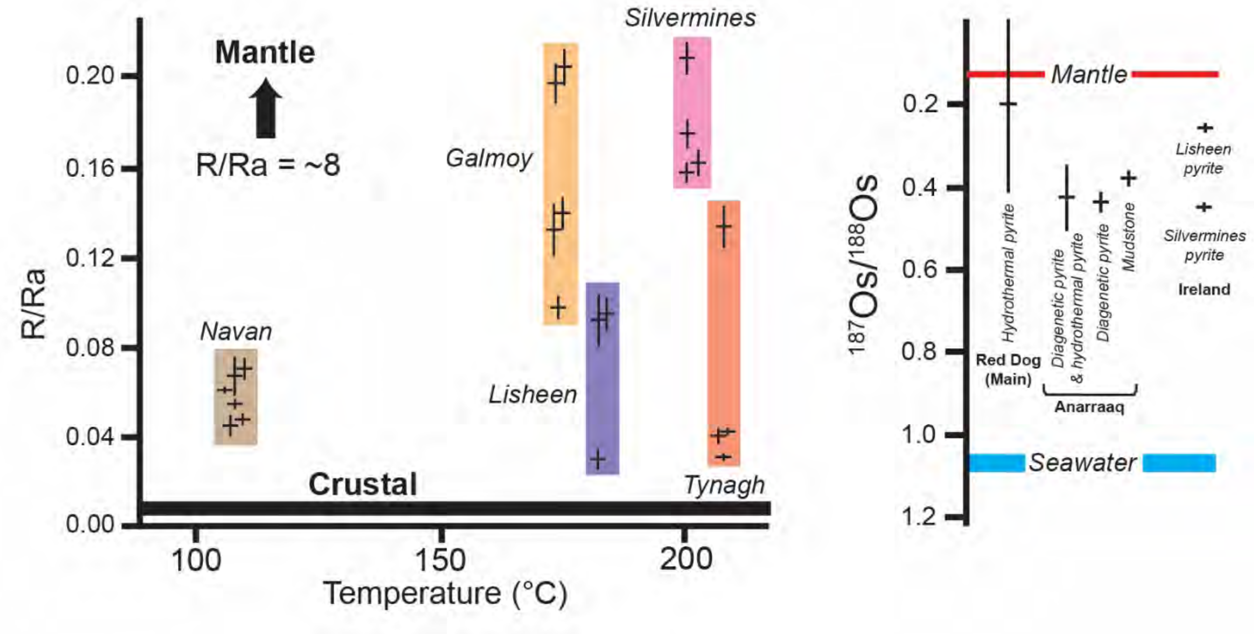

Figure 3. *The He isotope composition (R/Ra) of fluid inclusions plotted against homogenization temperatures (modified from Davidheiser-Kroll et al., 2013). The $^{187}Os/^{188}Os$ composition of pyrite from the Red Dog (Main) deposit, Anarraaq deposit, and Irish Orefield (Lisheen and Silvermines). Compiled from Reynolds et al. (2021), Morelli et al. (2004), Hnatyshin et al. (2014), Davidheiser-Kroll et al. (2013).*

2004). The igneous rocks are regionally scarce, low volume, and restricted to base of Kivalina unit or Kayak Shale (Ayuso *et al*., 2004). Genetic relationships with the base metal mineralization are unclear, although age of mafic intrusions near the Aqqaluk deposit (biotite $^{40}Ar/^{39}Ar$ = 344 ± 3Ma; Werdon *et al*., 2004) overlaps the Re-Os age for mineralization (338 ± 5.8Ma; Morelli *et al*., 2004). At Drenchwater there are up to 300m of submarine felsic rocks and mafic tuffaceous rocks ($^{40}Ar/^{39}Ar$ = 335 to 337Ma; Werdon *et al*., 2004) in the Kuna Formation with trace element concentrations similar to volcanic rocks of the East African rift system (Young, 2004). The $^{187}Os/^{188}Os$ (Os^i) can also be used to trace mantle vs. crustal input (e.g., Morelli *et al*., 2004; Slack *et al*., 2015; Reynolds *et al*., 2021). The Os^i for pyrite from the main ore stage at Red Dog is 0.20 ± 0.21, which is consistent with Os sourced from either a relatively young crustal reservoir (< 410Ma) or the mantle (Morelli *et al*., 2004). The Os^i for the samples from Anarraaq are more precise (Fig. 3), and the isochrons for different samples (mudstone, pre-ore pyrite, ore stage pyrite) mean it is possible to delineate the source of Os with more confidence (Reynolds *et al*., 2021). Importantly, the similarity between Os^i of the mudstone isochron and hydrothermal pyrite (with pre-ore pyrite) can be explained without the input of mantle Os.

