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Clumped C-O isotope temperature constraints for carbonate precipitation associated with Irish-type Zn-Pb orebodies

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Abstract. Ireland hosts the greatest concentration of discovered zinc per square kilometre on Earth, with production from 5 carbonate-hosted deposits, including the giant Navan deposit. Clumped C-O isotope analyses of carbonates offer a powerful new technique to directly deliver accurate fluid temperatures and precise calculations of fluid O isotope compositions, offering a significant opportunity to refine the evolving genetic models, and develop new vectoring tools for exploration. We present the first clumped C-O isotope results for paragenetically-constrained carbonate generations from a number of Irish-type Zn-Pb deposits. Preliminary analysis of hanging-wall white matrix breccias from Lisheen show non-systematic temperature variation (~100 to 170˚C), with fluid $\delta^{18}O_{V\text{-}SMOW}$ increasing with temperature. Significant variations in temperature at the thin section scale may be indicative of fluid mixing and/or multiple phases of WMB dolomite brecciation. Post-ore pink dolomite at Lisheen, and crosscutting calcite veins formed at significantly lower temperatures (67 to 42˚C). Temperatures of 61 to 110˚C were obtained for sphalerite-bearing calcite veins in the hanging-wall of the Randalstown Fault near Navan. These veins contain coarse sphalerite interpreted to have been remobilised from the nearby Navan orebody by a single, cool fluid (Marks, 2015). Clumped C-O data will also be presented for samples from Galmoy, Kilbricken and Castlegard ("Pallas Green"), from which existing fluid inclusion constraints are available.

1 Irish-type Zn-Pb deposits

Irish-type Zn-Pb deposits are the mainstay of the Irish mining industry. In the last fifty years, five orebodies have been mined (Tynagh, Silvermines, Navan, Galmoy and Lisheen) and over twenty prospects discovered (e.g. Kilbricken, Pallas Green) (Fig. 1). With the closure of the Lisheen mine in late 2015 there is now a sense of urgency to establish robust vectors to Zn-Pb mineralization.

There is now a consensus that Irish-type Zn-Pb deposits are syn-diagenetic ores formed by the replacement of Lower Carboniferous limestones during shallow burial. Conditions required for their formation include dense networks of normal faults that allowed ascending, warm, metal-bearing fluids equilibrated with Lower Palaeozoic basement to mix with sinking, cooler, hypersaline brines that carried bacteriogenically reduced sulphide of ultimate seawater origin (Wilkinson and Hitzman 2015).

2 Clumped C-O isotope analysis

It is well established that temperature-dependent mineral-fluid C and O isotope fractionations occur when carbonates crystallize from aqueous fluids. Mineral C-O isotope compositions are therefore controlled by crystallization temperature and the isotopic composition of the fluid, as well as the speciation of carbon and oxygen. However, the heavy isotopes of these two elements (^{13}C,^{18}O) are now known to bond in carbonate minerals measurably more frequently than expected by stochastic (i.e. random) distribution (Huntington et al. 2011).

Clumped C-O isotope analysis relies on the degree of ordering of rare ^{13}C and ^{18}O isotopes in the carbonate mineral lattice. This degree of "clumping" is an inverse function of temperature, with an increasingly random distribution at higher temperatures (Huntington et al. 2011). Although the technique has been traditionally applied to low-temperature Earth systems (i.e. to obtain accurate paleo-temperature constraints from ice-cores, soil, bones and teeth), it is rapidly moving into higher temperature fields of Earth Science.

One of the most useful aspects of the clumped isotope technique is that in addition to providing temperature constraints for carbonate crystallization, $\delta^{13}C$ and $\delta^{18}O$ may be simultaneously determined. Fluid $\delta^{18}O$ may be calculated, because temperature is known, rather than modelled, elucidating processes responsible for mineralization (Dennis et al. in press).

