Diatremes act as fluid conduits for Zn-Pb mineralization in the SW Irish Orefield

Holly A. L. Elliott[1a*], Thomas M. Gernon[1], Stephen Roberts[1], Adrian J. Boyce[2] and Chad Hewson[3]

[1] School of Ocean and Earth Science, University of Southampton, National Oceanography Centre Southampton, SO14 3ZH, UK

[2]NERC Isotope Facility, Scottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, Scotland

[3]Teck Resources Limited, Vancouver, Canada

[a] Currently at: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE, UK

**Corresponding author email address: h.elliott@exeter.ac.uk*

ABSTRACT

'Irish-type' mineralization is commonly attributed to fault-controlled mixing of a seawater-derived, sulfur-rich fluid and basement-derived metal-rich fluid. However, maar-diatreme volcanoes discovered in close spatial and temporal association with Zn-Pb mineralization at Stonepark, in the Limerick Basin (SW Ireland) bring a new dimension to established geological models, which may increase the deposit-scale prospectivity in one of the world's greatest Zn-Pb districts. Stonepark exhibits many incidences of dolomitic black matrix breccias (BMB) with associated Zn-Pb mineralization, the latter typically occurring within 150 m of the diatremes. Highly negative δ^{34}S pyrite values within country rock-dominated BMBs (-

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

12 to -34 ‰) are consistent with sulfide precipitation from bacteriogenic sulfur reduction in seawater-derived brines. However, $\delta^{34}S$ values of Zn-Pb sulfides replacing BMBs (-10 to +1 ‰) reflect multiple sulfur sources. Diatreme emplacement both greatly enhanced country rock fracture permeability, and produced conduits filled with porous volcaniclastic material, that extend down to basement lithologies. Our $\delta^{34}S$ data suggest that diatremes provide more efficient fluid pathways for basement-derived fluids. The diatremes introduce another potential sulfur source, and facilitate a greater input of metal-rich basement-derived hydrothermal fluid into the system compared to other Irish-type deposits such as Navan and Lisheen, evidenced by Stonepark's more positive modal $\delta^{34}S$ value of -4 ‰. Irish-type deposits are traditionally thought to form in association with extensional basement faults, and are considered to be unrelated to extensive Carboniferous magmatism. Our results indicate that a direct link exists between diatreme volcanism and Zn-Pb mineralization at Limerick, prompting a re-evaluation of the traditional 'Irish-type' ore formation model where mineralization is spatially associated with volcanic pipes.

INTRODUCTION

The Irish Orefield hosts a number of globally important stratabound, carbonate-hosted Zn-Pb deposits of Viséan age (346.7-330.9 Ma), which exhibit strong spatial and genetic associations with reactivated Caledonian basement faults (Mitchell, 1985; Hitzman & Beaty, 1996; Everett et al., 1999; Hitzman, 1999; Blakeman et al., 2002; Wilkinson et al., 2005a; Hnatyshin et al., 2015; Ashton et al., 2016), and are designated 'Irish-type'. Mineralization in the Limerick region is typically hosted in dolomitized country rock breccias termed 'black matrix breccias' (BMB) (Hitzman et al., 2002; Wilkinson et al., 2005b; Redmond, 2010). The exact origin of these

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

deposits remains controversial as they share characteristics of both sedimentary exhalative (SEDEX; Wilkinson, 2014) and Mississippi Valley-type (MVT) deposits (Bradley & Leach, 2003). The 2010 discovery of base-metal mineralization associated with volcanic rocks in SW Ireland (Blaney et al., 2013; Redmond, 2010) challenged the traditional Irish-type model, which does not recognize a link to volumetrically minor, but regionally extensive Carboniferous magmatism that extends across Ireland, Scotland and the English Midlands (Woodcock and Strachan, 2000; Holland and Sanders, 2009; Elliott et al., 2015). Field observations at Limerick (Fig. 1) suggest a close spatial and temporal association between Zn-Pb mineralization and basaltic maar-diatreme volcanism (McCusker and Reed, 2013; Elliott et al., 2015), but the existence of a direct genetic link is yet to be established.

Here, we apply $\delta^{34}S$ analysis of sulfides from mineralized environments including volcanic facies and BMBs at Stonepark, Limerick to investigate the relationship between volcanism and ore deposition. Our data indicates that diatreme emplacement strongly influenced mineral deposit formation at Stonepark. Diatremes, such as those preserved at Stonepark (Elliott et al., 2015), are typically infilled with porous and permeable material (e.g. White and Ross, 2011; Afanasyev et al., 2014), and are associated with fracture networks and breccia bodies related to their explosive emplacement (Sparks et al., 2006). We propose that the relatively permeable diatremes served as conduits for mineralizing fluids, forming more efficient fluid pathways from the basement than the extensional fault systems widely observed within the Irish Orefield (e.g. Silvermines, Navan, Lisheen). Our data also suggest that large quantities of volcaniclastic material within the diatreme provided a third (magmatic) sulfur source.

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Context and Mineralization

Maar-diatremes (hereafter, diatremes) are formed during explosive volcanism (cf. Sparks et al., 2006; White and Ross, 2011). In the Limerick Basin, diatremes form a NE-SW orientated cluster, closely reflecting the regional Caledonian trend. This suggests that ascending magmas utilized pre-existing faults (cf. Kurszlaukis and Barnett, 2003; Jelsma et al., 2009). Phreatomagmatic eruption of these diatremes into a shallow-water graben resulted in the deposition of >450 m of extra-vent pyroclastic deposits (Knockroe Formation) interbedded with wackestones and cherts (Elliott et al., 2015). Stratigraphic constraints suggest diatreme emplacement occurred during the Viséan Stage (346.7–330.9 Ma) (Somerville et al., 1992; Holland and Sanders, 2009).

The Limerick Basin occupies a highly faulted section of the western Irish Midlands (Fig. 1). Here, shallow marine carbonates were deposited during the Lower Carboniferous (Holland and Sanders, 2009). Typically, it is the Waulsortian Limestone Formation that hosts high incidences of BMB. Three main types of BMB are recognized at Limerick (Fig. 2), all of which have a dolomite-rich matrix (≤80 wt. %). ‘Country Rock BMB’ (Type C) contains Waulsortian carbonate clasts, commonly with embayed edges set in a dark, relatively unmineralized matrix that exhibits limited pyrite replacement (Fig. 2A). ‘Replaced BMB’ (Type R) contains clasts and matrix completely or predominantly replaced by sphalerite, galena and pyrite (Fig. 2B). ‘Polymict BMB’ (Type P) contains a range of clast types including diatreme breccia, pyroclastics, crystalline igneous and country rock in a poorly-mineralized dolomite matrix (Fig. 2C) intruded by tuffisite dikes. Volcaniclastic material within the breccia occasionally shows evidence of deformation prior to lithification (Elliott, 2015), indicating that these clasts were still unconsolidated when they were incorporated into the breccia.

