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Establishing a geochemical baseline for the Lower Carboniferous stratigraphy of the Rathdowney Trend, Irish Zn-Pb orefield



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ABSTRACT

Carbonate-hosted Zn-Pb mineralisation within strata of the Irish Midlands can be subdivided between deposits forming on either Lower Carboniferous basin margin. Those on the southern side, known as the Rathdowney or Lisheen trend deposits, are hosted within the Waulsortian Mudbank formation and have been exploited for over 35 Mt of massive sphalerite-galena-pyrite ore since the 1960s. Additional occurrences of Irish-style mineralisation along the Rathdowney trend are numerous; however, questions remain regarding the extent and geochemical signature of the accompanying alteration haloes as, until now, no geochemical baseline was established.

Preliminary results from Rapla, an exploration prospect 15 km northeast of the decommissioned Lisheen mine, show that an unaltered stratigraphical geochemical baseline can be distinguished using bulk 4-acid ICP-AES/MS data, thus a chemostratigraphic sequence can be derived from select major elements (Ca, Mg, Al) and Σ REE concentrations. With Eu and Ce anomalies and redox sensitive elements (Mo-U-V) providing environmental conditions during formation.

pXRF analysis on the sample pulps show > 95% precision of 15 elements. Of these 5 elements display > 90% accuracy (Al, Ti, Fe, Cu, Rb), 4 elements > 80% accuracy (K, As, Cd, U), and finally 6 elements at > 50% accuracy (S, Ca, Mn, Zn, Se, Sr). Therefore confidence in data collected from powdered samples from rocks of this type by pXRF is high.

1. Introduction

The Irish midlands represents a world class Zn-Pb province with five deposits having been brought into production, including the giant Navan deposit (combined resource of 115 Mt at 10 wt% Zn + Pb; Ashton et al., 2015), and over 20 prospects discovered (Fig. 1). Mineralisation is hosted within two formations of Lower Carboniferous limestone: Tatestown or Navan trend deposits are hosted within the Navan Pale Beds, a series of clean micrites, grading into bio-grainstones and calc-arenites, with variable argillaceous beds throughout (Ashton et al., 1986). Those of the Rathdowney or Lisheen trend are hosted within the Waulsortian Mudbank formation, a relatively clean biomicrite (Wilkinson et al., 2005).

Irish Zn-Pb deposits are considered to represent hybrid deposits with characteristics of both sedimentary-exhalative (SEDEX) and Mississippi Valley type (MVT) classes (Leach et al., 2010). As such, they are commonly referred to as Irish-type in the literature (e.g. Wilkinson, 2010). Significant factors influencing the type of deposit that forms within this spectrum are: the activity of deep-seated syn-sedimentary faulting, the depth of sediment at the onset of mineralisation, and the progression of lithification (Leach et al., 2010). All styles of mineralisation require a metalliferous fluid stripping metals from the crust and being subsequently transported by deep listric structures (Leach et al., 2010). While SEDEX deposits form prior to, diagenesis, and MVT are post-lithification, Irish-type deposits are distinguished as syndiagenetic (Peace and Wallace, 2000; Peace et al., 2003; Wilkinson et al., 2005; Wilkinson and Hitzman, 2015). Mineralisation is dominantly stratform through the replacement of carbonate in the hanging-wall of extensional faults, which are, in turn, coupled to reactivated basement structures (Graham, 2009b; Worthington and Walsh, 2011). Sphaleritegalena-pyrite is the dominant sulfide assemblage, with variable amounts of barite, marcasite, chalcopyrite, pyrrhotite, and other sulfosalts (Wilkinson and Hitzman, 2015).

Although Irish Zn-Pb exploration has a history of successfully

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Fig. 1. Simplified geological map of Ireland with the prospective, decommissioned or active Zn-Pb sites highlighted alongside the projected trace of the Iapetus suture zone (ISZ) and the trend referenced in this study (Rathdowney Trend, RT), left. Larger scale map over the study area (Rapla) with the prospective formation (Waulsortian Mudbank) highlighted, right.

 Table 1

 Average concentration and standard deviations from unaltered samples.

