A Review of Fluid Inclusion Constraints on Mineralization in the Irish Orefield and Implications for the Genesis of Sediment-Hosted Zn-Pb deposits

J.J. Wilkinson

CODES, University of Tasmania, Private Bag 126, Hobart, Tasmania 7001, Australia

and

Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, Exhibition Road, London SW7 2AZ, UK

Abstract

Many fluid inclusion studies have been carried out in the Irish Midlands Basin orefield (Lower Carboniferous) since the earliest work by Ed Roedder in the late 1960s. Results show that, in the ore deposits, the total range in fluid salinity is 4-28 wt% NaCl equivalent but with the majority falling in the moderate salinity range between 8-19 wt%. This variability is interpreted in terms of mixing between moderate salinity ore fluids and low temperature brines during ore formation. The most northerly ore deposits of Navan and Abbeytown are distinct in containing fluids of both lower and higher salinity than is typical of the Waulsortian-hosted deposits further south (Tynagh, Silvermines, Lisheen and Galmoy). Subeconomic prospects tend to display a narrower range in salinity, mostly at the lower end of the range observed in the ore deposits. In some prospects, and on the margins of some ore deposits, evidence for dilution is observed, interpreted to reflect mixing between hydrothermal fluids and unmodified seawater. This process is inferred to be unfavorable for mineralization.

Homogenization temperatures, a reasonable proxy for true trapping temperatures in the orefield, range from 70-280 °C but with the majority falling between 130-240 °C. There is no evidence for systematic stretching or leakage of inclusions related to the post-entrapment heating implied by elevated thermal maturity indicators. The highest temperatures are observed in the Waulsortian-hosted systems, with peak temperatures of ~280 °C supported by local, high grade Cu and Ni mineralization. In the Navan and Abbeytown deposits, lower temperature fluids appear to have been more prevalent. The subeconomic prospects formed over essentially the same temperature range as

the ore deposits (90-270 °C), with the exception of the morphologically and texturally distinct MVT systems in the region (e.g., Kinnitty, Harberton Bridge) that formed at lower temperatures (50-100 °C).

Similar hydrothermal fluids to those recorded in both deposits and prospects are widely observed in dolomite (and sometimes calcite) cements within Courceyan-Arundian age rocks indicating hydrothermal fluid activity occurred over an extremely large area (>30,000 km^2) and probably over an extended time period. There is a broad regional division in fluid properties suggesting that the northwestern and southeastern provinces, separated by the trace of the Iapetus suture zone, may represent partly decoupled, large-scale flow regimes. Up to three, low temperature brine types are also recorded by cements in the host rock sequence, indicating a complex range of evaporation and fluid-rock interaction processes were ongoing in the shallow basin succession during the period of hydrothermal activity.

Halogen data show that fluids involved in mineralization were originally seawater-derived brines, produced by evaporation to varying degrees. Relatively high temperature, basement-interacted hydrothermal fluids were derived from partially evaporated seawater (molar Cl/Br = 559-825). Their compositions can be explained by dolomitization in the Carboniferous succession prior to circulation to depth; alkali exchange, reduction and metal-leaching from the Lower Paleozoic basement; and mixing with low temperature brines that locally penetrated the upper parts of the basement rock package. Fertile ore fluids appear to be characterized by higher $\delta^{18}O$ (+7 to +9 ‰), lower δD (-25 to -45 ‰) and much higher metal contents than otherwise similar fluids sampled in basement-hosted feeder veins distal to deposits. This may reflect highly efficient metal scavenging in deeper/higher temperature reaction zones that underlie the principal deposits. In the ore deposits, these fluids mixed with Br-enriched bittern brines (Cl/Br ~290) produced by evaporation of Carboniferous seawater past halite saturation. It is inferred that bittern brine generation occurred in the shallow marine shelf regions in the footwalls to the synsedimentary fault systems that controlled the localization of mineralization. These brines then migrated into hangingwall depressions where they ponded within permeable sediments and became enriched in H_2S via bacteriogenic sulfate reduction. The coincidence of structurally-controlled, high temperature reaction zones, brine-producing footwalls, and hangingwall traps, with bacterial blooms above upwelling plumes of hydrothermal fluids, can be interpreted as a self-organizing system that locally converged on ore-forming conditions. Understanding the first-order structural control of the ore systems will therefore be critical for predicting new deposits.

The Irish orefield presents arguably the best database available on the thermal and chemical characteristics of hydrothermal fluids involved in sediment-hosted ore genesis. The system shares much of the variety and complexity observed in other intracratonic basin-hosted Zn-Pb(-Ba) ore

districts. This includes the coexistence of contrasting styles of mineralization that are typically observed in the more distal and platform-marginal parts of the basinal environment. The thermal and chemical fluid heterogeneity observed is typical of modern intracratonic basin systems and should be expected in large paleohydrothermal systems where recharge of surface-derived fluids is involved.

Introduction

The Carboniferous Irish Midlands Basin hosts a remarkable concentration of base metals (~17 MT known) in a prospective area of approximately 200x150 km. In addition to the known prospects, operating mines at Navan, Lisheen and Galmoy, and the historical mines at Tynagh, Silvermines and Abbeytown, anomalous concentrations of Zn and Pb are common in the lower part of the Waulsortian Limestone Formation and pervasive in the Navan Group – the primary host rock sequences (Blakeman, pers. comm.). Such extensive mineralization implies the operation of a giant hydrothermal system of significant academic as well as economic interest. Indeed, the orefield has been important in a number of debates on the classification of sediment-hosted deposits and the nature of the hydrothermal systems that form them (Russell, 1978; Russell et al., 1981; Hitzman and Large, 1986; Lydon, 1986; Hitzman and Beaty, 1996; Everett et al., 2003; Wilkinson, 2003; Leach et al., 2005; Wilkinson et al., 2005a).

The purpose of this paper is to provide a historical review of fluid inclusion studies carried out in the Irish orefield, including investigations of individual mineralized systems (deposits and prospects) as well as regional studies in the host rock stratigraphy and underlying basement. The contribution of these data to the development of genetic models for mineralization is highlighted. Previously unpublished data are also presented that, in combination with the published results, provide an extensive dataset that constrains the nature of the fluid regimes operating in the region prior to, during, and subsequent to the main stages of ore formation. How these data impact on our understanding of the Irish paleohydrothermal system and the wider implications for models of sediment-hosted ore formation are considered.

Geological Setting and Mineralization

A thorough description of the geology and mineralization in Ireland is beyond the scope of this contribution and only a brief summary is presented here. For more detail and thorough reviews the reader is referred to Andrew et al. (1986), Hitzman and Large (1986), Phillips and Sevastopulo (1986),

Bowden et al. (1992), Andrew (1993), Anderson et al. (1995), Hitzman (1995), Hitzman and Beaty (1996), and Kelly et al. (2003).