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Mineralized or BMB clasts have not yet been observed in the diatreme fill, which has been dolomitized and subsequently haematitized causing a red coloration. Dolomitization of the diatreme fill starts at ~100-190 meters below sea level (mbsl), coinciding with higher incidences of BMB in the country rock (Fig. 1). Concentrations of dolomite within the upper diatreme fill range from 0.2 to 0.4 wt.%, increasing to 11-12 wt.% in the middle diatreme (110-190 mbsl) and 22 wt. % at >400 mbsl. Dolomite is a key BMB mineral phase, comprising ≤80 wt.% of the breccia matrix. Further, the lower diatreme-fill (>400 mbsl) exhibits the same mineral assemblage as BMB Type P clasts, comprising dolomite, illite, calcite and quartz, suggesting they experienced similar hydrothermal alteration (Elliott, 2015). The lower diatreme matrix contains higher concentrations of disseminated sphalerite, pyrite, rutile and galena than the upper and middle diatreme. These observations strongly suggest that diatreme emplacement pre-dated, or was synchronous with BMB formation and that mineralization post-dated both events.

BMBs are concentrated in fractured country rock adjacent to the diatremes, typically pinching out with distance from the diatreme margins (Fig. 1C). Major and trace element signatures of juvenile volcanic fragments in the Type P breccias, diatreme fill and Knockroe Formation pyroclastic material are geochemically near-identical (Elliott et al., 2015).

Role of faulting and hydrothermal fluids

There is some controversy surrounding the relative importance and timing of large-scale extensional basement faults that provided fluid pathways, however there is a general consensus that the majority of Irish-type deposits were formed by the epigenetic sulfide replacement of hydrothermal breccias (e.g. Hitzman and Beaty, 1996; Anderson et al., 1998; Hitzman et al., 2002; Wilkinson et al., 2005b; Redmond, 2010). The timing of mineralization at Lisheen and

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Silvermines have been constrained by Hnatyshin et al., (2015) to 346.6 ± 3.0 Ma and 334.0 ± 6.1 Ma, respectively, and within a similar timeframe to Stonepark.

Different BMB types have been recognized in the literature, however, some show evidence for formation by sedimentary processes within cavities, later overprinted by hydrothermal fluids (e.g. Lee and Wilkinson, 2002). However, typical BMBs are thought to have formed by hydrothermal fluids that utilized extensional faults, brecciating the carbonate host-rocks (Hitzman and Beaty, 1996; Hitzman et al., 2002). These breccias were later affected by large-scale sulfide precipitation (Wilkinson et al., 2005b) upon mixing of surface and basement-derived hydrothermal fluids (Banks et al., 2002; Wilkinson et al., 2005a). The surface fluid is thought to be a lower temperature (<140^{o}C) seawater-derived brine, enriched in reduced bacteriogenic sulfur (-25 to -5 per mil, mean -15 per mil; Fallick et al., 2001), which had evaporated to reach salinities of up to 25 wt% NaCl. The second, higher temperature (200-280^{o}C) hydrothermal fluid likely contained a high concentration of metals and minor reduced hydrothermal sulfur (0 to 15 per mil, mean 10 per mil; Fallick et al., 2001), leached from basement rocks (Fallick et al., 2001; Banks et al., 2002).

Sulfide description and paragenesis

Sulfide precipitation at Limerick is multi-stage, similar to other deposits in the Irish Orefield (e.g. Hitzman and Beaty, 1996; Hitzman et al., 2002; Wilkinson et al., 2004; Ashton et al., 2015). Early fine-grained, disseminated pyrite (pre-ore 1) is observed in all environments but can be associated with rounded aggregates of dark sphalerite within BMB horizons (Fig. 2D). Another void-filling pyrite mineralization stage follows (pre-ore 2), typically precipitated in layers or with a colloform habit (Fig. 2B and 2D). Within the diatreme fill, this stage is

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

represented by massive or coarse-grained pyrite locally replacing juvenile ash, rimming volcanic clasts or is associated with carbonate-filled voids (Fig. 2F).

The subsequent main ore-forming stage is represented differently in each environment. Unfortunately, sphalerite and galena crystals within the lower diatreme are too small to perform sulfur isotope analysis, but have been identified and imaged by Scanning Electron Microscope (SEM) (Fig. 2G). These minerals appear to co-precipitate as anhedral masses predominantly replacing volcanic lapilli or earlier pyrite. Earlier pyrite within BMB samples are brecciated or replaced by ore minerals at this stage (Fig. 2B and 2C). Within Type R BMB, galena is typically observed as large anhedral crystals and sphalerite as creamy yellow-brown anhedral intergranular masses, often associated with carbonate filling voids (Fig. 2B). A similar assemblage is observed within the Waulsortian Limestone environment, as veins, replacing crackle breccias or sediment infilling voids. Sphalerite is typically found at the edge of veins or rimming clasts in breccias, and is occasionally layered, whereas anhedral galena and carbonate fill the voids (Fig. 2C and 2E). Pure sphalerite veins within the limestone consist of elongate brown crystals. Sphalerite and galena are sparse within Type P BMB samples, but can replace the matrix and earlier layered or colloform pyrite (Fig. 2D).

Post-ore fine-grained veins of pyrite intrude, brecciate and in some cases replace earlier stages of mineralization (Fig. 2B and 2C). This is observed in all sampled environments except the volcanic material, in which sphalerite and galena are the latest mineralization stages identified.

ANALYTICAL TECHNIQUES

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Sulfides (pyrite, sphalerite and galena) from BMBs, sedimentary rocks, intrusions, diatremes and veins were separated from gangue by crushing and picking or micro drill extraction, and analyzed for sulfur isotopes following the approach used by Robinson and Kusakabe (1975). Samples of fine-grained sulfides and those exhibiting intergrown sulfide textures were prepared as polished blocks and combusted by in-situ laser analysis (Wagner et al., 2002). The laser spot size was ~100 μm, significantly smaller than the scale of intergrowths, which typically range from 400-6000 μm. Reproducibility based on repeat analysis of internal and international standards was ~ ±0.3 ‰ for both methods. All data are reported in $\delta^{34}S$ notation as per mil (‰) variations from the Vienna Canyon Diablo Troilite (V-CDT).