Formation	Al (wt%)	Ca (wt%)	Mg (wt%)	Na (wt%)	K (wt%)	Ti (wt%)	Fe (wt%)	Mn (ppm)	TREE (ppm)
BA DUR AGH CPK W ABL RING MEL ORS	$\begin{array}{c} 0.05 \ \pm \ 0.02 \\ 0.36 \ \pm \ 0.28 \\ 0.29 \ \pm \ 0.47 \\ 0.32 \ \pm \ 0.33 \\ 0.3 \ \pm \ 0.25 \\ 2.35 \ \pm \ 1.65 \\ 5.74 \ \pm \ 2.07 \\ 5.65 \ \pm \ 1.46 \\ 3.97 \ \pm \ 0.15 \end{array}$	$\begin{array}{r} 36.2 \pm 1.04 \\ 31.19 \pm 3.94 \\ 33.51 \pm 3.38 \\ 28.46 \pm 6.87 \\ 20.15 \pm 0.49 \\ 22.95 \pm 6.68 \\ 9.74 \pm 6.03 \\ 4.71 \pm 0.57 \\ 2.16 \pm 2.53 \end{array}$	$\begin{array}{c} 0.27 \ \pm \ 0.13 \\ 1.61 \ \pm \ 2.9 \\ 1.35 \ \pm \ 2.2 \\ 5.41 \ \pm \ 5.45 \\ 12.49 \ \pm \ 0.7 \\ 2.63 \ \pm \ 3.33 \\ 1.8 \ \pm \ 0.9 \\ 2.15 \ \pm \ 0.23 \\ 1.14 \ \pm \ 1.16 \end{array}$	$\begin{array}{c} 0.01 \ \pm \ 0 \\ 0.03 \ \pm \ 0.01 \\ 0.02 \ \pm \ 0.02 \\ 0.03 \ \pm \ 0.01 \\ 0.03 \ \pm \ 0.01 \\ 0.11 \ \pm \ 0.12 \\ 0.2 \ \pm \ 0.16 \\ 0.26 \ \pm \ 0.03 \\ 0.08 \ \pm \ 0.04 \end{array}$	$\begin{array}{c} 0.02 \ \pm \ 0.01 \\ 0.15 \ \pm \ 0.12 \\ 0.13 \ \pm \ 0.21 \\ 0.16 \ \pm \ 0.16 \\ 0.15 \ \pm \ 0.14 \\ 1.26 \ \pm \ 0.91 \\ 3.15 \ \pm \ 1.14 \\ 2.88 \ \pm \ 0.61 \\ 2.87 \ \pm \ 0.17 \end{array}$	$\begin{array}{c} < 0.005 \\ 0.02 \ \pm \ 0.01 \\ 0.03 \ \pm \ 0.03 \\ 0.02 \ \pm \ 0.01 \\ 0.13 \ \pm \ 0.08 \\ 0.31 \ \pm \ 0.11 \\ 0.38 \ \pm \ 0.02 \\ 0.19 \ \pm \ 0.03 \end{array}$	$\begin{array}{c} 0.03 \ \pm \ 0.02 \\ 0.23 \ \pm \ 0.16 \\ 0.17 \ \pm \ 0.26 \\ 0.28 \ \pm \ 0.23 \\ 0.65 \ \pm \ 0.74 \\ 1.35 \ \pm \ 0.84 \\ 3.05 \ \pm \ 1.25 \\ 3.06 \ \pm \ 1.04 \\ 1.23 \ \pm \ 0.79 \end{array}$	$\begin{array}{r} 124 \ \pm \ 118.12 \\ 172.53 \ \pm \ 250.3 \\ 114.39 \ \pm \ 101.08 \\ 277.77 \ \pm \ 285.09 \\ 331.43 \ \pm \ 342.18 \\ 466.24 \ \pm \ 490.97 \\ 741.71 \ \pm \ 739.19 \\ 1270 \ \pm \ 254.56 \\ 673.5 \ \pm \ 829.44 \end{array}$	$\begin{array}{c} 6.32 \ \pm \ 2.33 \\ 15.2 \ \pm \ 5.25 \\ 11.63 \ \pm \ 11 \\ 31.45 \ \pm \ 15.59 \\ 16.52 \ \pm \ 10.03 \\ 56.71 \ \pm \ 33.65 \\ 141.17 \ \pm \ 27.68 \\ 170.1 \ \pm \ 5.29 \\ 66.12 \ \pm \ 9.82 \end{array}$

utilising geochemical vectors (Wilkinson et al., 2011; Walker, 2010; Wilkinson and Hitzman, 2015; Marks, 2015), these methods are not necessarily cost effective and cannot be readily utilised in a purely greenfields context. Therefore, increased exploration success requires the development of new tools to detect subtle geochemical halos distal to feeder zones, and at greater depths. To detect subtle hydrothermal signatures around new orebodies, the original, natural background geochemical concentrations must first be understood. Consequently, to aid exploration efforts within the Rathdowney Trend, we have determined a geochemical baseline for the Lower Carboniferous stratigraphy alongside of calibrating portable X-Ray Fluorescence (pXRF) acquisition for major and trace elements samples from the ore field. This will allow mineral explorers to potentially augment current analytical procedures to detect anomalies over introducing new isotopic or mineral-chemical methodologies (Table 1).

1.1. Regional geology

Irish geology is dominated, both in basement and overlying

Mesozoic cover, by the closure of the Iapetus Ocean. While Paleoproterozoic rocks in the northwest of the country are of Laurentian-affinity, those to the southeast of the Iapetus Suture are of Gondwanan affinity (Chew and Stillman, 2009). On the northern side of the Iapetus Suture, early ocean closure during the Late Cambrian to Early Ordovician (Grampian phase of the Caledonian orogeny) was denoted by the accretion of ophiolites, arcs and microcontinental blocks to the passive margin (Fig. 2, Draut et al., 2004; Hollis et al., 2012). The Longford - Down Terrane subsequently developed as an accretionary prism above a north-dipping subduction zone as ocean closure continued (Chew and Stillman, 2009). On the southern side of Iapetus, arc volcanism developed on rifted continental crust between the Lower and Upper Ordovician (Chew and Stillman, 2009). The closure of Iapetus culminated in the collision of these two continents (Laurentia and Ganderia-Avalonia) during the Late Caledonian phase of the wider Caledonian-Appalachian orogeny. This resulted in the emplacement of large granitoid batholiths across Ireland until c. 400 Ma (Fig. 2, Chew and Stillman, 2009). Erosion of the Caledonian mountain range followed, depositing quartzose feldspathic sediments into the extensional