Zinc-lead mineralization in the Irish Midlands is hosted by Lower Carboniferous (Dinantian) carbonate rocks (Fig. 1), within both the Waulsortian Limestone Formation and the Navan Group – the first major non-argillaceous carbonate units in a transgressive marine sequence. Beneath these rocks lie red, terrestrial mudstones, sandstones and conglomerates (Old Red Sandstone, ORS) that in turn unconformably overlie an eroded Lower Paleozoic volcanosedimentary succession that was deformed and underwent low grade metamorphism in the Caledonian Orogeny. A crystalline basement is inferred at depth in the Midlands area (Strogen, 1974; Kennan et al., 1979) and likely comprises Grenvillian gneiss and schist to the northwest and late Precambrian, probably Avalonian, gneissic rocks to the southeast (Watson, 1978; Phillips and Sevastopulo, 1986).

The Waulsortian Limestone Formation developed in a ramp environment in the Courceyan as biomicrite mounds surrounded by argillaceous bioclastic limestones (ABL) at moderate water depths of up to several hundred meters. Waulsortian banks dominate in the south and west Midlands, where they coalesced to form thicknesses in excess of 750 m (Andrew, 1993) in the Shannon Trough (Fig. 1). The Navan Group, of similar age, comprises near-shore, shallow marine, largely high-energy deposits, including oolitic and bioclastic grainstones, birdseye micrites and minor sandstones (Philcox, 1984). These were deposited in the northern Midlands on the southern margin of the Laurasian landmass, now marked by the Longford Down inlier (Fig. 1).

The host rocks underwent early diagenesis that included extensive calcite cementation and dolomitization (Lees and Miller, 1995; Rizzi and Braithwaite, 1997; Gregg et al., 2001; Lee and Wilkinson, 2002; Wilkinson, 2003; Nagy et al., 2004). It is widely considered that these processes were initated upon deposition of the carbonate sediments, with significant cementation occurring within a few tens of meters of the seafloor (cf. Dix and Edwards, 1996). Early dolomitization is pervasive in the southeastern Midlands, fringing the Leinster Massif (Phillips and Sevastopulo, 1986; Hitzman and Beaty, 1996; Gregg et al., 2001; Nagy et al., 2004), but is also widely developed elsewhere (Gregg et al., 2001). Sulfides appear to generally postdate early dolomite cements and are themselves accompanied by a variety of replacive, breccia-cementing and vein- and vug-filling calcite and dolomite, plus variable barite and minor quartz (Fig. 2).

Mineralization in the ore deposits principally occurs as massive sulfide displaying a complex range of textures (Boast et al., 1981; Taylor, 1984; Ashton et al., 1986; Anderson et al., 1998; Hitzman et al., 2002; Fusciardi et al., 2003; Lowther et al., 2003; Wilkinson et al., 2005b). In sub-economic mineralization, a variety of massive, disseminated, breccia- and vein-filling styles occur (e.g. Holdstock, 1982; Emo, 1986; Grennan, 1986; Trude and Wilkinson, 2001). Abundant ore minerals are sphalerite, galena and pyrite, with lesser but variable marcasite and minor chalcopyrite, tennantite

and other sulfosalts. Orebodies are broadly stratiform but in most cases have been shown to be strictly stratabound and occur as single or multiple lenses hosted by favorable horizons within the hostrock packages. For the deposits of Lisheen and Galmoy, this is a breccia unit of variable thickness, located close to the base of the Waulsortian Limestone.

The Reliability of Fluid Inclusion Data

A fundamental assumption in fluid inclusion studies is that inclusions have maintained their integrity since their time of formation (Roedder, 1984). In the Irish Midlands, the validity of fluid inclusion data has been questioned by some authors (Hitzman, 1995; Hitzman and Beaty, 1996; Peace, 1999; Reed and Wallace, 2001) because vitrinite reflectance and conodont color analyses suggest that the Carboniferous rocks have been subject to late Carboniferous heating (Clayton et al., 1989). The highest maturation values are observed in the Munster Basin in southern Ireland where Variscan deformation and metamorphism have occurred. However, high values extend into the southeast and west Midlands where, taken at face value, vitrinite reflectance values (R_m >4%) imply peak temperatures in excess of 300 °C and conodont alteration indices (CAI) of 5-7 imply temperatures of 300 to >550 °C. Any re-equilibration toward lower density (greater inclusion volume) by plastic stretching, or partial leakage of inclusions, as a result of overheating would result in anomalously high homogenization temperature (T_h) values and an overestimate of ore fluid temperatures. Thus, although no textural evidence for inclusion re-equilibration (e.g. Bodnar, 2003a) has been described from the Irish Midlands, it is nonetheless important to consider this issue before discussing the data in detail.

Laboratory studies have shown that the potential for inclusion re-equilibration during overheating is largely a function of inclusion size and host mineral strength (e.g. Bodnar and Bethke, 1984; Burruss, 1987; Bodnar et al., 1989). Consequently, a plot of inclusion size against T_h should show a positive correlation if partial re-equilibration has occurred and this effect would be more pronounced for softer minerals in which inclusions can deform under lower internal overpressures (e.g. calcite, barite). In addition, modification is more likely to affect some inclusions in a given inclusion assemblage than others due to variations in size, shape, or proximity to defects. This would result in variable T_h data within individual inclusion populations and the elimination of systematic differences between different growth stages of a single mineral grain, or between different paragenetic stages.

The first application of a size/T_h test for different host minerals was presented by Everett et al. (1999a) for data from Lower Paleozoic-hosted veins. These data are supplemented here and compared with results from regional carbonates and deposits (Fig. 3A). For all datasets (with the possible exception of deposit barite), no positive correlation is apparent for any mineral host.

Sphalerite and quartz are the strongest host minerals and therefore might be expected to preserve a putative lower temperature population, especially in smaller inclusions. In fact, the opposite is observed, with these minerals generally hosting higher T_h inclusions. The broad T_h differences between the minerals (quartz>calcite>dolomite>pink dolomite) and the notable bimodality in sphalerite values cannot be easily explained by re-equilibration and are likely to reflect features of genetic significance, principally differences in precipitation temperature.

A similar plot for regional Lower Carboniferous carbonates (Fig. 3B) again shows no size-T_h correlation, appears to show a bimodality in dolomite data, and illustrates low T_h values in the weakest mineral, calcite.

For the deposit data, sphalerite T_h values are the highest, followed by dolomite and then calcite – the opposite of what might be expected for stretching populations. At some of the prospects (e.g. Harberton Bridge; Trude and Wilkinson, 2001) calcite hosts monophase inclusions that could not have been preserved if post-entrapment temperatures had exceeded 300 °C. Barite also contains monophase inclusions at some localities (e.g. Silvermines; Samson and Russell, 1987) that would be impossible to preserve during such overheating. However, variable degrees of filling are commonly observed in barite and a weak positive correlation between size and T_h is observed in the deposit data (Fig. 3C) suggesting leakage (during post-entrapment burial or laboratory analysis) is a problem for this mineral. Consequently, T_h data (but not necessarily compositional information) from barite are treated as generally unreliable (cf. Bodnar and Bethke, 1984; Ulrich and Bodnar, 1988).