SULFUR ISOTOPE RESULTS

The Waulsortian Limestone Formation hosts the diatremes, BMB and also contains pyrite-carbonate filled veins and breccias. Limestone-hosted sulfides (pyrite, sphalerite and galena – see Supplementary Table A1) consist of pre-ore stage 1, stage 2 and ore stage minerals that returned predominantly negative $\delta^{34}S$ values (-45 to -1 ‰), with a mean of -10.9 ‰. Only three samples out of the 16 analyzed, show fine-scale inhomogeneity, displaying values up to +12 ‰ (Fig. 3A). Ore stage sulfides display a more positive mean $\delta^{34}S$ value of -7.5 ‰ compared to pre-ore stages (-17 to -14 ‰).

Type C BMBs contain pre-ore stage pyrite with negative $\delta^{34}S$ values (-34 to -13 ‰; Fig. 3B, Supplementary Table A2). In contrast, >70 % of Type R BMB $\delta^{34}S$ values (pyrite, sphalerite and galena) lie in the range -10 to +1 ‰ (mode -4 ‰). Pre-ore stage 2 sulfides (mean -7‰) and ore stage sulfides (mean -5‰) display similar ranges of $\delta^{34}S$ values. However, pre-ore stage 1 sulfides display more negative $\delta^{34}S$ values (mean -20 ‰). Type P BMBs are variably

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

mineralized with pyrite and minor sphalerite and galena, reflected in the wide distribution of $\delta^{34}S$ values (-44 to +10 ‰, Fig. 3B and Supplementary Table A2). Compared to the other BMB environments, Type P ore stage sulfides exhibit more positive $\delta^{34}S$ values (mean 6‰).

Sulfides (predominantly pyrite) from volcanic rocks exhibit a more restricted range of $\delta^{34}S$ values, largely between -10 and +10 ‰ (Fig. 3C). Due to their disseminated nature in the diatreme fill, ore stage sulfides were only able to be sampled from intrusions, which displayed a mean $\delta^{34}S$ value of 5.5 ‰. Pre-ore stage 1 sulfide minerals within diatreme and intrusion samples exhibit more negative $\delta^{34}S$ values (mean -4 and -7 ‰ respectively) than pre-ore stage 2, which typically show more positive $\delta^{34}S$ values (mean 2 and 3 ‰ respectively).

Comparison with other deposits in the Irish Orefield

Sulfides at Silvermines show a bimodal $\delta^{34}S$ distribution with modes at -21 and -36 ‰ (Fig. 3E). In contrast, minerals from Lisheen show a unimodal $\delta^{34}S$ distribution with a mode of -10 ‰ (Fig. 3F). Our data from Stonepark (Fig. 3D) have a distinctly more positive distribution with a mode of -4 ‰ (Supplementary Table A2) compared to the other two deposits. A highly negative pyrite peak is common to all deposits, visible between -40 to -35 ‰ (Fig. 3).

Sulfides adjacent to faults at Navan and Lisheen typically exhibit more positive $\delta^{34}S$ values (Blakeman et al., 2002; Wilkinson et al., 2005b), suggesting they accommodated basement-derived fluids (Blakeman et al., 2002; Wilkinson et al., 2005b). To some extent this relationship is observed at Limerick, where positive $\delta^{34}S$ values of sphalerite and galena are solely observed proximal to the diatremes (<116 m). However, negative $\delta^{34}S$ values of these sulfides are observed at all distances from the diatremes, up to 410 m (Fig. 1B and C).

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Sulfur isotope data for the adjacent Pallas Green deposit (currently owned by Glencore PLC) are sparse, but those available indicate a similarly positive value (~+10 ‰, Wilkinson and Redmond, 2010). A number of volcanic centers have also been identified at Pallas Green, in addition to many dikes, sills and intrusive breccia plugs (Tyler, 2007), with the latter likely to be diatremes. Tyler (2007) also describes breccia dikes containing <30 % igneous clasts, comparable with Type P BMBs described herein, which are often associated with ore-grade mineralization.

DISCUSSION & CONCLUSIONS

Grades of Zn and Pb mineralization are high within BMB horizons proximal to the diatremes (≤27 wt.% - see Supplementary Table A3), and reduce significantly with distance from the diatreme margins (Fig. 5). This pattern supports the hypothesis that basement-derived metal-rich fluids preferentially utilized the diatremes. Anomalously high Zn concentrations (>20 wt.%) occur at shallower depths adjacent to diatremes in the northwest (Fig. 4C), compared to the southeast (Fig. 4D). Lead concentrations show a similar pattern, displaying <30 wt.% at shallower depths surrounding the northern diatreme-related boreholes (Fig. 4A), however comparable concentrations to the south are observed at 350 m (Fig. 4B). This could be related to the thick composite intrusions observed within diatreme 19 (Fig. 1B and C) acting as a barrier, and focusing fluids in to the surrounding country rock at greater depths to the southwest.

Negative $\delta^{34}S$ values within Type C BMBs are consistent with a bacteriogenic sulfur origin, most likely precipitated from seawater-derived brines. The light sulfur isotopes and lack of ore stage minerals support the hypothesis that metal-rich basement-derived fluids never reached these breccias. In contrast, Type R BMBs show evidence for a shift to more positive

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

values, which could be explained by mixing of two fluids, resulting in extensive sulfide precipitation (Fig. 5B). Early pre-ore stage 1 sulfides display highly negative δ^{34}S values, indicating they precipitated from seawater-derived brines. The introduction of metal-rich, basement-derived fluids containing heavier sulfur isotopes, resulted in more positive isotopic signatures in the later pre-ore stage 2 and ore-stage sulfides.

Type P BMB sulfides exhibit the widest range of δ^{34}S values, consistent with bacteriogenic sulfate reduction (-45 ‰) and more positive sulfur leached from basement rocks (+10 ‰). Heavier sulfur isotopes may also have been leached from the large volumes of diatreme, intrusion and Knockroe-related material hosted in these breccias, with means between -2.1 and +3.8 ‰ (see Supplementary Table A2). Country rock-hosted sulfides exhibit predominantly negative δ^{34}S values (see Fig. 3A). These data suggest that seawater-derived fluids utilized both fractured country rock and diatreme pathways, whereas basement-derived fluids were restricted to the diatremes and subsequently formed Type P BMBs (Fig. 5B). Fluid mixing in Type R breccias led to extensive sulfide precipitation.