Fig. 2. Generalised Lower Carboniferous stratigraphy of the Rathdowney trend (left) with representative photos derived in part from the sampled drill holes at the Rapla prospect (mapped right).

basins generated through orogenic-collapse (Figs. 1, 2). Initially this subaerial material was coarse, but gradually, during marine transgression, the sequence becomes finer grained (Graham, 2009a). Continuing orogenic root collapse resulted in a transition from subaerial deposition into submarine sedimentation. Shelf, ramp and deep-sea carbonate-rich sediments were formed during the Lower Carboniferous, grading into deltaic cyclic sedimentation through the Upper Carboniferous (Philcox, 1984).

1.2. Devonian to Lower Carboniferous stratigraphy of the Rathdowney Trend

The simplified stratigraphy for the Upper Paleozoic geology of the Rathdowney Trend is presented in Fig. 2. Sub-aerial medium grained sandstones of the Old Red Sandstone transition through the inter-tidal Lower Limestone Shale group (Mellon House, Ringmoylan and Ballymartin formations) into the pre-reef sub-marine Ballysteen formation bearing the oolitic Lisduff member, a minor host of Zn-Pb-Cu mineralisation at Lisheen (Wilkinson et al., 2005). Biomicrites conformably overly, and make-up the generally dolomitised Waulsortian Reef Mudbank formation, a major host for Irish-type mineralisation (Wilkinson and Hitzman, 2015). Post-reef strata are represented by the basal-shelf flank argillaceous limestones of the Crosspatrick formation followed by the deep-water carbonates of the Aghmacart, Durrow and Ballyadams formations (Fig. 2). The unconformable Namurian/Westphalian age deltaic coal-bearing sequences (inc. Moyadd Coal formation) are found towards the top of the Carboniferous sequence (Sevastopulo, 2009). However, these are commonly eroded, sub-cropping below recently-developed lacustrine and peat bog sediments (Mitchell, 2009).

A Courceyan-Visean transtensional dextral relay-ramp system, utilising reactivated structural features from the northeast-southwest trending Caledonian orogenic belt, controls much of the mineralisation with normal faults along the trend (e.g. Lisheen, Galmoy and Rapla deposits: Worthington and Walsh, 2011; Bonson et al., 2012; Kyne et al., 2017; Torremans et al., 2017). Later thrusting and strike-slip movement associated with Variscan compression are the most recent features reactivating the older fault network and generating northwestsoutheast structures (Graham, 2009b; Bonson et al., 2012; Kyne et al., 2017).

2. Methodology

In order to develop a baseline chemostratigraphy for the Rathdowney Trend, 297 half and 30 quarter NQ (46.3 mm) core samples drilled by Vedanta Exploration Ireland Ltd. were collected for whole rock geochemical analysis (Table 2). With no single drill hole intersecting a complete stratigraphic sequence, 140 samples across 14 holes, becoming progressively distal to mineralisation, were compiled to examine the background geochemical variation. An additional hole, distal to any known mineralisation, was used as an end-member monitor. These drillholes were fully described and photographed in late 2015 during Vedanta's regional exploration programme. Drillhole locations are shown in Fig. 2.

For whole rock geochemistry, half core samples of 0.15–0.30 m length were taken at, approximately 50 m intervals in unaltered units, and 25 m in altered zones (Table 2). At sample locations, sampling occurred along sections which reflected the average variability across

Table 2									
Frequency	breakdown	of	the	number	of	un-			
altered samples present in each formation.									

Formation	Count
Ballyadams	3
Durrow	15
Aghmacart	49
Crosspatrick	13
Waulsortian	7
Ballysteen	34
Ringmoylan	7
Mellon House	2
Old Red Sst	2

5–10 m of core. Where geological contacts were present, the frequency was increased and samples were collected within 5 m either side of the contact. Quarter core samples were only taken in areas of existing sampling, where the same sample frequency was used but the length of sample extended to 0.25–0.4 m (so more material was available for analysis).

Samples were analysed for 60 elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr, Dy, Er, Eu, Gd, Ho, Lu, Nd, Pr, Sm, Tb, Tm and Yb) at ALS Laboratories, Loughrea, Ireland (laboratory package code ME-MS61r). Samples were homogenized using mild-steel rotary crushing and ceramic grinding prior to four-acid (nitric, hydrochloric, perchloric and hydrofluoric acids) digestion and analysis via Inductively Coupled Plasma Mass Spectroscopy/Atomic Emission Spectroscopy (ICP-MS/AES).

Matrix and grade matched quality control samples (blanks, standards and duplicates) were added both at the sampling and laboratory stage yielding aggregate results, at two sigma, of 93% accuracy and 94% precision. Accuracy is determined by the proportional count of analysis which falls within the 2 sigma limit of the certified value, while precision is calculated by half absolute relative difference. A total of 66 sample pulps were subsequently duplicated by ICP-AES following peroxide fusion digestion for 12 element oxide and Loss on Ignition (LOI) values with QAQC returning 90% accuracy and 95% precision. Results resolved below the detection limit and those at the detection limit were nulled. Data greater than the detection limit, all sulfide-related, underwent additional analysis and after satisfactory interrogation was subsequently combined with the existing data of the respective element.