The last, and perhaps most convincing, evidence for preservation of inclusion integrity is the petrography which demonstrates that individual inclusion populations (such as within a single dolomite growth zone) typically display a relatively narrow range of T_h values that is much less than within a sample as a whole, or between samples. Furthermore, systematic variations in microthermometric data can be observed that relate to changes in fluid properties during crystal growth (Fig. 4). These features would not be preserved if post-entrapment re-equilibration was widespread.

The contradiction between Devonian and Carboniferous maturation data and Lower Carboniferous fluid inclusion data is problematic. Although higher temperatures are plausible in the Munster Basin to the south, where the rocks have been subjected to Variscan thrusting and have developed a cleavage, it is difficult to credit rock temperatures of up to 550 °C in the Midlands Basin, (except immediately adjacent to minor intrusions) given the lack of evidence for recrystallization at such high temperatures, lack of mineralogical indicators, and perfect preservation of delicate fossils and low-temperature diagenetic fabrics. Consequently, it has been suggested that CAI and R_m values recorded in the Midlands do not reflect true maximum temperatures (Everett, 1999; Wilkinson et al., 2003). The reason for this is uncertain, although it is most likely due to hydrothermal overprinting

(e.g. Rejebian et al. 1987) by the unusually extensive flow that has affected much of the stratigraphy in the Midlands area, and which may have been active over a long period of time (e.g. Hitzman, 1995; Wright et al. 2000; Gregg et al. 2001; Wilkinson, 2003).

The modification of CAI values by fluids is suggested by a number of features of the dataset presented by Clayton et al. (1989). In particular, reddened limestones, commonly inferred to be related to hydrothermal activity (Hitzman et al., 1995), display elevated CAI values of 6-7 compared with values of 5-5.5 in normal limestones from the same drillhole or nearby (e.g. Meelin No.1 borehole, Co. Cork; Rocky Island, Co. Cork; Fig. 1). Also, dolomitized intervals can display higher CAI than undolomitized intervals in the same drillhole (e.g. Ballyragget No. 1 borehole, Co. Kilkenny) and there is often a variation of up to 1 CAI in single samples. Local vertical reversals in thermal gradients down boreholes also suggest a complex thermal regime probably involving advective heating (Goodhue and Clayton, 1999). This conclusion is supported by Jones (1992) who noted that CAI values in Ireland are influenced by proximity to major mineral deposits and follow Caledonoid trends, these structures also being implicated as the major infrabasinal flow conduits. Numerical modeling has shown that anomalous organic maturity can be accounted for by free thermal convection in the continental crust beneath intracratonic basins (Nunn, 1994). Consequently, the weight of evidence supports widespread preservation of fluid inclusion integrity in the Midlands area and therefore in the discussion below T_h values are considered reliable except where standard petrographic evidence indicates otherwise.

Historical Review of Fluid Inclusion Studies

Fluid inclusion studies in the Irish orefield have played an important part in the development of genetic models and the debate surrounding the timing and depth of mineralization. Opposing views can be distilled down to purely epigenetic models invoking largely lateral fluid flow and replacement/ cavity-filling mineralization at depth, during burial, from fluids close to thermal equilibrium with their host rocks (Hitzman and Beaty, 1996; Reed and Wallace, 2001; Peace et al., 2003); and SEDEX models, in which near-seafloor and underlying epigenetic mineralization occurred during diagenesis of the host rocks from elevated temperature fluids in the updrafts of a convective flow system (Boyce et al., 1983; Russell, 1978, 1986). The more recent evidence that much mineralization probably formed by host rock replacement in the shallow sub-seafloor environment (Anderson et al., 1998; Blakeman et al., 2002; Lee and Wilkinson, 2002; Wilkinson et al., 2003, 2005a, 2005b) and a relaxed definition of the term “SEDEX” (Leach et al., 2005) means that the deposits can be classified as carbonate-replacement SEDEX type.

In the following review, only fluid inclusions interpreted to be of primary (or pseudosecondary) origin and constrained paragenetically to be associated with the principal mineralizing stages are considered, except where otherwise stated. In the summary of fluid properties (Table 1), the modes and ranges given are considered to be the best reliable estimates based on published information; these may omit outlying data which are noted and, in some cases, have necessitated a degree of interpretation of results that may be equivocal. Most of the results discussed are salinity data inferred from final ice melting (as the last solid phase), or in some cases hydrate melting temperatures ($T_m$hyd), together with T_h values which, in the Irish system, can be considered to be a reasonable proxy for trapping temperatures (e.g. Wilkinson and Earls, 2000). Additional chemical or isotopic data acquired from fluid inclusion analyses are also discussed.

Ore Deposits

It is appropriate for this volume that the history of fluid inclusion research in Ireland was started by Ed Roedder himself in the late 1960s. The earliest data reported, obtained on sphalerite from the Keel deposit (Fig. 1), are attributed variously in the literature but were in fact acquired by Ed Roedder (unpublished USGS memorandum to T.B. Nolan, 1968), listed in Roedder (1976), on samples collected by Nolan on a visit to the deposit. Patterson (1970) cites these data and quotes from Roedder's report:

"*The samples had clear euhedral, yellow to brown, unzoned sphalerite crystals up to 8 mm as a crust on [Lower Paleozoic] quartzite. These sphalerite crystals contained reasonably good primary and pseudo secondary fluid inclusions yielding the following data: (no distinction in the measurements could be made between the two types of inclusions):*

Freezing temperatures:	*10 inclusions all between -7.35 ± 0.5 and -8.0 ± 0.2 °C*
	1 inclusion -6.0 ± 0.1 °C
Filling [homogenization] temperature:	*3 inclusions 176 ± 5 °C*
	5 inclusions 185 ± 3 °C

Thus <u>this sample</u> (if not the whole deposit), formed from rather hot brines, with a salinity in the range of 11-12 per cent salts in solution."

These were the first data to shed light on the nature of the fluids responsible for formation of the Irish deposits and suggested that they formed at higher temperatures and from lower salinity fluids than those typical of carbonate-hosted deposits of Mississippi Valley-type (MVT).