It is well established that diatreme-filling deposits have high initial porosity and permeability (Sparks et al., 2006; Stripp et al., 2006), allowing enhanced hydrothermal fluid flow (Afanasyev et al., 2014). Further, diatreme-forming eruptions produce radial fracture networks (cf. Barnett and Lorig, 2007), allowing fluid flow in and out of the diatremes. The localization of BMB adjacent to, and radiating out from the diatreme margins (Fig. 1B and C), most likely reflects exploitation by fluids of fracture networks associated with diatreme emplacment. High Zn and Pb grades (<22 and 7.5 wt.% respectively) are also observed <50 m from the diatremes, and reducing significantly with distance from the diatreme margins (Fig. 4).

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Hydrothermal components increase in importance during the later stages of Irish-type ore formation (e.g. Lisheen; Wilkinson et al., 2005b). The Stonepark deposit exhibits a more positive sulfur isotope signature in later sulfide precipitation stages compared to other Irish Orefield deposits. We attribute this to enhanced hydrothermal fluid flux from the basement, via 1-2 km deep diatremes, which would increase the amount of hydrothermal sulfur relative to bacteriogenic sulfur in the mineralizing system. In summary, the evidence for enhanced fluid flow from the basement via diatremes is as follows: (1) dolomite, a key BMB mineral, overprints the lower diatreme fill; (2) the occurrence of mineralization within the lower diatremes; (3) high Zn-Pb mineralization grades proximal to diatreme margins (Fig. 4); and (4) the more positive sulfur isotope signatures observed in the Stonepark deposit (Fig. 3C). The latter is enhanced by the leaching of a third magmatic sulfur source (mean -0.4 ‰, see Supplementary Table A1 'Intrusion (original)') from basaltic glass-rich pyroclastic diatreme-fill (estimated minimum volume for a given vent ~5 – 7.5 x 10^6 m^3; Elliott et al., 2015) during hydrothermal alteration (cf. Afansyev et al., 2014).

The timing of mineralization in the Irish Orefield (Chadian to Arundian; Hitzman and Beaty, 1996; Anderson et al., 1998; Reed and Wallace, 2004; Ashton et al., 2015) overlaps with extensive magmatic and volcanic activity, including that in the Limerick Basin (Somerville et al., 1992; Elliott et al., 2015; Hnatyshin et al., 2015; Wilkinson and Hitzman, 2015). Textures such as plastic deformation of diatreme-derived material within BMB Type P indicates that BMB formation occurred during the waning stages of diatreme activity. Therefore, a close temporal association between volcanism, hydrothermal activity and mineralization exists at Stonepark, and raises the interesting possibility that volcanism is a key process in the localization of Zn-Pb mineralization. The temporal associations at Limerick are consistent with a scenario in which

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

magmatism elevated heat flow and hydrothermal circulation in the Carboniferous Irish Orefield (Praeg, 2004; Wilson et al., 2004; Davidheiser-Kroll et al., 2014; Hnatyshin et al., 2015; Wilkinson and Hitzman, 2015).

This study has implications for the origin of diatreme-related mineralization in other regions, for example gold deposits such as those of Kelian, Indonesia and Cripple Creek, USA (Davies et al., 2008). Our results suggest that diatreme breccias can focus metal-rich hydrothermal fluids, facilitating epithermal metal deposit formation. The direct link between volcanic activity and Zn-Pb mineralization at Limerick prompts re-evaluation of the traditional ‘Irish-type’ model for ore formation in regions where mineralization is spatially associated with magmatism and volcanic pipes.

ACKNOWLEDGMENTS

The authors would like to thank Teck Ireland Ltd for supporting this study and Group Eleven Resources for their cooperation. We acknowledge and thank Dr Jon Neades for creating the 3D model portrayed in Figure 4. Funding for isotope analysis was obtained from the Natural Environment Research Council (IP-1397-1113). We would also like to thank the expert staff at the SUERC isotope facility in East Kilbride.

REFERENCES CITED

Afanasyev, A. A., Melnik, O., Porritt, L., Schumacher, J. C. and Sparks, R. S. J., 2014, Hydrothermal alteration of kimberlite by convective flows of external water: Contributions to Mineralogy and Petrology, v. 168, p. 1038-1055.

Anderson, I.K., Ashton, J.H., Boyce, A.J., Fallick, A.E. and Russell, M.J., 1998, Ore depositional processes in the Navan Zn-Pb deposit, Ireland: Economic Geology, v. 93, p. 535-563.

Ashton, J. H., Blakeman, R. J., Geraghty, J. F., Beach, A., Coller, D., Phicox, M. E., Boyce, A. J. and Wilkinson, J.

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

J., 2015, The giant Navan carbonate-hosted Zn-Pb deposit – a review, in Archibald, S. and Piercey, S., eds., Current perspectives on zinc deposits: Dublin, Irish Association for Economic Geology, p. 85-122.

Banks, D. A., Boyce, A. J. and Samson, I. M., 2002, Constraints on the origins of fluids forming Irish Zn-Pb-Ba deposits: Evidence from the composition of fluid inclusions: Economic Geology, v. 97, p. 471–480.

Barnett, W. and Lorig, L., 2007, A model for stress-controlled pipe growth: Journal of Volcanology and Geothermal Research, v. 159, p. 108–125.

Blakeman, R. J., Ashton, J. H., Boyce, A. J., Fallick, Anthony, E. and Russell, M. J., 2002, Timing of interplay between hydrothermal and surface fluids in the Navan Zn + Pb orebody, Ireland: evidence from metal distribution trends, mineral textures, and δS^{34} analyses: Economic Geology, v. 97, p. 73–91.

Blaney, D., Tennant, S. and Tyler, P., 2013, Geology, alteration and mineralization of the Pallas Green block, Country Limerick, Ireland, in Kelly, J. G., Andrew, C. J., Ashton, J. H., Boland, M. B., Earls, G., Fusciardi, L. and Stanley, G., ed., Europe's major base metal deposits: Dublin, Irish Association for Economic Geology, p. 533-544.

Davidheiser-Kroll, B., Stuart, F. M. and Boyce, A. J., 2014, Mantle heat drives hydrothermal fluids responsible for carbonate-hosted base metal deposits: evidence from 3he/4he of ore fluids in the Irish Pb-Zn ore district: Mineralium Deposita, v. 49, p. 547–553.

Davies, A. G. S., Cooke, D. R., Gemmell, J. B. and Simpson, K. A., 2008, Diatreme breccias at the Kelian gold mine, Kalimantan, Indonesia: Precursors to epithermal gold mineralization: Economic Geology, v. 103, p. 689-716

Elliott, H. A. L., 2015, Pb-Zn mineralisation within the Limerick Basin (SW Ireland): A role for volcanism? PhD thesis, Southampton, UK, University of Southampton.