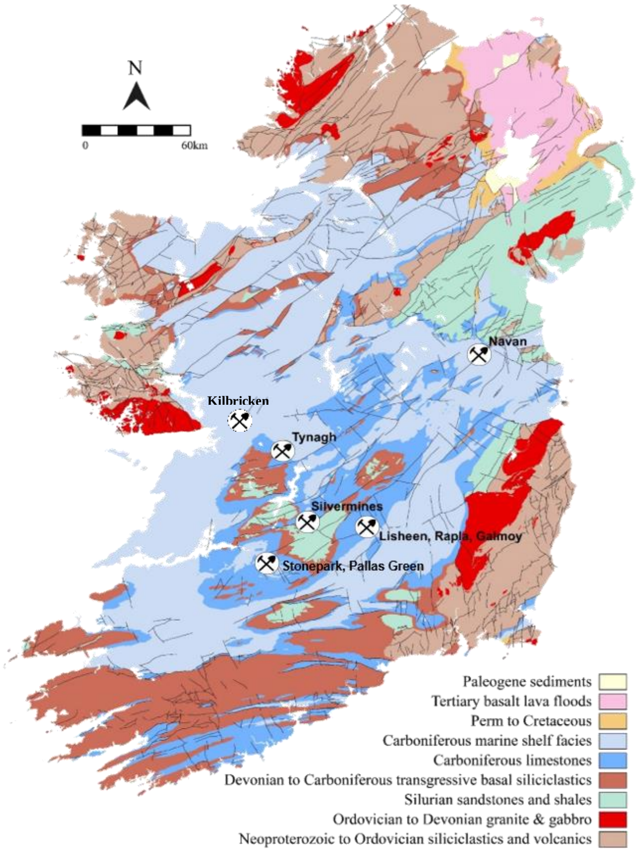

Figure 1. A simplified geological map of Ireland showing significant mined Zn-Pb deposits in Ireland and the Pallas Green and Kilbricken prospects.

3 Methods

Approximately 110 samples were obtained from drillcore across the Lisheen Zn-Pb deposit, including the Lisduff Oolite Member, and Waulsortian-hosted Main Zone, Derryville and Island Pod orebodies (Fig. 2). These samples were examined in thin section to identify carbonate generations according to the paragenesis of Wilkinson et al. (2005). Carbonate powders were obtained from thin section-matched billets using a hand held drill.

Samples of sphalerite-bearing carbonate veins from the hanging-wall of the Randalstown Fault, to the west of the Navan deposit, were also analysed. These samples were previously characterised by Marks (2015). Additional carbonate powders from Galmoy, Kilbricken and Castlegarde ("Pallas Green") (Fig. 1) were sampled from doubly polished wafers, previously characterised for fluid inclusion analysis (e.g. Eyre 1998; Wilkinson 2010, unpublished). Material sampled from fluid inclusion wafers was picked and crushed using an agate mortar and pestle.

Carbon dioxide was produced by reacting ~4 mg of carbonate powder with 102% orthophosphoric acid in vacuo at 25˚C for a period of 12 hours for calcite and 5 days for dolomite. The evolved CO_2 was collected by cryo-distillation according to the methodology of Dennis et al. (in press). Potential hydrocarbon and chlorocarbon contaminations were stripped using porapak Q ion exchange resin at -20˚C.

Sample gases were analysed for their isotope values, δ^{45} - δ^{49} on a custom-built MIRA (multiple isotope ratio analyser) dual-inlet mass spectrometer at the University of East Anglia (UEA), with analytical conditions as in Dennis et al. (in press). Details for calculating Δ47 are provided in Huntington et al. (2011). Temperatures are calibrated using natural and synthetic biogenic and inorganic calcites using the following in house equation (Dennis et al. in press):

$$\Delta 47 = ([0.0389 \times 10^{6}]/T^{2}) + 0.2139,$$

where T is in Kelvin.

External precision for sample analysis is estimated as ± 0.014 ‰, with temperature errors corresponding to ± 2˚C at Earth surface temperatures, rising to ± 12˚C at 200˚C. Sample contamination is monitored through Δ48 and Δ49 (Dennis et al. in press). Fluid $\delta^{18}O_{V\text{-}SMOW}$ values were calculated according to Kim and O'Neill (1996) for calcite, and Horita (2014) for dolomite.