Irish Midlands

In the Limerick Basin (SW Ireland), Lower Carboniferous alkali basaltic diatremes that define a regional NE-SW trend immediately south of the Iapetus suture zone (Somerville *et al*., 1992). These diatremes erupted through the Waulsortian, and are genetically linked to overlying pyroclastic deposits (Elliott *et al*., 2015). The diatremes are part of larger scale magmatic and volcanic activity across Europe that resulted from N-S back-arc extension and reactivation of NE-SW trending Caledonian basement faults (Wilson *et al*., 2004). At the Stonepark deposit, it has been suggested that intrusions pre-date hydrothermal dissolution, and intrusions proximal to breccias and mineralization have been extensively altered to sericite and pyrite (McCusker & Reed, 2013). There is a spatial relationship between zones of high Zn and the volume of igneous material, and it is possible that intrusions provided a pathway of enhanced permeability (fracture) that focused mineralizing fluids.

The initial Os ($^{187}Os/^{188}Os$) for the pyrite isochrons at Lisheen and Silvermines are both relatively low, which could indicate mantle derived Os ($^{187}Os/^{188}Os$ ~0.13; Meisel *et al*., 2001). However, it is also possible that Os with a similar composition was sourced from early Palaeozoic volcanic arc rocks that comprise the basement (Hnatyshin *et al*., 2015b). Fluid inclusions trapped in ore stage sulphides record more convincing evidence of a small but potentially significant component of mantle-derived He (Fig. 3; Davidheiser-Kroll *et al*., 2014).

Metal source (Pb isotopes)

Red Dog district

The overlapping Pb isotope composition of galena and sphalerite from different deposits in the Red Dog district (Fig. 4) has been used to infer that the Pb was derived from a from a homogenous regional source, mixing of lead during leaching and fluid transport, or mixing at site of deposition (Ayuso *et al*., 2004). The metals are generally considered to have been leached from oxidized fluvial-deltaic rocks in the Endicott