Elliott, H. A. L., Gernon, T. M., Roberts, S. and Hewson, C., 2015, Basaltic maar-diatreme volcanism in the Lower Carboniferous of the Limerick Basin (SW Ireland): Bulletin of Volcanology, v. 77, p. 37-59.

Everett, C. E., Wilkinson, J. J. and Rye, D. M., 1999, Fracture-controlled fluid flow in the Lower Palaeozoic basement rocks of Ireland: implications for the genesis of Irish-type Zn-Pb deposits, in K. J. W. McCaffrey, L. Lonergan and J. J. Wilkinson, ed., Fractures, fluid flow and mineralization: London, Geological Society, v. 155, p. 247-276.

Fallick, A. E., Ashton, J. H., Boyce, A. J., Ellam, R. M. and Russel, M. J., 2001, Bacteria were responsible for the magnitude of the world-class hydrothermal base-metal orebody at Navan, Ireland: Economic Geology, v. 96, p. 883-888

Hitzman, M. W. and Beaty, D. W., 1996, The Irish Zn-Pb-(Ba) Orefield: Society of Economic Geologists Special Publication no. 4, p. 112–143.

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Hitzman, M. W., Redmond, P. B. and Beaty, D. W., 2002, The carbonate-hosted Lisheen Zn-Pb-Ag deposit, County Tipperary, Ireland: Economic Geology, v. 97, p. 1627– 1655.

Hitzman, M. W., 1999, Extensional faults that localize Irish syndiagenetic Zn-Pb deposits and their later compressional fate, in K. McCaffery, L. Lonergan, and J. Wilkinson, ed. Fractures, Fluid Flow and Mineralization: London, Geological Society, Special Publications v. 155, p. 233-245.

Hnatyshin, D., Creaser, R. A., Wilkinson, J. J. and Gleeson, S. A., 2015, Re-Os dating of pyrite confirms an early diagenetic onset and extended duration of mineralization in the Irish Zn-Pb ore field: Geology, v. 43, p. 143-146.

Holland, C. H. and Sanders, I. S., 2009, The Geology of Ireland, 2nd .ed: Dunedin Academic Press.

Jelsma, H., Barnett, W., Richards, S. and Lister, G., 2009, Tectonic setting of kimberlites: Lithos, v. 112S, p. 155–165.

Kurszlaukis, S. and Barnett, W., 2003, Volcanological and structural aspects of the Venetia kimberlite cluster - as case study of South African kimberlite maar-diatreme volcanoes: South African Journal of Geology, v. 106, p. 145–172.

Lee, M. J. and Wilkinson, J. J., 2002, Cementation, hydrothermal alteration, and Zn-Pb mineralization of carbonate breccias in the Irish Midlands: textural evidence from the Coleen Zone, near Silvermines, County Tipperary: Economic Geology, v. 97, p. 653-662.

McCusker, J. and Reed, C., 2013, The role of intrusions in the formation of Irish-type mineralisation: Mineralium Deposita, v. 48, p. 687–695.

Mitchell, A. H. G., 1985, Mineral deposits related to tectonic events accompanying arc-continent collision: Transactions of the Institution of Mining and Metallurgy, v. 94, p. 115-125.

Praeg, D., 2004, Diachronous Variscan late-orogenic collapse in response to multiple detachments: a view from the Internides in France to the foreland in the Irish Sea, in M. Wilson, E. R. Neumann, G. R. Davies, M. J. Timmerman, M. Heeremans and B. T. Larsen, ed., Permo-Carboniferous Magmatism and Rifting in Europe: Geological Society of London, v. 223, p. 89 – 138.

Redmond, P. B., 2010, The Limerick Basin: An important emerging subdistrict of the Irish Zn-Pb orefield: Society of Economic Geologists Newsletter, v. 82, p. 21–25.

Reed, C. P. and Wallace, M. W., 2004, Zn-Pb mineralisation in the Silvermines district, Ireland: a product of burial diagenesis: Mineralium Deposita, v. 39, p. 87–102.

Robinson, B. W. and Kusakabe, M., 1975, Quantitative preparation of sulfur dioxide, for $^{34}S/^{32}S$ analyses, from

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

sulfides by combustion with cuprous oxide: Analytical Chemistry, v. 47, p. 1179–1181.

Somerville, I. D., Strogen, P. and Jones, G. L., 1992, Biostratigraphy of Dinantian limestones and associated volcanic rocks in the Limerick Syncline, Ireland: Geological Journal, v. 27, p. 201–220.

Sparks, R. S. J., Baker, L., Brown, R. J., 2006, Dynamical constraints on kimberlite volcanism: Journal of Volcanology and Geothermal Research, v. 155, p. 18-48.

Stripp, G. R., Field, M., Schumacher, J. C., Sparks, R. S. J. and Cressy, G., 2006, Post- emplacement serpentinization and related hydrothermal metamorphism in a kimberlite from Venetia, South Africa: Journal of Metamorphic Geology, v. 24, p. 515–534.

Tyler, P. A., 2007, An evaluation of potential, Pallas Green Property, Co. Limerick and Tipperary, Ireland: Unpublished report prepared for Minco Plc, Durham, England.

Wagner, T., Boyce, A.J. and Fallick, A.E., 2002, Laser combustion analysis of $\delta^{34}S$ of sulfosalt minerals: determination of the fractionation systematics and some crystal-chemical considerations: Geochimica Cosmochimica Acta, v. 66, p. 2855-2863.

White, J. D. L. and Ross, P.-S., 2011, Maar-diatreme volcanoes: a review: Journal of Volcanology and Geothermal Research, v. 201, p. 1–29.

Wilkinson, J. J., Everett, C. E., Boyce, A. J., Gleeson, S. A. and Rye, D. M., 2005a, Intracratonic crustal seawater circulation and the genesis of subseafloor zinc-lead mineralization in the Irish orefield: Geology, v. 33, p. 805–808.

Wilkinson, J. J., Eyre, S. L. and Boyce, A. J., 2005b, Ore-forming processes in Irish- Type carbonate-hosted Zn-Pb deposits: Evidence from mineralogy, chemistry, and isotopic composition of sulfides at the Lisheen Mine: Economic Geology, v. 100, p. 63–86.

Wilkinson, J. J. and Redmond, P. B., 2010, Irish Zn-Pb: New insights, new discoveries: IAGOD Symposium conference presentation, Adelaide, Australia.

Wilkinson, J. J., 2014, Sediment-hosted zinc-lead mineralization: Processes and Perspectives, in H. D. Holland and K. K. Turekian, ed., Geochemistry of Mineral Deposits: Oxford, Elsevier, p. 219-249.