Pulps from the samples were also compressed into 15 mm deep, 25 mm diameter pucks which were then analysed by an Olympus Delta X pXRF device. Both the 40 and 10 kV beams were exposed for 60 s perpendicular to the surface of the puck and without any medium between the sample and the pXRF analyser. This data is then compared to the ICP-AES/MS values to produce calibration factors for any subsequent work in the Irish Midlands.

Of the 327 samples, 132 were unaltered, the univariate statistics of which produced a chemostratigraphic column. This is devised using the sample mid-points and normalising the sample position in the intersected formation relative to the maximum observed thickness of the same formation in the local area. The samples are then averaged at 10 m intervals down the 1.55 km composite section with any data outliers subject to additional scrutiny and potential removal. In addition, Immobile element and rare earth element (REE) ratios were used for sedimentary provenance with Sr-U-V-Mo and Ce-anomalies determining palaeo-redox conditions. Maps and sections are derived from the Geological Survey of Irelands' (GSI) 1:100,000 bedrock data modified with drilling data supplemented by the Vedanta Exploration drill log database.

3. Chemostratigraphy

Modelling and characterising the natural geochemical variation of a sedimentary sequence is required to properly interrogate any trends within strata that have been modified post-formation. That said, the emplacement of mineral deposits after pervasive dolomite replacement complicates the picture within the Irish Midlands, as both occur late in the diagenetic process. $\delta^{18}O_{SMOW}$ values of the pervasive dolomitisation suggest a sea-water derived source (Hitzman et al., 1992). This can be interpreted as a result of surface-related environmental changes during lithification, and thus part of the natural background variation in the Rathdowney Trend (Fig. 4).

Univariate statistics from the discrimination of sample data into their respective geological formations was used to categorise each formation and thus present a robust dataset for the automatic characterisation of lithologies by the Irish minerals industry (Fig. 5). Ranges given are the 1st and 3rd quartile of the dataset. Bivariate and multi-variate statistics are used to describe potential mineral or inter-mineral chemical relationships, constrained by petrographic observations; all correlations are defined as greater 0.9 or less than -0.9 unless otherwise specified.

3.1.1. Old Red Sandstone

The lowermost continuous stratigraphic unit is characterised by relatively moderately-high Al (3.8-4.6 wt% Al) with associated K (2.8-3.0 wt% K), moderate Fe (0.7-1.8 wt% Fe) and low Ca and Mg (0.4-3.9 wt% Ca, 0.3-2.0 wt% Mg). The formation bears the highest Ba (> 890 ppm) content decreasing with younging units. Other major and trace elements are within the bottom quartile, excluding the immobile elements (Ti, Y, Nd, Al, Nb, Zr), which exhibit a rapidly decreasing trend from the overlying Mellon House formation with depth. Only two samples were taken within the upper 10 m and therefore bivariate and multivariate statistics are inconclusive.

3.1.2. Mellon House formation

The Mellon House formation forms a unit of transitional deposition between alluvial/fluvial systems and shallow water reef development. Many of the major and minor trace-element compositions are gradational with the contacting Old Red Sandstone and Ringmoylan formations (4.3–5.1 wt% Ca, 4.6–6.7 wt% Al, 2.4–3.1 wt% K). Major element exceptions include Fe (2.3–3.8 wt%), Mn (1090–1450 ppm) and S (0.4–1.5 wt%), with Σ REE (160–170 ppm) exhibiting the highest concentrations from the entire pre-reef stratigraphy. As with the underlying group, only 2 samples were recovered from a single drill hole and therefore other statistical analysis is not possible.

3.1.3. Ringmoylan formation

Argillaceous content within the stratigraphic column is highest, and is defined by, the group of beds in the Ringmoylan formation. Aluminium concentrations are highest here (4.9–6.9 wt% Al), along with associated elements (K-Ti-Be-Bi-Co-Ga-Rb-Sc-V-W), including Al/K ratios of 2–2.1. Calcium concentrations increase through the Lower Limestone shale (5.4–12.9 wt% Ca) and Mg remains low (1.2–2.9 wt% Mg). However, the Ringmoylan formation is not homogenous; Al, Ca, Mg concentrations, and associated minor elements, decrease with depth inversely to SiO₂. Zr-Ta-Nb-Hf and S-Fe-As-Sb-Cu-Co-Ni exhibit correlative behaviour with residual Fe/S ratios > 1.

3.1.4. Ballysteen formation

Including the Ballymartin Shale horizon, the Ballysteen formation is the thickest stratigraphic unit intersected (340 m), covering a transition that is contemporaneous with oolitic deposition in the Lisduff Oolite Member. Chemical constituents reflect this and consequently this formation is discussed in three parts.