279 Early results were also reported by Greig et al. (1971) from Silvermines. Only three datapoints
280 (possibly averages of individual samples) were presented on a plot of T_h vs. distance from the
281 Silvermines fault zone; these indicated T_h values of 190-280 °C for inclusions hosted by quartz,
282 sphalerite and barite. Further reconnaissance results were presented by Probert (1983; cited in
283 Andrew, 1993) from locations in the northern Midlands including the Navan deposit and the Keel,
284 Moyvoughly and Tatestown prospects (Fig. 1). The absence of paragenetic or spatial control makes
285 interpretation of these results risky, but some comparisons with subsequent studies can be made
286 (Table 1). More recent and carefully-constrained results from Navan (this study) do not replicate
287 these early measurements although it should be noted that the high grade core of the deposit was
288 mined out in the 1980s-1990s.
289 *Silvermines:* The first detailed fluid inclusion study was carried out principally on the lower
290 (epigenetic) orebodies and Old Red Sandstone-hosted footwall veins from the Silvermines deposit
291 (Samson, 1983; Samson and Russell, 1983). Homogenization temperature and salinity data (modelled
292 in the NaCl-H_2O system) were reported from inferred primary and pseudosecondary liquid-vapor
293 fluid inclusions in quartz, sphalerite, calcite and dolomite, and salinity data from the predominantly
294 monophase liquid inclusions in barite. Extended results, including the addition of the first bulk
295 analytical (crush-leach) chemical and isotopic (decrepitation, crushing) data and the observation and
296 identification of trapped phases (calcite) in some inclusions were presented in a comprehensive,
297 benchmark study by Samson and Russell (1987).
298 Wide ranges in microthermometric properties were observed (Table 1) and the occurrence of
299 some vapor-rich inclusions in quartz was taken as evidence for episodic boiling; similar inclusions in
300 carbonate and barite were discounted. Since then, vapor-rich inclusions have not been reported
301 from the orefield (apart from in one Lower Paleozoic basement-hosted vein sample; Everett et al.,
302 1999a) so it is likely that boiling was not a common process in the district (Wilkinson et al., 2003). A
303 broad negative correlation between T_h and salinity was interpreted as the first direct evidence for
304 fluid mixing in the Irish deposits, previously suggested based on sulfur isotope data and the chemical
305 conditions of sulfide deposition (Boast et al., 1981). An important detail within this correlation is that
306 samples from different geographic locations and paleodepths within the system tend to fall in
307 different parts of the array, consistent with a relatively stable mixing zone between higher
308 temperature, less saline fluids at depth (and possibly also on the fringes of the system) and more
309 saline, cooler fluids higher up and in the center, proximal to the main ore zones.
310 *Tynagh:* Tynagh, the first Zn-Pb deposit to be discovered in the Lower Carboniferous of the
311 Midlands Basin, was the subject of a fluid inclusion study by Banks and Russell (1992). Primary and
312 secondary inclusion data were reported from limestone-hosted vein sphalerite from epigenetic
313 mineralization in Zones 2 and 3, the principal ore zones in the deposit (Boast et al., 1981), together

with results from barite (monophase liquid inclusions predominant) and quartz (Table 1). Quartz-hosted inclusions were measured both from rare, euhedral quartz replacing carbonates in the ore zones and in quartz overgrowths in the ORS within 1 m of the Tynagh Fault in the deposit footwall. Although there is some ambiguity in the timing of these overgrowths, the inclusions were interpreted as relating to the main stages of ore formation.

As with Silvermines, a negative correlation was observed between T_h and salinity in the inferred ore-stage fluids, interpreted in terms of fluid mixing. The principal spread in salinities occurs in the footwall quartz overgrowths and in barite implying that these either formed during mixing, and/or were overprinted by fluids undergoing mixing. By contrast, and similar to Silvermines, the sphalerite data show little spread in salinity suggesting precipitation under somewhat different conditions. Data from quartz within the ores were not fully reported.

Banks and Russell (1992) also presented data from "post-ore" calcites that hosted four inclusion types. Because the paragenesis of the samples and the petrography of the inclusions within them are not described it is difficult to interpret these results. However, their Group 1 fluid inclusions (T_h 109-196 °C; salinity 5.1-10.2 wt% NaCl equivalent; $T_m$hyd -24.9 to -22.4 °C) coincide with the data reported by Probert (1983), as well as ore-stage fluids elsewhere (Table 1), and are therefore considered likely to be related to mineralization, although this was discounted by the authors. Some of the calcite samples were associated with a dolomite-chalcopyrite assemblage typical of the post-ore pink dolomite and later calcite widely developed in the Midlands Basin (the D_5 and C_6 of Wilkinson et al., 2005b; Fig. 2). This "copper dolomite" event is interpreted to represent a basin-wide brine migration, probably related to the onset, or relaxation, of Variscan compression (Andrew, 1993; Wilkinson, 2003; Wilkinson et al., 2005b). The Group 3 inclusions of Banks and Russell (1992) are potentially associated with this stage based on similarities with microthermometric data from pink dolomite elsewhere (e.g. Eyre, 1998; Wilkinson, 2003). The Group 4 inclusions contained low salinity fluids and displayed anomalous hydrate melting behavior, with hydrate and ice coexisting above -20.8 °C, interpreted in terms of sulfate or bicarbonate presence. These are comparable to the dilute fluids typical of the C_6 cement stage (Fig. 2) that are strongly oxidizing and may therefore reflect groundwaters enriched in sulfate, possibly locally as a result of sulfide oxidation.

Abbeytown: The historic small mine of Abbeytown in Co. Sligo, studied by Hitzman (1986), lies well to the northwest of the main orefield (Fig. 1) and its genetic relationship to it remains enigmatic. A small number of two-phase fluid inclusions were analysed by R.J. Bodnar (cited in Hitzman, 1986) from the main mineralizing stage (sphalerite and calcite) and from late ore-stage calcite-pyrite breccias. These predominantly showed moderate salinities of 10-13 wt% NaCl equivalent, salinities that are typical of ore-related inclusions throughout the Midlands Basin. T_h values varied from 85-180 °C with the majority in calcite falling at the upper end of this range and those in sphalerite at the

lower end. A minor population of more saline inclusions was also observed in ore-stage calcite but their timing was not discussed. No evidence for fluid mixing was observed and it was suggested that mineralization probably formed from a single fluid, perhaps due to cooling and/or neutralization by hostrock dissolution.

Lisheen: The discovery of Galmoy in 1986 (Doyle et al., 1992) focused exploration attention on the Rathdowney Trend in the southeast Midlands (Fig. 1), and proved a significant factor in the subsequent discovery of the Lisheen deposit (Hitzman et al., 1992). Initial fluid inclusion studies were reported in conference abstracts (Thompson et al., 1992; Eyre et al., 1996), with the first detailed results presented by Eyre (1998). In this study, fluid inclusion analyses from Galmoy, Lisheen and a number of prospects in the Rathdowney Trend were constrained with respect to the mineral paragenesis observed in the samples (see Wilkinson et al., 2005b for details), synthesized in Figure 2.