Wilkinson, J. J. and Hitzman, M. W., 2015, The Irish Zn-Pb Orefield: The view from 2014, in S. M. Archibald amd S. J. Piercey, ed., Current perpective on zinc deposits: Dublin, Irish Association for Economic Geology, p. 59-72.

Wilson, B., Neumann, E. R., Davies, G. R., Timmerman, M. J., Heeremans, M. and Larsen, B. T., 2004, Permo-Carboniferous Magmatism and Rifting in Europe: London, Special Publication, Geological Society of London.

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Woodcock, N. H. and Strachan, R., 2000, Geological history of Britain and Ireland: Oxford, Blackwell Science.

FIGURE CAPTIONS

Fig. 1. A: Summary geologic map of the study area outlined with a white line, showing inferred diatreme outlines (resolved by drill-core and magnetic surveys) and boreholes intersecting diatremes. Inset map of Ireland shows the location of Limerick. B: South-west to north-east cross section. C: West to east cross section (see A for locations) showing diatremes and adjacent BMBs. Dotted lines on diatremes indicate upper extent of dolomitization and subsequent hematization overprinting basal parts of diatremes. Y-axis depicts height relative to sea level.

Fig. 2. A: Summary of the mineralogy and relative importance of each stage of volcanism, dolomitization and mineralization within the studied categories. Note that Dol: dolomite, Ap: apatite, It: illite, Pyr: pyrite, Sph: sphalerite, Gal: galena, Carb: carbonate. B: Sample 6476 – Replacement of BMB (Type R) by layered pre-ore stage 2 pyrite and ore stage minerals brecciated by post-ore fine-grained pyrite. C: Sample 6508 – Replacement of limestone breccia by the same mineral assemblage seen in B. D: Sample 6470 – Polymict breccia (Type P) replaced by layered and colloform stage 2 pyrite, later replaced by ore stage spherules of sphalerite. E: Sample 6500 – Ore stage vein of sphalerite, galena and carbonate cross-cutting Waulsortian Limestone. F: Sample 6496 – Pyrite replaced by sphalerite rimming clasts in diatreme fill. G: Sample S17 – SEM image of sphalerite replacing matrix of diatreme clast. H: Country rock breccias (Type C) - Weakly mineralized with minor pyrite and Waulsortian Limestone clasts displaying embayed edges and often jigsaw or float textures (borehole TC-

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

2638-036, 223.1 mbsl). I: Polymict breccias (Type P) - diatreme clasts and matrix partially replaced by pyrite (borehole TC-2638-047, 0.6 mbsl).

Fig. 3. Histograms of sulfur isotope results (raw data available in Supplementary Table A1). A: Data categorized by environments: BMB, limestone and volcanic rock-hosted sulfides. B: BMB data categorized by type. Type R contain high concentrations of sulfides; Type P moderate concentrations, predominantly pyrite; and Type C are typically unmineralized. C: Volcanic-hosted sulfide data generalized in Figure 3A, is here categorized by host-rock (diatreme fill, intrusions or extra-crater deposits of the Knockroe Formation). D: Sulfur isotope results categorized by mineral type from all environments. For comparison, sulfur isotope data from (E) Silvermines (Boyce et al., 2003) and (F) Lisheen (Wilkinson et al., 2005b) are shown categorized by mineral type.

Fig. 4. 3D box models displaying variations in concentration of lead and zinc (ppm), showing plan sections through the model at varying depths within the northeast section of the Limerick license area. Grey lines show depths within boreholes where assay Zn and Pb concentrations have been measured (see Supplementary Table A3). The model was created by extrapolating these values in all directions. Dotted blue lines show traces of diatreme-related boreholes identified by the number above, and depth is recorded as metres below sea level (mbsl). 3D box models display lead concentrations with plan sections at 100 mbsl (A) and 350 mbsl (B) in addition to zinc concentrations with plan sections at 120 mbsl (C) and 250 mbsl (D).

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Fig. 5. Schematic summary of the relationship between diatremes, fluid flow and BMBs. A: Late-stage magmatic intrusions within the diatremes and country rock. Hydrothermal fluids utilize the diatremes, causing dolomitization during the waning stages of eruption. Fluids were channeled into the fractured country rocks forming dissolution BMBs. B: Hydrothermal metal-rich and brine-derived hydrothermal fluids utilized the porous diatreme fill. Note $\delta^{34}S$ values shown are means for each category.

Corresponding author current address: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE

Figure 1 revised

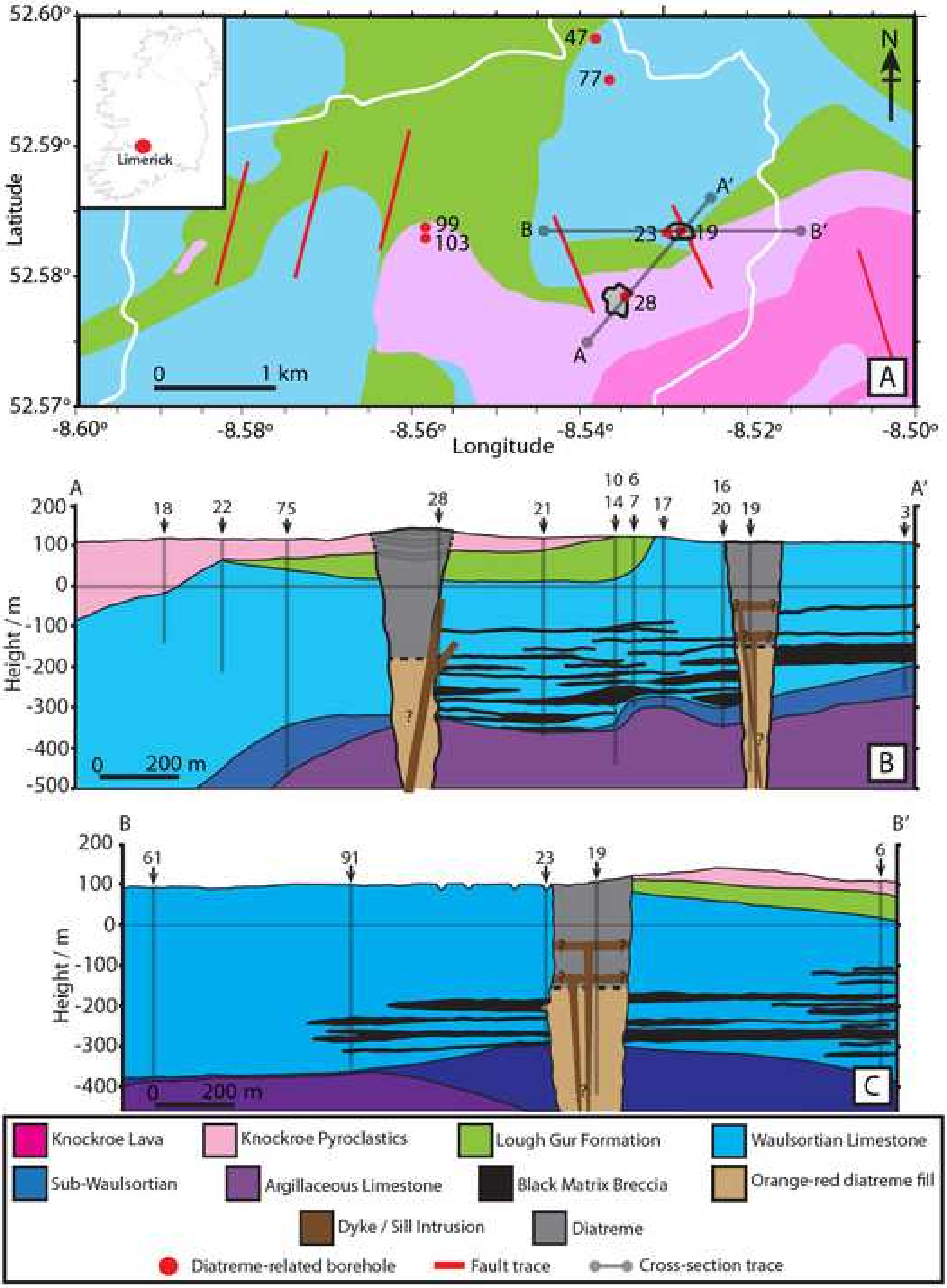
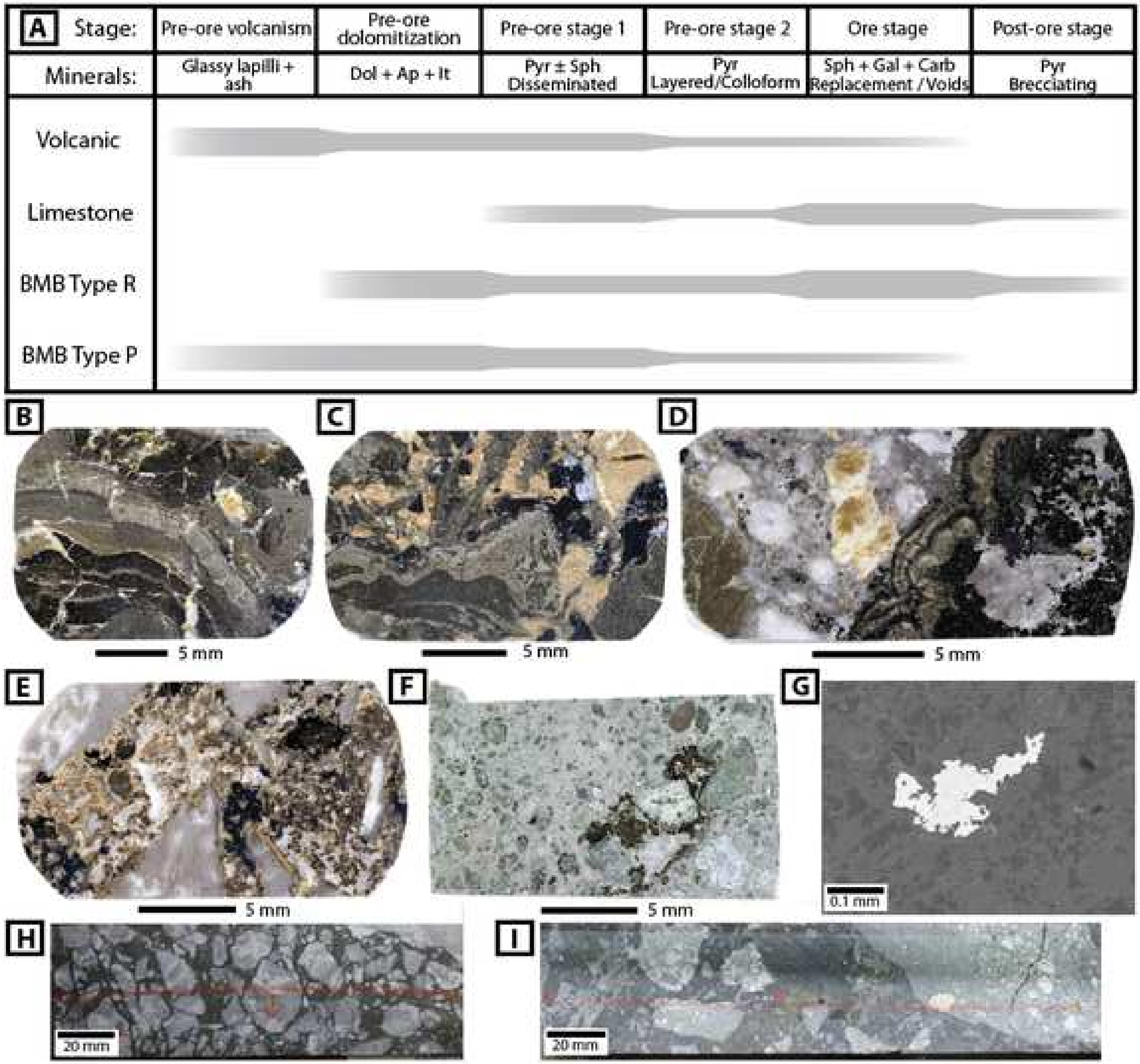


Figure 2



A
Stage:
Pre-ore volcanism
Pre-ore dolomitization
Pre-ore stage 1
Pre-ore stage 2
Ore stage
Post-ore stage
Minerals:
Glassy lapilli + ash
Dol + Ap + It
Pyr ± Sph Disseminated
Pyr Layered/Colloform
Sph + Gal + Carb Replacement / Voids
Pyr Brecciating
Volcanic
Limestone
BMB Type R
BMB Type P
B
C
D
5 mm
5 mm
5 mm
E
F
G
5 mm
5 mm
0.1 mm
H
I
20 mm
20 mm