3.1.4.1. Lower Calcarenite member. Unlike the upper calcarenite member, the sedimentological and, therefore, primary chemical trends are linear in nature. Al, K, and all other analysed elements decrease with stratigraphic height. Ca displays antithetic behaviour to Al and K and increases with shallowing depth. Mg is low (0.67–1.12 wt %) and is bimodally distributed with separate associations separately for both Al and Ca. Where Mg is variable, this is likely related to Ca contained within carbonate. Sulfur is relatively significant (0.34–1.06 wt%) with at least one of the trends with Fe a 1:1 ratio and Co-Ni showing strong association with Zn-Pb-Cu-Sb-Tl are relatively elevated (40–248 ppm Zn) as an independent group with the only major element of significance Mg with Pearsons' correlation at 0.58.

3.1.4.2. Lisduff Oolite member. Relative to the other two members, the

central member of the Ballysteen formation is similar to the reef limestone with relatively enriched Mg-Mn (3.1–7.5 wt% Mg, 562–1060 ppm Mn) and significant enrichment of some chalcophile elements (S-Cu-Zn-As-Ag-Cd-Sb-Tl-Pb). All other chalcophiles are below detection or depleted along with K, Ti, Sr and Ni (0.4–0.7 wt% K, 0.04–0.07 wt% Ti, 91–217 ppm Sr, 7.6–18.0 ppm Ni) associated with many other minor lithophiles. Calcium and Ba concentrations (16.6–27.8 wt% Ca, 80–120 ppm Ba) are similar to that of the Upper Calcarenite member, however Ca is slightly enriched in comparison. Barium is slightly depleted in comparison to the Lower Calcarenite member.

3.1.4.3. Upper Calcarenite member. While many of the associations seen within the Lower Calcrenite member of the Ballysteen formation are similar in the upper member, the major element distribution is bipartite. Clean carbonate units form near the contacts, with significant argillaceous material within the centre of the member. The gradational upper contact with the Waulsortian Mudbank formation is commonly classified as an additional member (i.e. the nodular micrite, due to the unique inclusion of reworked micrite cobbles).

3.1.5. Waulsortian Mudbank formation

While sub-divided into further members, the Waulsortian Mudbank is relatively homogenous both in major and trace elements, when not associated with Zn-Pb mineralisation. Mg is consistently and characteristically > 10 wt% with interquartile Ca/Mg ratios of 1.62–1.92. Stoichiometric dolomite has a Ca/Mg ratio of 1.65. Residual Ca after dolomite ranges between 0.5 and 2.5 wt%. On average, there are increased Al-K values compared to supra-Waulsortian limestones, however other immobile elements (Ti-Zr-Y-Nd-Nb) show no change. Barium is strongly associated with Al-K. Other trace elements are relatively low with the exceptions of Zn-Fe-S-As-Ag-Cd-Tl-Pb, which are all elevated above values for the rest of the stratigraphy, the exchange between Mg-Ca and Fe-S causes a depletion trend (Mg, Ca) towards the base of the Waulsortian.

3.1.6. Crosspatrick formation

Syn-sedimentary deformation gives rise to varying thicknesses of interbedded bioclastic micrites and shaley horizons during the start of the Visean (346.7-330.9 Ma) epoch. Chert nodules are commonly present at the base of the Crosspatrick formation, but can be observed throughout the strata. However, pervasive silicification, which primarily is restricted to the base or contact with the Waulsortian below is difficult to identify. Bounded by clean lower-shelf carbonates (Aghmacart formation) and homogenous carbonaceous mud mounds (Waulsortian Mudbank formation) the Crosspatrick Formation is distinct in its elevated Al-K contents and related lithophile elements (LILE) which is normally distributed between the formation contacts. Al/K ratios indicate the presence of illite. Chondirite normalised REE plots show that these are LREE enriched. Magnesium is not distinctive as it is highly variable within this formation. Ca/Mg ratios at the upper levels of the Crosspatrick formation are high and decrease exponentially to the basal contact. Calcium decreases with depth, initially exchanging for Si however this is overtaken by Mg which continues to the concentrations found across the Waulsortian with the Si decreasing at the lower contact.

3.1.7. Aghmacart formation

Major-element variability away from clean carbonate compositions within the thick carbonate Aghmacart formation is minimal (29–35.4 wt% Ca) with variability due to dolomitisation in the middle of the formation and within the basal grainstone unit, a spary oolite. Further variation is reflected by grading of sequences bearing argillaceous sediments; although, this only produces 0.1–0.2 wt% Al concentrations with minor trace-element increases. Sr displays a strong negative trend with depth. The upper contact averages 800–900 ppm

Sr, however the basal contact only has concentrations of 50-200 ppm.

3.1.8. Durrow formation

There are few stratigraphic differences between the Durrow Formation and the overlying Ballyadams formation. The presence of siphonodendron (an extinct rugose coral) is used to define this formation. The stratigraphic similarity is reflected in the chemistry with little variation between the two units. Notably, Sr is anomalously enriched (77–890 ppm) towards the base and decreases with depth, this is associated with locally elevated Al-K-S contents.

3.1.9. Ballyadams formation

The shallowest 4 samples collected in this study belong to the > 200 m thick and, relatively, homogenous Ballyadams formation. The unit is a clean limestone, with 35.9-36.9 wt% Ca and only minor Mg (0.2–0.4 wt%). Ca decreases with increasing Mg towards the basal contact. Sr maintains contents of 279–306 ppm yet has an element of inverse linear correlation (-0.6) with Mg. All other concentrations are below or close to the detection limit of the analytical method.