All analyzed fluid inclusions from Lisheen were of liquid-vapor type and showed simple low temperature phase behavior with first melting temperatures in the range -54 to -39 °C, best interpreted in terms of the NaCl-$CaCl_2$-H_2O system. Fluid inclusions in sphalerite showing permissive evidence for a primary origin displayed $T_m$hyd of -22.6 ± 0.3 °C indicating the dominance of NaCl (e.g., see Bodnar, 2003b). These yielded salinities mostly in the range 10.2-18.0 wt% NaCl equivalent. A marked polymodal distribution of salinities was observed (Table 1), including an unusually low salinity grouping from the outlying North Zone (Wilkinson et al., 2005b). Liquid-vapor homogenization temperatures (to the liquid) were mainly in the range 140-210 °C (up to 241 °C) with the highest mode observed for samples from the central Derryville Zone. Excluding the low salinity population, the groups define points along a trend of decreasing temperature and increasing salinity, similar to the data from Silvermines and Tynagh. Secondary, low T_h brine inclusions were commonly recorded.

Results from ore-stage and late ore-stage gangue phases fill out this trend with a more continuous data distribution. Measurements from a ferroan calcite-cemented “white matrix breccia” (drillhole LK262-100 m) from the Derryville Zone overlap most closely those from sphalerite. Rare data from quartz fall at the more saline end of the distribution. Data from post ore-stage pink dolomite (D_5) and secondary inclusions in calcite veins (and in sphalerite) fall at the end of this array indicating the late-stage infiltration of low temperature brines into the deposit. Although these brines appear to represent a viable end-member for the suggested mixing process (Eyre, 1998; Wilkinson et al., 2005b), the pink dolomite itself is thought to significantly postdate mineralization and is related to extensive sulfide dissolution. Thus it is inferred that multiple brine types infiltrated the deposit during and subsequent to mineralization.

Galmoy: Fewer results are available from Galmoy but these show broadly similar characteristics to Lisheen (Table 1). Sphalerite data display several salinity clusters in the range 10.8-16.3 wt% NaCl

equivalent and a relatively narrow range of homogenization temperatures between 129-179 °C (Table 1), notably lower than at Lisheen. Hydrate melting was recorded in one sample at -22.4 ±0.2 °C indicating predominance of NaCl over $CaCl_2$. Low T_h secondary inclusions were again common but no salinity data are available. The sphalerite data overlap significantly with results from white matrix breccia dolomite (D_3; see Fig. 2), consistent with a syn- ore-stage timing for these breccias as inferred at Lisheen (Wilkinson et al., 2005b). Limited measurements on late ore-stage dolomite and calcite yielded a wide range in T_h (111-228 °C) and salinity but are consistent with the possible mixing trend defined at Lisheen.

Subeconomic Prospects

Studies of the subeconomic prospects in the orefield have been important in order to constrain relative timing of mineralization in less intensely altered environments and to compare geological characteristics with the larger systems to evaluate controls of economic mineralization. However, no systematic comparison of the characteristics of the fluids involved has been carried out.

Keel: The Keel prospect and the adjacent Garrycam barite deposit (Fig. 1) have been widely studied but never in great detail. The Keel deposit comprises stratabound breccia and fracture-fill mineralization, localized by faults, that is hosted in rocks extending from the uppermost Silurian basement slates up to the top of the Navan Group "Mixed Beds" (Slowey, 1986). It is distinctive in that much of the sulfides occur as relatively coarse, euhedral crystals cementing breccias.

Subsequent to the initial study by Roedder, both Probert (1983) and Thompson (1992; cited in Slowey et al., 1995) obtained T_h values in the range 110-187 °C and salinities of 11-24 wt% NaCl equivalent but without detailed paragenetic control. Higher T_h values from barite at Garrycam were considered to be unreliable. Later work reported data within this same range (Caulfield et al., 1986), confirmed in this study on primary inclusions hosted by color-zoned sphalerite (Table 1). Late, pale-yellow and transparent sphalerite trapped the coolest and lowest salinity fluids, interpreted to reflect dilution of earlier, more saline and Fe-rich fluids. This pattern is similar to that recognized in carbonate-base metal-gold epithermal deposits (Corbett, 2004). Post-sphalerite quartz contains the most dilute inclusions (4.4-9.1 wt% NaCl equivalent; Collins, unpublished MSci dissertation, Imperial College London, 2005; This study) suggesting that dilution eventually quenched ore formation. The polymodal salinities observed at Keel-Garrycam, lack of evidence for mixing (with the exception of the late dilution noted above), and range in T_h values suggest a complex history involving injection and cooling of a number of fluid pulses.

Harberton Bridge: Harberton Bridge, located in Co. Kildare in the eastern part of the Midlands (Fig. 1), is one of a number of small sulfide- and carbonate-cemented breccia deposits of Mississippi Valley-type (Holdstock, 1982). The Kildare District has been widely cited as hosting an end-member

of the spectrum of styles of deposit in the orefield (Andrew, 1993; Wilkinson, 2003). Marcasite and sphalerite are the dominant (commonly interbanded) sulfides with minor amounts of galena that sometimes shows a recrystallized dendritic form (Trude and Wilkinson, 2001). The typical paragenesis is early marcasite-calcite, often replacing or overgrowing limestone host rock, followed by polymetallic marcasite-sphalerite-galena-calcite mineralization overprinted by late calcite (Holdstock, 1982, 1983). Dolomite and pyrite are uncommon. This sequence is similar to that described for the other Kildare deposits by Dixon (1990).

Preliminary T_h measurements of ~100 °C from Harberton Bridge were reported in a personal communication by Finlow-Bates, cited in Emo (1986). The only systematic study, on representative samples from one drillhole, found that monophase primary and secondary inclusions were abundant in calcite, although two-phase inclusions of probable primary origin were also present (Trude and Wilkinson, 2001). These yielded T_h values of 48-70 °C with an average of 61.5 °C, interpreted to represent the upper end of the range likely for the calcite studied and indicating a very low temperature origin for this style of mineralization. Hydrate melting was sometimes observed, ranging from -37.2 to -21.8 °C, suggesting variable Ca:Na ratios. Salinities varied from 10.1 to 19.3 wt% NaCl equivalent, possibly indicative of mixing.

Kinnitty: The Kinnitty prospect, located on the northwestern flank of the Slieve Bloom inlier (Fig. 1), is hosted by undolomitized Waulsortian Limestone and comprises stratabound calcite veins, calcite-cemented breccias, and cavity infillings. Iron sulfides are dominant, mainly layered marcasite-pyrite and melnikovite, and are typically interbanded with colloform sphalerite that contains galena, sometimes with dendritic habit. A later overprint of calcite-pyrite veins and breccia is also observed.

Calcite associated with sphalerite-galena-marcasite assemblages hosts two-phase inclusions with T_h values of 45-80 °C and modal salinity of 20-21 wt% with a total range of 8-22 wt% NaCl equivalent (Table 1). Hydrate was commonly observed with a modal melting temperature of -21.3 °C indicating dominance of Na over Ca (Strongman, unpublished MSci Dissertation, Imperial College London, 2001). The partial preservation of melnikovite, which converts to pyrite above 75 °C (Lepp, 1957), is consistent with the very low temperatures. The spread in salinity suggests mineralization could have been driven by mixing between a moderate salinity fluid (~14 wt%) and a more predominant brine (~21 wt%). Variable mixing proportions could account for the strongly oscillating chemistry and pH implied by the multiple interbanding of calcite(-melnikovite/pyrite) and marcasite.