Figure 3

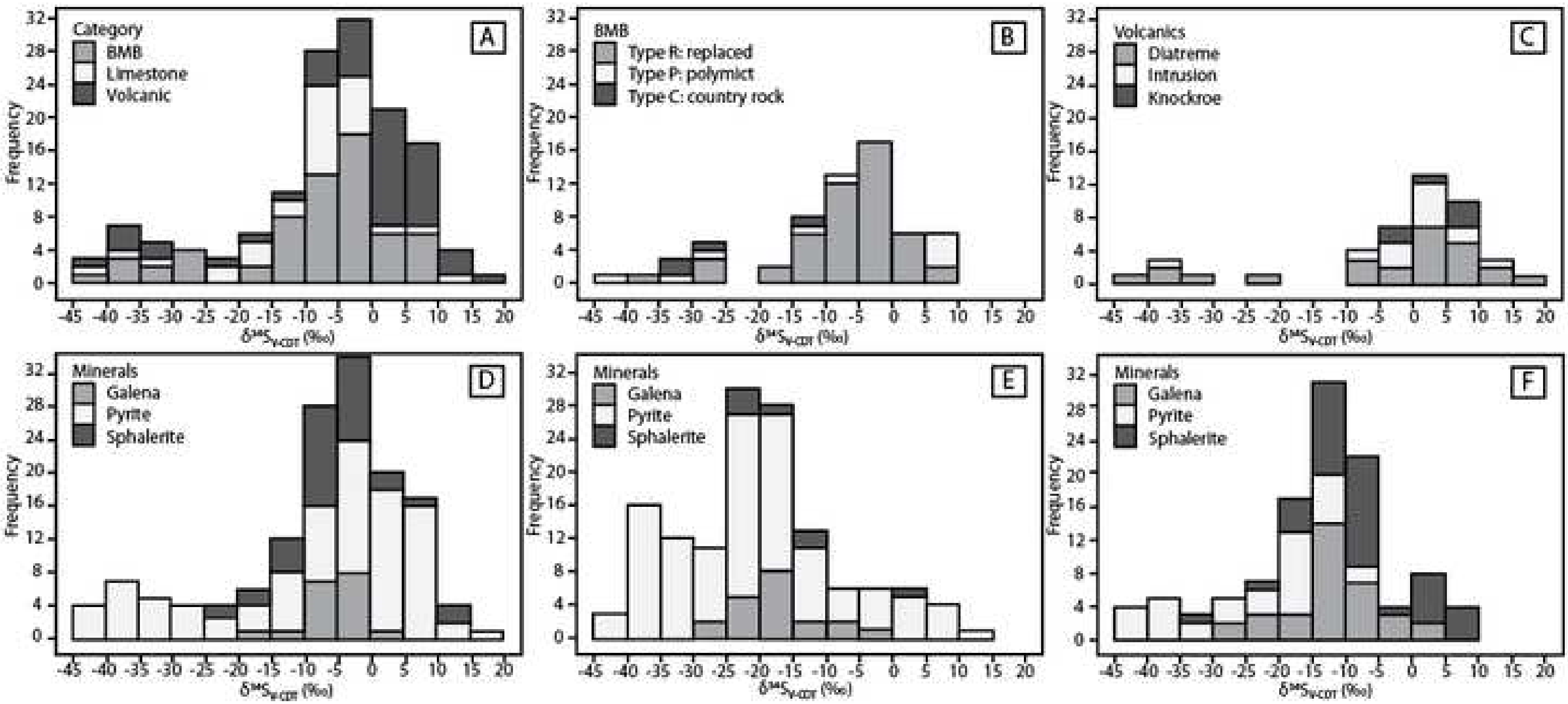

Category
BMB
Limestone
Volcanic
A
BMB
Type R: replaced
Type P: polymict
Type C: country rock
B
Volcanics
Diatreme
Intrusion
Knockroe
C
Minerals
Galena
Pyrite
Sphalerite
D
E
F
Frequency
$\delta^{34}S_{V\text{-}CDT}$ (‰)

Figure 4

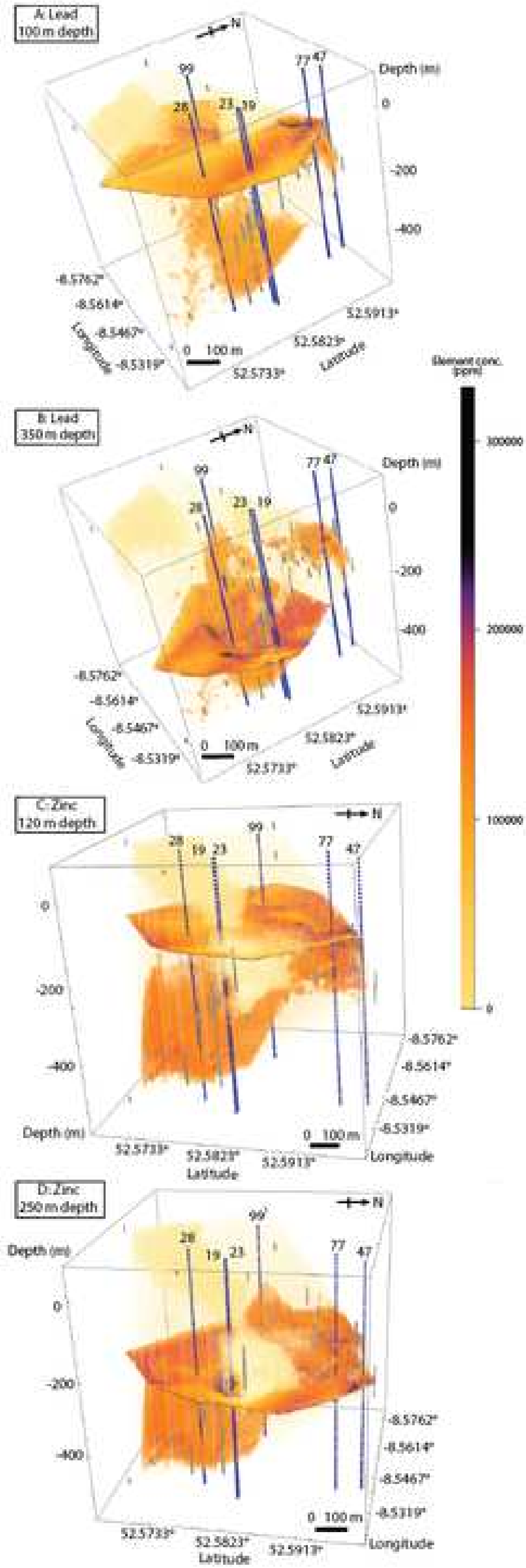

A: Lead
100 m depth
B: Lead
350 m depth
C: Zinc
120 m depth
D: Zinc
250 m depth
N
Depth (m)
0
-200
-400
99
28
23
19
77
47
-8.5762°
-8.5614°
-8.5467°
-8.5319°
Longitude
52.5733°
52.5823°
52.5913°
Latitude
0 100 m
Element conc. (ppm)
300000
200000
100000
0

Figure 5 revised