3.1.10. REE results

As part of the ICP-MS package a full suite of rare earth elements were analysed, albeit with a four-acid digestion. These measurements are therefore potentially not fully representative of the samples as a whole, especially if REE bearing resistant mineral phases (e.g. monzonite, zircon) were present. That said, the signatures adequately represent REE contents in carbonate minerals and it is still possible to discern correlations with the data obtained. This is important, as exploration companies rarely have use for high quality fusion lithogeochemistry, but use the four-acid method routinely.

Rare earth element profiles normalised to C1 Chondrite (McDonough and Sun, 1995) display LREE enrichment trends within all Lower Carboniferous sediments analysed (Fig. 3, top right). REE concentrations increase up to 2 orders of magnitude towards the Devonian contact. Minor HREE enrichment is present in these units, whereas in the post-reef stratigraphy this enrichment has not been detected. Negative Eu anomalies (Eu/Eu* < 1: Taylor and McLennan, 1985) are present throughout the entire stratigraphy analysed, excluding the Aghmacart formation. The strength of Eu anomalies increase upwards from the Devonian contact (Fig. 3, d). Cerium anomalies do not show the same trend, with only the Ballyadams, Crosspatrick and Waulsortian formations displaying prominent negative Ce anomalies. These strata form a separate group in calculated Ce/Ce* values (Fig. 3, d) where the formations below the Crosspatrick formation form a logarithmically increasing sequence towards the underlying Old Red Sandstone. When plotted against total REE concentrations, the Ce/Ce* values show two trends (Fig. 3, c), that of the dominantly clean carbonates (Ballyadams, Durrow and Aghmacart) and those bearing argillaceous contents. The Crosspatrick formation is anomalous as it fits on neither of these trends, a feature reflected by immobile element plots.

Additionally, chondrite normalised spider diagrams (Fig. 3, a) show further anomalies useful to distinguish between different formations. Lead is significantly enriched in the Waulsortian and Ballysteen formations yet is depleted in the Lower Calcarenite member of the Ballysteen formation, the Ringmoylan formation, Mellon House formation and Old Red Sandstone. U and K are generally enriched, with P and Ti depleted across the entire stratigraphy. Strontium is enriched within the post-reef stratigraphy, and depleted in the pre-reef strata. Data from (Rollinson, 1993, p. 143) indicates a larger negative anomaly within the Nb-Ta data and a minor enrichment of Y within post-reef formations.

Redox-sensitive trace elements, Se and Mo have been suggested by Large et al. (2014) to trace ocean oxygenation via Se/Co and Mo/Co ratios as incorporations within pyrite. While this study does not analyse pyrite directly, these elements are only correlative with S, and so the bulk geochemical data can be assumed to reflect the appropriate



Fig. 3. Chondrite (top left) and REE C1 Chondrite (top right) normalised values for unaltered samples taken at the Rapla prospect. All samples show LREE enrichment with Ba-Nb-Ta-P-Tl-Ce-Eu negative anomalies. Pre-reef stratigraphy has positive Sr anomalies while post-reef is negative. Eu anomalies (after Taylor and McLennan, 1985) increase with time (bottom right) while Ce anomalies can be used to model detrital input (bottom left).

signatures.

4. pXRF calibration

Handheld portable X-ray fluorescence has a number of errors, which compound to reduce the accuracy and precision of in instrument relative to laboratory techniques (Fisher et al., 2015). However, the rapid data acquisition with minimal preparation renders it a useful tool for geochemical exploration. As the resulting error is linear, determining the appropriate correction factors for the material being analysed can ensure increased accuracy, over factory settings, with minor decreases in precision (Piercey et al., 2013).

In the Irish ore field, the most common method of ICP-MS analysis uses four-acid digestion. The current study compares four-acid ICP-MS results to those of pXRF for 31 elements. In addition peroxide fusion ICP-AES analyses were completed on 90 samples for major element oxides. Si concentrations are taken from this data (Fig. 6).

31 elements (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, W, Hg, Pb, Th, U) are detected. by pXRF Although Sn is rejected at the outset with low counting (n = 5) statistics with P, Cd and Sb returning < 50 data points above detection limits from 726 samples. Assuming linear correlation, the components (*a*, *b*) of a linear function (y = ax + b) are calculated along with the Pearsons' moment correlation coefficient (r^2). The latter value can be



Fig. 4. Discriminant projection plot of the calculated first and second (left), second and third (right) components showing the end member and interaction of the two major sedimentary constituents within the samples.

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Fig. 6. Comparison of ICP-MS (4-acid) and pXRF data on the same samples. Raw/corrected bivariate plots for a selection of elements (top), summary plot of the linear correction factors (a and b from y = ax + b) with data point size relative to the correlation (larger sizes displaying poorer correlation) calculated by Pearsons (REF, bottom).

interpreted as the precision of the pXRF measurement against ICP-MS while the linear components describe the transformation away from the line of perfect accuracy (a = 1, b = 0).