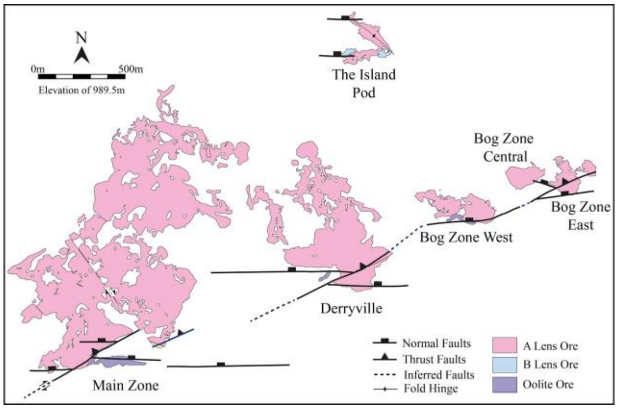

Figure 2. Orebodies and main structural elements of the Lisheen Zn-Pb deposit (modified after Kyne et al. 2017).

4 Preliminary results and conclusions

All data referred to in this section are plotted on Figure 3.
Navan:

- Temperatures of 61 to 110˚C (n=4; mean 92 ˚C) were obtained for sphalerite-bearing calcite veins in the hanging-wall of the Randalstown Fault near Navan. These veins contain coarse sphalerite interpreted to have been remobilised from the nearby orebody by a single, cool fluid (Marks, 2015).
- Calcite $\delta^{18}O_{V\text{-}SMOW}$ for these samples varies from +16 to +21 and calculated fluid $\delta^{18}O_{V\text{-}SMOW}$ ranges from -4.6 to +6.0 (mean 0.3) with higher values associated with higher temperature.
- One sample yielded a Δ_{47} temperature of 89˚C,

consistent with existing fluid inclusion constraints (81˚C mean, range 68-92˚C: Marks, 2015). This highlights the potential of the clumped technique to reproduce temperatures obtained by conventional fluid inclusion analysis. Fluid inclusions from other samples will be analysed in coming months.

Lisheen:

- Samples of coarse white dolomite, drilled from white matrix breccias (WMBs) of the high-grade Island Pod orebody (Doran et al. 2017 – this volume), yielded $\delta^{13}C_{V\text{-}PDB}$ (+2.6 to +3.3) and $\delta^{18}O_{V\text{-}SMOW}$ (+21.2 to +24.4) values similar to the rest of the deposit (i.e. Main Zone, Derryville, Bog Zone).
- The coarse white dolomites from Island Pod WMBs also have similar $\delta^{13}C$ and $\delta^{18}O$ isotopic compositions to clasts of regional dolomite from the same samples, and regional dolomite elsewhere in the deposit, similar to results reported by Wilkinson (2003). This suggests that the WMB dolomite may have been buffered by early regional dolomite or was precipitated from a fluid with similar $\delta^{18}O$, heated to ~180˚C (see below).
- Temperatures of 98 to 172˚C were obtained for the Island Pod WMB dolomites. The samples were all collected from one drillhole (from directly above mineralization to ~80 m in the hanging-wall). There is no systematic variation in temperature, or carbonate δ13C or $\delta^{18}O$ towards mineralization in the preliminary dataset.
- Calculated fluid $\delta^{18}O_{V\text{-}SMOW}$ values for WMBs dolomites range from +0.7 to +8.6, with higher values associated with higher temperatures, as at Navan. Interestingly, the WMB samples plot on the same array as the post-ore carbonates described below. This array is consistent with fluids in isotopic equilibrium with regional dolomite, calculated from Horita (2014) over a range of temperatures and $\delta^{18}O_{dol}$ of +19.5 to +26 (data from Eyre 1998; Hitzman et al. 1998).
- Samples of black dolomite drilled from black matrix breccias (BMBs) at Lisheen also yield similar $\delta^{13}C$ and $\delta^{18}O$ isotopic compositions to clasts of regional dolomite from the same samples and across the deposit (Fig. 3).
- A temperature of 67˚C was obtained for post-ore pink dolomite from the Lisheen deposit, with a fluid $\delta^{18}O_{V\text{-}SMOW}$ value of -0.7.
- A late white calcite vein yielded a temperatures of 63˚C, with a calculated fluid $\delta^{18}O_{V\text{-}SMOW}$ value of -2.6.
- Temperatures of 42 and 43˚C were obtained for late yellow calcite (which crosscuts the late white calcite), with fluid calculated $\delta^{18}O_{V\text{-}SMOW}$ values of -3.5 to -6.2.