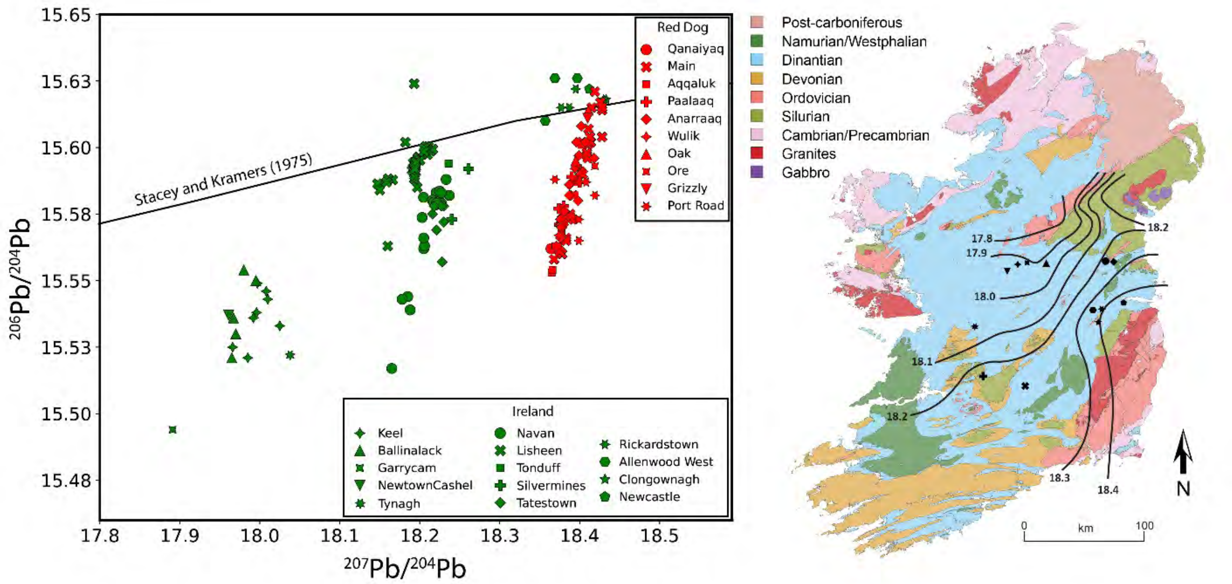

Figure 4. *The Pb isotope composition of galena from the Irish Orefield and Red Dog district presented as $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ and a geological map of Ireland annotated with contours for $^{207}Pb/^{204}Pb$ (modified from Everett et al. 2000). Data compiled from Ayuso et al. (2004), Caulfield et al. (1986), LeHuray et al. (1987), Yesares et al. (2019).*

Group (Moore *et al.*, 1986; Leach *et al.*, 2004), which is supported by Pb isotope compositions that overlap with the sulphide deposits (Ayuso *et al.*, 2004).

Irish Midlands

A large amount of Pb isotope data has been generated on sulphide minerals from Irish type deposits (Fig. 4). In terms of published data, sulphide minerals from individual deposits preserve relatively homogenous Pb isotope compositions, but systematic variation across Ireland reflects the pre-Caledonian basement geology (Caulfield *et al.*, 1986; LeHuray *et al.*, 1987; Yesares *et al.*, 2019) rather than Pb sourced from the overlying Old Red Sandstone (Everett *et al.*, 2003). The least radiogenic Pb is located in samples from the northwest, whereas the most radiogenic is located in samples from the southeast. The uniformity of Pb isotope compositions within individual deposits indicates Pb was well mixed at the source, rather than site of deposition.

Fluid constraints (T, X, fO_2)

Red Dog district

An early study reported homogenization temperatures between 187 and 329°C and relatively low salinities (0 to 8 wt.% NaCl) in fluid inclusions from vein quartz and massive sulphide from the Red Dog Main deposit (Forrest, 1983). Werdon (1998) reported similar salinities (3.9 to 6 wt.% NaCl) were reported for fluid inclusions in a quartz vein from a vein-breccia occurrence (Kady), albeit with lower homogenization temperatures (100 to 145°C). A fluid inclusion study of samples from the Red Dog Main and Aqqaluk provided constraints for stage 3 sphalerite (vein ore), with homogenization temperatures between 115 and 180°C and salinities of between 14 and 19 wt.% NaCl (Leach *et al.*, 2004). As the aquifer unit contains ferric iron the fluids are considered to have been oxidizing (Kelley *et al.*, 2004b).

Irish Midlands

A large amount of fluid inclusion data has been produced on samples from the Irish Orefield, making it one of the most well described districts for the thermal and chemical characteristics of fluids responsible for sediment hosted mineral systems (Wilkinson 2010). A negative correlation between temperature and salinity supports a general model in which there was fluid mixing between moderate salinity, metal-bearing fluid (principal ore fluid) and low temperature, high salinity, sulphur bearing brine. A wide range of salinities are reported (4 to 28 wt.%), although the majority form a narrower range between 8 and 19 wt.%. Evaporated seawater provided the main source of salinity to the ore fluids, as halogen data provide no evidence that halite dissolution was involved in brine generation (Wilkinson, 2010). Homogenization temperatures (T_h) are between 70 to 280°C, with the majority between 130 and 240°C. Homogenization temperatures in sphalerite tend to be highest, followed by dolomite and then calcite (Wilkinson, 2010). In terms of spatial variability in the district, the highest temperatures are recorded in the Waulsortian hosted deposits (S and E), whereas lower temperatures are recorded in Navan and Abbeytown (N and W Midlands) (Fig. 3).