Of the 31 elements measured, 28 return statistically significant values to proceed. Within these 15 display correlation statistics > 95% (Mg, Al, SI, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Nb, Pb) and a further 4 between 90 and 95% (As, Zr, Cd, U), beyond this precision decreases exponentially with 5 more elements 50–90% (P, S, V, Se, Y) and the final 4 elements with < 50% precision (Mo, Sb, W, Th). Poor correlation statistics are a function of two major mechanisms, firstly, elemental interferences at high mass ranges (Y, Mo, Sb, W, Th) and inappropriate ICP analytical methods (S).

Slope and intercept values are a function of the accuracy of the pXRF method relative to the ICP data. 5 elements display > 90% accuracy (Al, Ti, Fe, Cu, Rb) with a further 4 elements > 80% accuracy (K, As, Cd, U). At > 50% accuracy another 6 elements are bracketed (S, Ca, Mn, Zn, Se, Sr) with the remainder < 50% accurate in comparison to 4-acid ICP analysis (Fig. 6). However with the intercept value, which within this dataset represents consistent over or under-recording on concentrations, the accuracy can be increased to levels near 100%. This is achieved by taking the original pXRF data points, multiplying by the calculated slope and adding the intercept value. This linear correction can be inbuilt into the pXRF, but it also is required to be completed on the QAQC data points to determine the usefulness of the data (Piercey et al., 2013, 2014; Fisher et al., 2015).

5. Discussion

5.1. Chemostratigraphy

Major and trace elemental trends throughout the constructed chemostratigraphy are fundamentally controlled by the mineralogy present: carbonate by Ca + Mg, the abundance of siliciclastic material by Si and Al, and clay/felsic proportions inferred by Si/Al ratios. Elements attributed to mineralisation in the area are not found to be elevated, confirmed by petrographic observations. Wilkinson and Hitzman (2015) conclude that the Waulsortian was dolomitised during diagenesis, so although this unit is visibly altered, the presented chemostratigraphic sequence represents the chemistry of the units up until the end of diagenesis with no evidence for post-diagenetic hydrothermal or surface-based processes (karst) affecting the samples collected.

While there is increased geochemical variation at the Waulsortian-Ballysteen contact, due to the sample frequency in the highly heterogenous layer, this marks a change in sedimentary regimes, and many plots also exhibit this change geochemically. Younger formations are carbonate dominant and become progressively pure with respect to the calcite contents. Older formations have much lower carbonate contents, at the expense of detrital siliciclastics and argillaceous material, but with an increased mixing of felsic material culminating in the Old Red Sandstone.

Dolomitisation occurs with varying consistency throughout the stratigraphy, although this is not always easy to discern at a macroscale. While the entire Waulsortain reef has been transformed, no other formation displays alteration to the same extent and intensity. Dolomitisation appears to occur locally, or along preferential horizons, in the Crosspatrick and Ballysteen Formations, in addition the basal grainstone member of the Aghmacart exhibits strong dolomitisation. Both pervasive replacement and breccia styles of dolomitisation are present within the Waulsortain related to sedimentary-hosted strata form replacement Irish-type Zn-Pb mineralisation. Work by Wilkinson et al. (2005) suggests that the individual phases can be characterised by

major element data; however, no work further work investigating the trace element and rare earth systematics of the various phases exists.

Multivariate analysis utilising linear discriminants on the chemical suite allows for the generation of source-specific components, simplifying complex chemical relationships into single plots.

5.2. Palaeoenviromental reconstruction

Work by (Tribovillard et al., 2006) shows that by using a combination of Ni-Co-Cu-Zn-Cd-Cr-U-V-Mo the redox (fO_2) conditions within or close to the sea water column can be derived through bulk geochemical analysis. That said, given as these samples are collected close to known hydrothermal activity, any interpretation using Cu-Zn-Cd has been avoided. Other elements are normalised to carbonate by Ca + Mg. Using the relationship of Mo-U-V it is possible to determine the approximate fO_2 conditions at the sediment-seawater interface. When all three elements (Mo, U, V) are elevated euxinic conditions can be inferred. By contrast, increases in U-V only designate suboxic to anoxic conditions (Tribovillard et al., 2006). The Crosspatrick and Ballysteen formations display suboxic to anoxic conditions while the post-Crosspatrick formations are euxinic.

A spike in Ni/Co-V-Hf/Zr exists at the top of the Crosspatrick Formation thought to be a result of additional volcaniclastic input (mafic-intermediate) accompanying the detrital components in the sediment budget. Tuffs are present throughout the Lower Carboniferous sequence, notably two horizons within the Ballysteen formation just below the contact with the overlying Waulsortain reef (Philcox, 1984). Neither these, nor the signature present in the Crosspatrick Formation, have been traced to a specific volcanic event. However, both the Limerick and Croghan Hill volcanics have been dated relatively to a similar period (Elliott, 2015; Timmerman, 2004; Sommerville et al., 1992).

5.3. Exploration implications

With corrected data, Mg, Fe, Si, Zn, Rb and Pb satisfy a 2 sigma accuracy test for QAQC data taken by four-acid ICP-MS analysis. Ca is an additional standard deviation from the certified value. Certified elements were not attainable for P, V, Cr, Mn, CI, Nu, Cu, As, Se, Sr, Zr, Nb, Mo, Ag, Sn, Sb, W, Hg, Bi and U. All other elements acquired by pXRF fall outside the 2 sigma range in correlating with four-acid ICP-MS data, or are on the lower end of the detection limit with this analytical technique.