4 Future work

The preliminary clumped C-O isotope results presented here highlight the potential of the technique to better understand the formation of both Irish-type and MVT Zn-Pb deposits. Additional samples will be analysed in the coming months (March-May 2017). These include samples from the following deposits, for which existing fluid inclusion data are available: (1) Galmoy – white matrix breccias; (2) Kilbricken – ore stage calcite; (3) Castlegard – ore stage calcite; (4) Lisheen – regional dolomite, white matrix breccias, pink dolomite, late calcite; (5) Rathdowney Trend – regional dolomite, black matrix breccias (6) Navan – ore stage carbonates.

We will also analyse samples of black matrix breccia from across the Lisheen deposit (i.e. Lisduff oolite, Main Zone, Derryville Zone: Fig. 2) to determine whether systematic temperature or fluid $\delta^{18}O$ variations occur away from faults which helped focus hydrothermal fluids from depth.

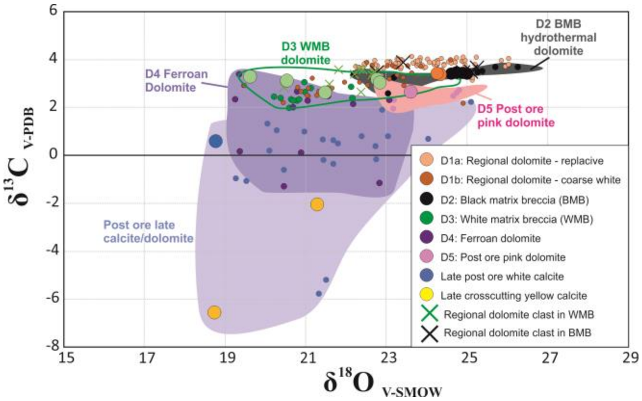

Figure 3. Compiled and new C and O isotope data from the Lisheen Zn-Pb deposit (includes data from Eyre, 1998; Hitzman et al. 1998). New data is represented by large symbols.

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References

Dennis PF, Myhill DJ, Marca A (in press) Episodic, rapid flow of fluids in a mineralized fault system in the Peak District, UK. J. Geol Soc, Lon.

Doran AL, Menuge JF, Hollis SP, Güven, Dennis PF (2017) Enhancing current understanding of Irish Zn-Pb mineralization: a closer look at the Island Pod orebody, Lisheen deposit. Abstract for SGA Québec 2017.

Eyre SL (1998) Geochemistry of dolomitization and Zn-Pb mineralization in the Rathdowney Trend, Ireland. Unpublished PhD thesis, University of London, 414p.

Hitzman MW, Allan JR, Beaty DW (1998) Regional dolomitization of the Waulsortian Limestone in southeastern Ireland: evidence of large-scale fluid flow driven by the Hercynian orogeny. Geology, 26, 547-550.

Horita J (2014) Oxygen and carbon isotope fractionation in the system dolomite-water-CO_2 to elevated temperatures. Geochim Cosmochim Acta, 129: 111-124.

Huntington KW, Budd DA, Wernicke BP, Eiler JM (2011) Use of clumped-isotope thermometry to constrain the crystallization temperature of diagenetic calcite. JSR, 81:656-669.

Kim ST, O'Neill JR (1996) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochim Cosmochim Acta, 61:3461-3475.

Kyne R, Torremans K, Doyle R, Güven J, Walsh J (2017) The role of fault segmentation and relay ramp geometries on the formation of Irish-type deposits. Joint Assembly of TSG-VMSG-BGA. January 4th-6th Liverpool, p130.

Marks FR (2015) Remote detection of Irish-type orebodies: an investigation of the Navan halo. Unpublished PhD thesis, University College Dublin.

Wilkinson JJ (2003) On diagenesis, dolomitisation and mineralisation in the Irish Zn-Pb orefield. Mineralium Deposita, 38, 968-983.

Wilkinson JJ (2010) A review of fluid inclusion constraints on mineralization in the Irish orefield and implications for the genesis of sediment-hosted Zn-Pb deposits. Econ Geol, 105: 417-442.

Wilkinson JJ, Eyre SL, Boyce AJ (2005) Ore-forming processes in Irish-type carbonate-hosted Zn-Pb deposits: evidence from mineralogy, chemistry, and isotopic composition of sulfides at the Lisheen mine. Econ Geol 100:63 - 86.

Wilkinson JJ, Hitzman MW (2015) The Irish Zn-Pb Orefield: the view from 2014. In: Current Perspectives on Zinc Deposits, conference book. IAEG, Dublin, pp 59 – 72.