Cooleen: The Cooleen Zone is a satellite of the Silvermines system (Lee and Wilkinson, 2002) that was explored by Ennex International in the 1990's before being abandoned as uneconomic. Mineralization is replacive and is focused within partially and wholly dolomitized sedimentary breccias. It comprises stratiform massive, semi-massive and disseminated sulfides dominated by pyrite with lesser sphalerite and minor galena. Galena is intimately associated with sphalerite,

sometimes forming bands of cubic crystals or dendrites located within and often at the core of growths of colloform sphalerite. Mineralized calcite and dolomite veins underlie and crosscut massive sulfides.

Fluid inclusion data were obtained from late ore-stage dolomite and calcite veins that cut massive sulfide mineralization and which have walls intermittently lined by euhedral, pale brown to orange-brown sphalerite and galena (Lee, 2002). Inclusions were usually two-phase liquid-vapor type, although monophase inclusions were also observed in the calcite veins. A clear distinction was noted between inclusions hosted by dolomite (modal T_h = 180-190 °C; salinity = 10.8-17.6 wt% NaCl equivalent) and calcite (modal T_h = 150-160 °C; 4.8-14.2 wt% NaCl equivalent) with the former data showing a cluster and the latter displaying a trend from this cluster toward lower T_h and salinity values, interpreted to represent dilution. The few sphalerite-hosted inclusions measured fell into two groups: vein-hosted sphalerite contained inclusions comparable to those hosted by dolomite whereas a fragment of sphalerite interpreted to be a reworked clast in a sedimentary breccia hosted inclusions with much lower T_h and salinity values (Table 1).

Rathdowney Trend: In the Rathdowney Trend (Fig. 1), prospects at Holycross, Durrow and Rathdowney East were sampled for reconnaissance studies by Eyre (1998). A variety of mineralization styles are observed, principally disseminated, replacement and fracture-fillings associated with hydrothermal black (D_2) and white (D_3) dolomite.

Sphalerite- and vein dolomite-hosted inclusions from Holycross display a prominent mode in T_h at 170-180 °C with salinity modes at 10-11 and 16-17 wt% NaCl equivalent (Table 1), very similar to Lisheen. Hydrate melting was observed at -22.7 °C, identical to Lisheen and Galmoy sphalerites (Table 1). Relatively high and variable homogenization temperatures of 155-267 °C (principal mode 210-220 °C) were recorded for primary inclusions hosted by coarse white dolomite-cemented breccias. On average, these inclusions display higher T_h and slightly lower salinity than sphalerite-hosted inclusions in the Rathdowney Trend deposits or prospects and could represent high-temperature, end-member ore fluids prior to fluid mixing. Pink dolomite (D_5) in the Rathdowney Trend contains similar inclusions to those observed in the same phase at Lisheen and Galmoy but with a slightly higher modal T_h range (110-120 °C compared with 90-100 °C and 80-90 °C respectively). Secondary, low T_h brine inclusions (28-29 wt% NaCl equivalent), similar to those in pink dolomite, are common in the Rathdowney Trend prospects.

Courtbrown: The Courtbrown prospect is located in the southwest Midlands, west of Limerick (Fig. 1). Mineralization occurs as replacement and disseminated styles and is commonly associated with solution seams (Grennan, 1986). Two-phase fluid inclusions in ore-stage calcite yielded T_h values mainly in the range 160-190 °C (Reed and Wallace, 2001). Freezing data were not reported. Although these results are within the most common range for fluids in the orefield (Table 1), no petrographic

evidence for stretching was described, and no size-T_h relationship exists, the authors concluded that the inclusions must have undergone post-entrapment modification based on inferred overheating to ~310 °C (Reed and Wallace, 2001).

Pallas Green: The Pallas Green prospecting licences are located in the southwest Midlands (Fig. 1). Five massive sulfide lenses have been discovered in the area: two small zones at Castlegarde and three larger lenses at Tobermalug, Caherconlish South and Srahane West. This area is currently undergoing intense exploration and is arguably the most prospective greenfield region in the orefield. Mineralization at Castlegarde comprises a variety of replacement, breccia and cavity-fill styles. Early marcasite and pyrite, which may form massive intervals in drillcore, partly replace early calcite cements and Waulsortian hostrock clasts. Sphalerite is often very finely color-banded, partly replaces earlier Fe sulfides, and contains later euhedral and dendritic galena (Crowther and Wilkinson, unpublished report to the Noranda-Minco joint venture, 2002).

Two-phase fluid inclusions were analyzed in calcite that infills sulfide-lined vugs and is sometimes replaced by sulfides. The majority of T_h values ranged from 132-181 °C with a mode of 150-160 °C. Salinities varied from 16.1 to 4.3 wt% NaCl at approximately constant T_h possibly indicative of a dilution trend.

Regional Carbonate Cements

Fluid inclusion studies on cement phases within the Lower Carboniferous host rock sequence began in the early 1990's. However, a clear picture of the relationship between cementation stages and hydrothermal events did not begin to emerge until more detailed fluid inclusion studies were carried out on exploration drillcore through the late 1990's (Wilkinson, unpublished data, 1996-2000) and a regional study of the Lower Carboniferous cements and their associated fluid inclusion populations was begun (Gregg et al., 2001; Johnson et al., 2001, 2009).

Fine replacive dolomite (D_{1a}): Reliable fluid inclusion data have not been obtained from the early (pre-ore) diagenetic planar dolomite (Fig. 2) due to its fine grain size. Based on textural and isotopic constraints, this has been interpreted as an early, seawater-related diagenetic product (Gregg et al., 2001).

Coarse white dolomite (D_{1b}): A few T_h data were reported from aqueous liquid-vapour inclusions in coarse white "regional" dolomite (Fig. 2) in the 1990's (Allan et al., 1992; Eyre, 1998) suggesting precipitation temperatures up to 233 °C and apparently ruling out a simple diagenetic origin (cf. Hitzman, 1995; Hitzman et al., 1998). Subsequent work on similar, non-planar replacement dolomite yielded rare data from two-phase aqueous inclusions with T_h values of 170-200 °C and salinities of ~2-15 wt% NaCl equivalent (fluid "Type 2": Gregg et al., 2001). It was concluded that this cement probably originated via partial neomorphic recrystallization and overgrowth of the early planar

dolomite in the presence of late diagenetic or hydrothermal fluids. More recent studies have reported the common occurrence of aqueous liquid-vapour fluid inclusions, distributed along growth zones, in Waulsortian-hosted samples of coarse white dolomite from throughout the Midlands (Wilkinson, unpublished data; Wilkinson, 2003). T_h data are in the range 140-240 °C with salinities of 10-15 wt% NaCl equivalent, identical to the majority of hydrothermal fluids observed in the deposits (Table 1).