The high barium concentrations in analyses of both bulk fluid inclusions and single inclusion analyses indicates that the ore fluids were probably reduced (Wilkinson *et al.*, 2005; 2007). This is further supported by a positive europium anomaly in hydrothermal dolomite from Lisheen and Galmoy (Wilkinson *et al.*, 2011). Fluids must have contained low total sulphur if reduced, similar to other sediment hosted ore systems (Tornos & Heinrich, 2008).

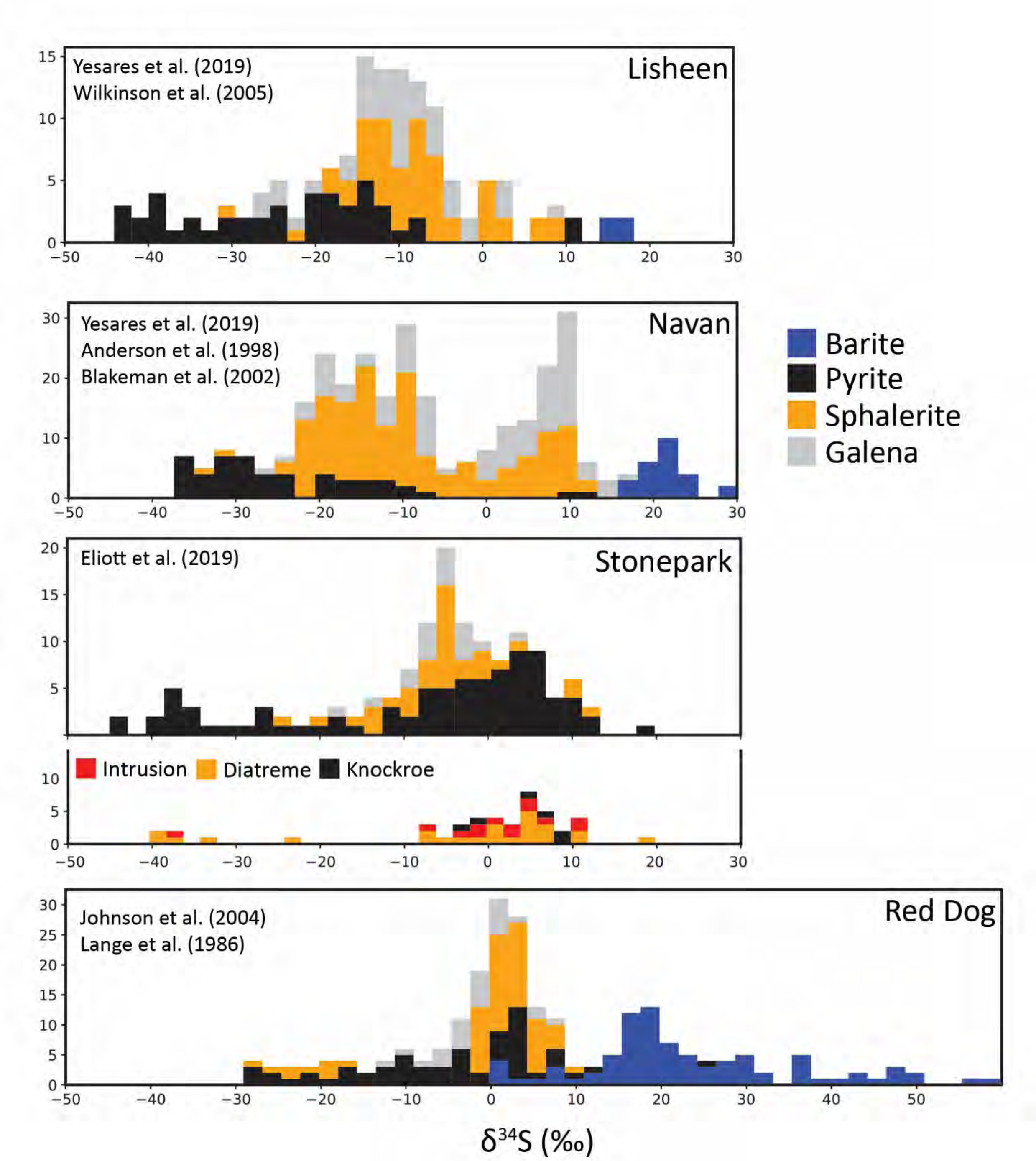

Figure 5. *A compilation of $\delta^{34}S$ values presented as summary histograms for deposits from the Irish Orefield and the Red Dog district. The histograms for Stonepark have been subdivided by mineral phase and also host rock.*

Sulphate reduction and the metal trap

The $\delta^{34}S$ value of Mississippian seawater (15 – 17‰; Claypool *et al.*, 1980) is preserved by barite in both districts, although a much larger range of $\delta^{34}S$ values are recorded in the barite from the Red Dog district.

Red Dog district

Barite deposits are regionally widespread in the Red Dog district, but are also spatially associated with the sulphide orebodies (e.g., Kelley *et al.*, 2004a; Reynolds *et al.*, 2021). The sulphur and oxygen isotope composition of barite in the Red Dog district is comparable to modern diagenetic cold seeps (Johnson *et al.*, 2004). The highly positive $\delta^{34}S$ values that are preserved in barite are typical of sulphate that has been fractionated during bacterial sulphate reduction (BSR) in diagenetic pore fluids (Johnson *et al.*, 2009).

The earliest generation of sphalerite and pyrite preserves strongly negative $\delta^{34}S$ values, consistent with reduced sulphur generated during open system BSR; in contrast, the main ore stages (2 and 3) preserve much higher values (Kelley *et al*., 2004b). Temperature constraints for yellow brown and red brown (stages 2 and 3) sphalerite are between 100 and 200°C, which is in the range of thermochemical sulphate reduction (TSR); the fractionation between sphalerite and barite (approx. 