As precision and accuracy limits are within 95%, there is an appropriate level of confidence for Mg, Fe, Si, Zn, Rb and Pb analysed by pXRF equivalent to that of normal laboratory techniques utilising ICP analysis. In addition, the reproducibility of results for Al, K, Ca, Ti, Mn, Ni, Cu, Sr, Nb, As, Zr, Cd and U suggests that trends that can be identified in these datasets are real albeit with a minor one-dimensional transformation (Fig. 6).

Previous work has concluded that, in addition to others, that Al-Rb-U-Zr could be used as a lithogeochemical vectoring tool in terrains hosting Irish Zn-Pb deposits (Washbrooke, 2006). Our research concludes that the increase in these elements is due to the proximity of Waulsortian-Ballysteen contact and the reduction in argillaceous deposition with time.

Many geochemical exploration techniques utilise normalisation to some defined background concentrations based on unaltered material. From this study it is apparent that using a single data point to normalise an entire sequence can be simplistic, particularly when multiple processes exist which are difficult to identify or constrain. Thus, modelling the variation stratigraphically provides an appropriate context prior to



Fig. 7. Simple chemical discrimination for Lower Carboniferous formations in the Rathdowney Trend.

any subsequent sampling, de-risking exploration targeting by providing results of increased confidence.

6. Conclusions

Chemical observations herein confirm what has been previously described through sedimentological studies by earlier workers (Sevastopulo, 2009; Philcox, 1984; Phillips and Sevastopulo, 1986; Graham, 2009a). The area sampled generally shows increasing water depth and an increased distance from major terrigenous sediment source with younging, this however does not include the possibility of local variations. Elemental associations indicate a switch from predominantly feldspathic to argillaceous deposition within the Mellon House formation, with the replacement of calcite for dolomite (postformation) occurring relatively early in the sequence within the Ringmoylan Formation.

As the defined geological formations are chemically distinct using uni- and bivariate statistics it is possible to derive a heuristic methodology for chemical classification. The youngest three formations, Ballyadams, Durrow and Aghmacart, have > 28 wt% Ca with the Ballyadams < 0.025 wt% K. Samples > 10 wt% Mg are typically from the Waulsortian formation and $> 190 \text{ ppm } \Sigma \text{TREE}$ are from the Mellon House formation. Ringmoylan formation material is identified by > 5wt% Al and $< 190 \text{ ppm } \Sigma \text{TREE}$ with the basal formation, Old Red Sandstone, characterised by < 5 wt% Ca, $< 190 \text{ ppm} \Sigma \text{TREE}$ and < 5 wt%wt% Al. The Ballysteen and Crosspatrick formations have 5-28 wt% Ca, however, Crosspatrick Zr/TREE ratios are < 0.3 while those of the Ballysteen are > 0.3. In addition, the calculated Ce and Eu anomalies (Taylor and McLennan, 1985) show that within the Crosspatrick formation, the values are relatively equivalent, as they are within the Waulsortian. In the Ballysteen formation Ce anomalies are 30-40% greater than corresponding Eu anomalies (Fig. 7).

Immobile element ratios (Y/Al, Ti/Nd, Zr/Nd) indicate that the ratios within the Crosspatrick Formation are not consistent with the rest of the sequence. As these strata are forming synchronously with mineralisation. Either the material is being altered by ore-forming fluids or an episodic change in source material is occurring. Given that many ratios associated with the petrogenetic tracing of igneous material (Ni/Co, Nb/Th, Zr/Nb) show appropriate signals, this may therefore reflect the input of volcanogenic material or a fluid derived from magmatic processes. Negative cerium anomalies occur in the same samples which would seem to support the idea of a change in environment or original source material.

Elements associated with the precipitated carbonate phases (Sr-Mo-U-V) can be used to determine constraints on the environmental conditions of the water-sediment interface. High Sr/Ca correlates with increased amounts of fossiliferous fragments in units, which is further evidence for increased biological productivity at certain times. The youngest units (Ballyadams Formation) are highly productive, but this then decreases through the Durrow formation with depth (and time). With the onset of deposition of the Aghmacart Formation biological productivity then steadily rises to a peak during periods of Crosspatrick and Waulsortian sedimentation, dropping off with the strong influence of detrital sedimentation towards the Old Red Sandstone.

Relative to ICP standards, accurate and precise data can be obtained with an appropriate analytical and QAQC protocol for Mg, Fe, Si, Zn, Rb and Pb in the carbonate rocks found in Ireland by pXRF. Al, K, Ca, Ti, Mn, Ni, Cu, Sr, Nb, As, Zr, Cd and U can also be obtained using pXRF with some degree of confidence, however the acceptance of these elements will fall at a lower threshold. With an appropriately deigned and introduced standard many of these elements will lie within the constraints required to deem them suitable for pXRF acquisition only.

In summary, the classification of formations found along the Rathdowney trend in Ireland can be achieved chemically through chemostratigraphic discrimination utilising calibrated pXRF technology, appropriate sampling methodology and QAQC.

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