White dolomite-cemented breccias: Breccias cemented by planar to non-planar white dolomite (Fig. 2) are similar to the white matrix breccias associated with mineralization (Doyle et al., 1992; Hitzman et al., 2002; Wilkinson et al., 2005b) in terms of texture, cathodoluminescence and primary liquid-vapor fluid inclusion properties (Wilkinson, 2003; Table 1). These inclusions have similar salinities but slightly higher T_h values than those hosted by coarse white dolomite and some develop clathrate on cooling, indicative of elevated CO_2, as previously reported from deposit sphalerite and Lower Paleozoic-hosted quartz-carbonate veins (Everett et al., 1999a).

An unusual dolomite with uncertain paragenetic position has also been studied. This generally comprises fine- to coarse-grained, planar-subhedral turbid crystals that commonly display a pearlescent appearance and cream to pinkish color in hand sample. It appears to be replacive in origin and is texturally similar to the fine replacive regional dolomite (Fig. 2) except for its coarser grain size. It is often overgrown by translucent dolomite, occasionally with red or brown ferroan growth bands, that displays weak, non-planar form (Fig. 4B). Late, transparent vug-filling calcite may be present, possibly equivalent to C_6 (Fig. 2). Primary inclusions in growth bands are common in the translucent dolomite and these have similar properties to those observed within some of the earlier turbid dolomite; therefore, they are both thought to have precipitated from the same fluid type. Average first melting temperatures of -53.2 °C indicate the predominance of NaCl and $CaCl_2$. Final ice melting temperatures are unusually low, ranging from -23.0 to -35.3 °C (Fig. 4B) and, where observed, hydrohalite melting occurs after ice with a mean temperature of -1.7 °C (Table 1). These data imply distinctive Ca-rich brine compositions.

Black dolomite: Breccia samples from Ballinasloe in the west-central Midlands (Fig. 1) yielded the only fluid inclusion data yet to be acquired from fine planar black dolomite of the type elsewhere associated with ore in the Waulsortian-hosted deposits (Wilkinson and Earls, 2000; Fig. 2). This yielded T_h values of 146-204 °C, salinities of 13.5-19.9 wt% NaCl equivalent and $T_m$hyd in a few inclusions close to -22 °C indicating NaCl-dominant compositions comparable with inferred ore-stage fluids at Silvermines, Tynagh, Lisheen and Galmoy. The spread in salinity was considered to be due to mixing of a moderate salinity (~12 wt%), higher temperature fluid with a low temperature brine; this process induced rapid supersaturation and precipitation of the characteristic dolomite type. Slightly earlier white to translucent dolomite that formed reaction rims around breccia clasts hosted two-

559 phase inclusions with T_h values of 144-203 °C and salinities of 10.3-13.5 wt% NaCl equivalent, similar
560 to coarse white dolomite elsewhere.
561 *Pink dolomite:* Paragenetically late, coarse grained, cream to pink dolomite (Fig. 2), is widely
562 observed in the Midlands as a replacement, vug- and vein-filling cement phase (e.g., Boast et al.
563 1981; Andrew 1986; Eyre 1998), and has also been described cutting mineralized veins in the Lower
564 Paleozoic basement (Everett et al., 1999a). It displays a well-developed saddle morphology and
565 shows pronounced compositional zoning in CL (Wilkinson, 2003). It commonly occurs as an
566 overgrowth of earlier coarse white dolomite in vugs and, as a result, may be confused with this
567 earlier dolomite. Minor sulfides (mainly pyrite, chalcopyrite and sphalerite) are occasionally observed
568 encrusting pink dolomite crystals which may explain why this dolomite has been interpreted as pre-
569 ore (Wright et al., 2000). However, where observed in the deposits, it is always post-ore and is
570 associated with extensive dissolution of sulfides (Boast et al., 1981; Eyre, 1998).
571 The pink dolomite contains two-phase liquid-vapour inclusions with very consistent properties
572 (Table 1). Homogenization temperatures are mostly in the range 91-137 °C and salinities are 23.7-
573 24.7 wt% NaCl equivalent. First melting is normally observed below -50 °C indicating significant $CaCl_2$,
574 but combined ice and hydrate melting temperatures (average -17.9 °C) indicate that these brines
575 have Na>Ca.
576 *Other dolomite data:* Gregg et al. (2001), Mulhall (2003) and Johnson et al. (2001, 2009) identified
577 three main types of fluid in the Midlands based on inclusions hosted by “late diagenetic” saddle
578 dolomite cements, but the relative timing of the hosting dolomites was not fully resolved. Based on
579 analogy with known fluids elsewhere in the Midlands it is considered probable that the saddle
580 dolomite that hosts inclusions homogenizing in the range 100-270 °C and with salinities of 0-17 wt%
581 NaCl equivalent (“Type 2” and “Type 3” fluids: Gregg et al., 2001) is correlatable with coarse white
582 and/or white matrix breccia dolomite (Fig. 2), whereas the white to pink saddle dolomite cements
583 hosting inclusions with T_h values of 70-120 °C and salinities of 19 to >26 wt% NaCl equivalent are
584 likely to be equivalent to the late (post-ore) pink dolomite described above. The difficulty in
585 distinguishing between some of the dolomite types is probably due in part to the development of
586 epitaxial overgrowths. For the late pink dolomite, its field distinction is largely based on a coloration
587 that is not always developed. Significantly, the “Type 3” fluid, that has comparable properties to the
588 ore-forming fluids (Table 1), was not observed in Supra-Waulsortian lithologies (Johnson et al., 2001,
589 2009), consistent with a principal high-temperature hydrothermal event that predated their
590 deposition (e.g., Lee and Wilkinson, 2002).
591
592 *Footwall stratigraphy*