15 ‰) is in the range expected for TSR at these temperatures (Ohmoto & Lasaga, 1982). The late stage breccias at Red Dog preserve low $\delta^{34}S$ values for all sulphides, which indicates a switch back to BSR dominated system (Kelley *et al*., 2004b).

Irish Midlands

A similar wide range of $\delta^{34}S$ values are preserved in the sulphide minerals in the Irish Orefield (Caulfield *et al*., 1986; Anderson *et al.*, 1998; Fallick *et al*., 2001; Blakeman *et al*., 2002; Wilkinson *et al*., 2005; Yesares *et al.*, 2019). At the Lisheen deposit, barite in an assemblage with ore stage sulphides preserves $\delta^{34}S$ values between 14.3 and 18.1‰, overlapping with Carboniferous seawater (Wilkinson *et al.*, 2005). The lowest $\delta^{34}S$ values are preserved by the pre-ore disseminated pyrite, and the 35 to 45 ‰ offset from seawater sulphate is typical of BSR under open system conditions.

Compilations of $\delta^{34}S$ values from ore stage sulphides can have a bimodal distribution (e.g., Fig. 5; Navan), with more positive values considered to have developed from TSR. At Navan, sulphides with relatively high values (> 0 < 17‰) are associated with steeply dipping normal faults that are considered to have acted as permeability conduits for hydrothermal fluids (Blakeman *et al*., 2002). Bacteriogenic sulphur tends to occur away from the faults and makes up the dominant source of sulphur (Anderson *et al*., 1998; Fallick *et al.*, 2001). Similar bimodality is also preserved at the sample scale. For example, different domains from colloform banded sphalerite in samples from Galmoy have been targeted using in situ laser sulphur isotope analysis, allowing for differentiation between end member $\delta^{34}S$ values associated with bacteriogenic (-25‰) and hydrothermal (+10‰) sources (Barrie *et al*., 2009).

At Stonepark, where sulphides are also hosted by volcanic rocks, a more restricted range of $\delta^{34}S$ values is preserved (between -10 and +10), although there are some pre-ore sulphides with more negative values (Fig. 5; Elliott *et al.*, 2019). Overall, Stonepark $\delta^{34}S$ values are more positive, which probably reflects a greater contribution of hydrothermal sulphur relative to bacteriogenic Sulphur in the system (Elliott *et al*., 2019).

Discussion

Metallogenesis in the Irish Midlands Orefield and Red Dog district benefited from the alignment of common factors, which resulted in contemporaneous ore formation on opposing margins of Laurentia (Fig. 2). These factors occurred both on a geodynamic and local subbasin scale.

Key geodynamic factors

On a geodynamic scale, both margins overly basement terranes with a complex accretionary evolution (Smit *et al.*, 2018; Anderson & Meisling, 2021). In Ireland, the faults that controlled the Carboniferous extensional basins are suggested to originate from Caledonian structures in the underlying basement, and E- to NE-trending faults that reflect the closure of the Iapetus Ocean during the Caledonian Orogeny (Walsh *et al*., 2018; Kyne *et al.*, 2019). The influence of the basement is also reflected by the systematic variability of Pb isotope data in the Irish Orefield, which indicates the contribution of Pb from differing terranes either side of the Iapetus Suture zone (LeHuray *et al.*, 1987; Everett *et al.*, 2003). In the Red Dog district, the basinal clastic succession is considered to have been the source of metals (Ayuso *et al*., 2004), although the tectonic overprint means it is more difficult to reconstruct potential fluid pathways into basement terranes. Differing flow paths would have been important factors controlling the ore fluid chemistry; in the Irish Orefield, the ore fluids are thought to have been reducing (Wilkinson & Hitzman, 2014) whereas ferric iron in the aquifer units in the Red Dog district would have effectively buffered hydrothermal fluids to a more oxidized state (Kelley *et al.*, 2004b). Higher heat flow would have been an important factor on metal solubilities under more reducing conditions; in the Irish Orefield, the magmatic activity in the SW does appear to correspond with higher fluid temperatures (Fig. 3).

From the Mid Devonian to Mississippian, the Laurentian craton occupied equatorial latitudes and was covered by shallow seas, in a configuration that favoured low latitude carbonate platforms, brine generation, high levels of biological productivity and organic carbon burial. Both the Irish Midlands and red Dog district preserve evidence of brine development and near surface sulphur traps in the form of highly saline fluid inclusions and bacteriogenic reduced sulphur. The composition of the host rock, however, is one of the key differences between the deposits of the Red Dog district and Irish Orefield; whereas the mineralized rocks in the Irish Orefield are carbonate-hosted, the host rock in the Red Dog district (Kuna Formation) is a bio-siliceous and organic rich mudstone, with some carbonate intervals.

It is tempting to link the differences in host rock composition with a slightly different position relative to the paleo-shoreline of the Laurentian margin. However, trace fossils in the Red Dog Mine area provide evidence of an inner to outer shelf paleoenvironment, similar to the Irish Orefield, although the lack of trace fossils at Anarraaq could indicate deeper water facies (Reynolds *et al.* 2015). Instead, it is likely that fundamental differences in depositional environment controlled the composition of the host rock succession in the Red Dog district and Irish Orefield. For example, the Kuna Basin was a heterozoan dominated cool-water system, where productivity was driven by nutrient upwelling (Dumoulin *et al*., 2014), whereas biotically induced precipitation and the buildup of mud mounds were more important factors in the Irish Orefield (Lees & Miller, 1985). The development of Waulsortian mud mounds is a characteristic feature of the sub-equatorial latitudes of the Mississippian Laurentian margin, where the most laterally extensive distribution (> 30,000 km^2) and thickest accumulations are in Ireland (Lees & Miller, 1995).

A number of factors influence the differing modes of carbonate precipitation, including ocean currents, upwelling, and terrestrial sediments (Reijmer, 2021). In terms of basin scale factors that contribute to these differing carbonate regimes, the sub-equatorial latitudes of Laurussia were perhaps more protected,

	Irish Orefield[¥]	Red Dog[□]	References
Tectonic setting	Passive margin with episodic back-arc extension	Passive margin	[¥]Davies *et al.* (2012), Smit *et al.* (2018) [□]Moore *et al.* (1986)
Basin stratigraphy (*host rock)*	Terrigenous sandstones; marine limestones, marls and shales (*limestones, marls, mudstones)*	Marine siltstones and mudstones *(mudstones)*	[¥]Philcox, (1984) [□]Dumoulin *et al.* (2004)
Igneous activity	Close spatial and temporal association in Limerick province	Minor (Drenchwater Creek area)	[¥]McCusker & Reed (2013), Elliot *et al.* (2019) [□]Lange *et al.* (1985)
Metal source	Pre-Silurian basement	Post-rift Upper Devonian clastics (Endicott Group)	[¥]O'Keefe (1986), Everett *et al.* (1999), Hollis *et al.* (2019), Yesares et al. (2021) [□]Ayuso et al. (2004)
Geochronology	346.3 ± 3.0Ma & 334.0 ± 6.1Ma (Re-Os isochrons – ore stage pyrite, Lisheen & Silvermines) $^{187}Os/^{185}Os = 0.253 \pm 0.045$ & 0.453 ± 0.006	338.3 ± 5.8Ma (Re-Os isochron – ore stage pyrite, Red Dog) $^{187}Os/^{185}Os = 0.253 \pm 0.045$	[¥]Hnatyshin *et al.* (2013), Vafeas *et al.* (2023) [□]Morelli et al. (2004)
Ore fluid constraints (T, X, fO2, pH)	Reduced ($H_2S > SO_4^{2-}$) Weakly acidic ($pH \leq 6$) Moderate to high 150-260 °C 5-19 wt. % (NaCl equivalent)	Low to moderate 110-180 °C 14-19 wt. % (NaCl equivalent)	[¥]Wilkinson (2010) [□]Leach *et al.* (2004)
Sulphur source	Bacteriogenic sulphate reduction. Thermochemical sulphate reduction	Bacteriogenic sulphate reduction. Thermochemical sulphate reduction. Barite replacement	[¥]Fallick *et al.* (2001), Barrie *et al.* (2009) [□]Kelley *et al.* (2004), Reynolds *et al.* (2021)
Water depth	10s to 100s meters	100s meters	[¥]Lees & Miller (1985), Elliott *et al.* (2015) [□]Reynolds *et al.* (2015)
Depth of host rock replacement	10s to 100s meters beneath paleo-seafloor	10s to 100s meters beneath paleo-seafloor	[¥]Wilkinson et al. (2003; 2005), Reed and Wallace, (2001) [□] Kelley et al. (2004b)
Pre-mineralization events	Dolomitization	Barite formation	[¥]Hitzman *et al.* (2002), Wilkinson, (2003) [□]Johnson *et al.* (2004), Reynolds *et al.* (2021)
Post-mineralization events	Variscan orogeny	Brookian orogeny	[¥] Coller (1984), Wartho *et al.* (2006) [□]Blevings *et al.* (2013)

Table 1: *Comparatives of the Irish Orefield with Red Dog*

and less prone to nutrient upwelling from open ocean circulation that could otherwise inhibit mud-mound development. In contrast, the nutrient upwelling in the Kuna Basin appears to have contributed to other important components of the host rock, including major phosphogenesis and diagenetic barite formation associated with methane seep activity (Johnson *et al*., 2004; Dumoulin *et al*., 2014; Reynolds *et al.*, 2021).

Key local factors

In both districts, mineralizing fluids were focused along faults before migrating along the most permeable and/or reactive units leading to stratabound replacement. Although ore stage mineralogy is relatively simple, facies variability in the protolith means that mineralization is texturally complex. The timing of the bulk of the Zn-sulphide mineralization in both districts was syn-diagenetic, meaning it formed during diagenesis of the host rock sequence. Both districts preserve examples of colloform sulphides and open space growth (e.g., Anderson *et al*., 1998; Reynolds *et al.*, 2021); this indicates lithified host rocks (at least locally) otherwise the collapse of open space would prevent colloform growth. Large, mineralized cavities and breccias are also consistent with fully cemented host rock. However, since host rock lithification may have occurred early (particularly in the Irish systems), epigenetic textures may not necessarily mean that mineralization happened a long period after host rock deposition (Wilkinson, 2003).

Diagenetic processes were critical for ground preparation of the metal trap, and it is likely that diagenetic and hydrothermal fluids exploited similar fault-controlled flow paths in the shallow subsurface. However, differing host rock composition means that there were contrasting styles of diagenetic ground preparation in either district, associated with the different facies and type of productivity in the basins. It has been suggested that the massive sulphides in the Red Dog district were superimposed on a methane cold seep setting, which resulted in major diagenetic pyrite and barite formation (Johnson *et al.*, 2004; Kelley *et al.*, 2004a; Reynolds *et al.*, 2021). The formation of diagenetic barite was highly effective in concentrating sulphur in the host rock, and evidence for barite replacement by hydrothermal sulphides has been described in the Main, Aqqaluk, Paalaaq, Qanaiyaq, and Anarraaq deposits (Kelley *et al*., 2004a; Blevings *et al.*, 2013; Reynolds *et al.*, 2021). In contrast, there is much less barite in the Irish Orefield, and where it occurs, it is thought to have formed as hydrothermal barite where barium rich fluids mixed with sulphate-rich marine fluids. Nevertheless, it is still possible that bacterial productivity may have been enhanced by hydrothermal leakage into sub-seafloor sediments, resulting in a positive feedback between hydrothermal fluid flow and sulphide generation (Wilkinson, 2003).

The abundance of fluid inclusion data that has been produced in the Irish Orefield has provided good evidence that a low temperature, Br-enriched, high salinity bittern brines may have played an important role in transporting reduced sulphur into the ore system (Banks *et al.*, 2002). The infiltration of the sulphur rich brines into faults and along permeable horizons could have potentially resulted in mixing with the upwelling ore fluids, providing a mechanism for sulphide precipitation (Wilkinson, 2010). The availability and reliability of fluid inclusion data is much more limited in the Red Dog district, owing to the tectonic overprint; however, both systems preserve negative $\delta^{34}S$ values in breccias, and at Red Dog these occur later in the paragenesis, after the main ore stages 2 and 3. In the Irish deposits, a major component of the mineralization is hosted in breccias. In either case this indicates bacteriogenic sulphur, perhaps in a low temperature brine, was introduced to the system via fracture permeability.

Implications

The deposits of the Red Dog district and Irish Midlands Orefield have more in common than they do differences, making them more than distant cousins in the broad family of sediment hosted massive sulphide deposits. In particular, the tectonic setting, role of bacteriogenic sulphur, and syn-diagenetic timing of mineralization mean the Irish-type deposits are more comparable to clastic-dominant (CD-type) than Mississippi-Valley type (MVT) deposits (see also Wilkinson, 2014). High value CD-type deposits are exceedingly rare in ancient sedimentary basins and appear to have developed in 'goldilocks zones' where there was the optimization of key processes and development of coupled feedbacks. The Mississippian Laurentian margin is clearly highly prospective; suture zones provide areas of crustal weakness, structural inheritance and potential fluid flow pathways. Good targets are where these zones overlap with host rocks deposited in productive environments, with the most potential for feedbacks between deeply circulating hydrothermal and shallow circulating diagenetic flow systems. For example, the deposits of the Maritimes Basin also fall along the south western extension of the Iapetus Suture zone, are hosted in slightly younger Mississippian units, and have been favourably compared to the deposits of the Irish Midlands (Chi *et al*., 1998; Sangster *et al*., 1998).

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