593 The first study of fluid flow at greater paleodepths investigated the structural, mineralogical and
594 isotopic characteristics of vein systems hosted by Lower Paleozoic rocks. This was coupled with fluid
595 inclusion data to test whether mineralizing fluids had circulated in fracture permeability within this
596 volcanosedimentary succession (Everett et al., 1999a). Three main vein types were identified that cut
597 dark grey-green Silurian greywackes, mudstones and sandstones in the southwest Irish Midlands at
598 locations up to 32 km WSW and 20 km ESE of Silvermines (Fig. 1):
599
600 1. Early hematitic calcite-quartz ± pyrite
601 2. Quartz-calcite ± sphalerite, galena, chalcopyrite, pyrite, barite
602 3. Ankerite-ferroan dolomite-quartz ± sphalerite, pyrite
603
604 Vein types 2 and 3 are associated with weak to locally intense sericite-chlorite-carbonate alteration,
605 and disseminated pyrite(-carbonate) is observed in the vicinity of well-developed vein systems. Clots
606 of a distinctive fine-grained pistachio green mineral are commonly observed within Type 2 veins and
607 along vein margins and more rarely in Type 3 veins. In some cases it is associated with pink dolomite
608 that cuts both vein types. Microprobe analyses indicate that these comprise phengitic K-mica,
609 sometimes intimately intergrown with chlorite.
610 The majority of the fluid inclusions observed were of liquid-vapor aqueous type with a minority of
611 secondary monophase, liquid-only inclusions. Inclusions within quartz which showed a highly variable
612 degree of fill from 5 to 75 percent liquid were recorded in one sample – possible evidence for boiling.
613 Some liquid-vapor and liquid-only inclusions contained trapped solid phases that showed no change
614 upon heating; these were interpreted to be calcite and K-mica.
615 Inclusions considered to represent the vein-forming fluids in Type 1 veins had low to moderate
616 salinities (0.2-10.8 wt% NaCl equivalent) and T_h values from 150-250 °C. Lower temperature (109-
617 189.9 °C), moderate to high salinity (12.2-23.8) secondary inclusions were also recorded. The origin
618 of the Type 1 veins is uncertain, although structural relationships are consistent with a Lower
619 Carboniferous age, and the occurrence of hematite, chlorite and calcite is similar to the early (pre-
620 sulfide) ironstones and associated hematite-bearing veins reported at several Irish base metal
621 deposits (Hitzman et al., 1995). However, the fluid properties are also comparable with inclusions
622 commonly associated with the Caledonian granites in Ireland, interpreted to represent widespread
623 meteoric circulation subsequent to their emplacement and crystallization (O'Reilly et al., 1997a,b).
624 Primary fluid inclusion data from vein Types 2 and 3 show T_h-salinity characteristics (123-238 °C,
625 9.7-20.6 wt% NaCl equivalent) that are comparable with data from Carboniferous-hosted
626 mineralization (Table 1). In addition, the highest T_h inclusions hosted by quartz and sphalerite

commonly contain CO_2 as noted elsewhere. These fluids are believed to represent ore fluids trapped en route to potential sites of mineralization.

Fluid Inclusion Constraints on Fluid Origins and Interactions

Although basic microthermometric data provide important constraints on fluid properties and variability within hydrothermal ore systems (e.g. Wilkinson, 2001), greater insights are provided by more complete fluid geochemical information. At the first level, this includes interpretation of ice and hydrate melting temperatures in the NaCl-$CaCl_2$-H_2O system which yields information on trends in the major cation compositions of the fluids. More detailed geochemical studies, using bulk methods (crush-leach or decrepitation-linked ICP analysis), have also been carried out in Ireland, principally to provide constraints on the origin of the ore-forming solutions. The use of laser ablation ICP-MS for the analysis of individual inclusions is just starting to be applied and is providing important new data on metal contents (Wilkinson et al., 2009).

Na:Ca ratios

In order to interpret fluid inclusion chemistry in chemical systems more complex than NaCl-H_2O from microthermometric data it is necessary to observe additional phase changes, such as hydrate melting. However, in studies of the Irish orefield this phase transition has been reported only rarely (Samson and Russell, 1987; Banks and Russell, 1992; Eyre, 1998). These results indicated that fluids generally had Na numbers (Na#: NaCl/[NaCl+$CaCl_2$]) greater than 0.5. Based on crush-leach data, Samson and Russell (1987) suggested that the moderate salinity ore fluids had high Na# and that two brine types existed, one with high Na# and one with low Na#.

Here, new data are presented from basement-hosted veins, regional carbonates, deposits (Silvermines) and prospects (Keel and Castlegarde). Excluding three outliers below -30 °C (probably erroneous observation), $T_m$hyd ranges from to -29.0°C to +1.1 °C, but is mostly between -22 and -24 °C (Table 1). Modelling ice and hydrate melting in the NaCl-$CaCl_2$-H_2O system (Naden, 1996) gives Na# mostly in the range of 0.66-0.95 for basement-hosted veins, 0.42-0.88 for regional carbonates, and 0.61-0.92 for deposits and prospects. The uncertainty for careful measurement of $T_m$hyd is ±0.2 °C and for ice melting ±0.1 °C which translates into a modeled uncertainty of +0.03/-0.01 in Na# and ±0.1 wt% in total salinity (wt% NaCl+$CaCl_2$ equivalent). The degree of uncertainty due to the presence of other cations or anions in the fluids cannot be assessed. Plotting Na# as a function of total salinity allows possible end-member fluids and mixing relationships to be identified (Fig. 5).

The regional carbonate data suggest that two brine compositions exist with Na# of ~0.75 (25 wt% salinity; Type B_1) and Na# ~0.60 (28 wt% salinity; Type B_2), in agreement with Samson and Russell

(1987). Type B_1 is principally associated with pink dolomite and has compositions similar to Triassic, red-bed derived, evaporitic brines recorded in Southwest England (Gleeson et al., 2001; Stoffell et al., 2004). It corresponds to the "Group 3" calcite-hosted inclusions of Banks and Russell (1992) at Tynagh. Type B_2 is associated with cream to pink, turbid, replacement dolomite or the more transparent dolomite that overgrows it. A third, calcic brine (B_3), sometimes spatially associated with the B_2 brines (Fig. 4), is inferred from inclusions that display very low ice melting temperatures (typically around -33 °C). Although hydrate melting generally was not observed, the topology of the $NaCl\text{-}CaCl_2\text{-}H_2O$ phase diagram indicates variably Ca-rich fluid compositions with Na# between ~0.2 and 0.6. These fluids have been found associated with Supra-Waulsortian dolomitized shelf limestones to the west of Ballinasloe and younger (up to Holkerian or early Asbian) shelf limestones southwest of Stradbally in Co. Laois (Fig. 1) indicating that they were present (although not necessarily exclusively) post-mineralization.

Results for moderate salinity fluids in basement-hosted veins (LP_1) indicate relatively high Na# (0.7-0.9), typical for ore fluids from Silvermines (Samson and Russell, 1987). Basement-hosted sphalerite typically displays average Na# ~0.75 at the lower end of this range. The variation in Na# as a function of total salinity could reflect $LP_1\text{-}B_2$ mixing in the upper parts of the basement immediately beneath the basinal succession or salinity-dependent siliciclastic buffering of fluid composition, with lower Na/Ca characterizing slightly higher salinity fluids (e.g., Yardley, 2005). However, there are insufficient data to properly constrain these possibilities at present.

Deposit-hosted sphalerite trapped fluids of distinct composition that are of relatively low salinity but more calcic than the LP_1 fluids. It is therefore possible that the actual ore-forming fluids were of somewhat different composition (particularly in their metal budget) to at least some of the fluids trapped in feeder veins in the basement as has recently been suggested on the basis of LA-ICP-MS analyses of inclusions (Wilkinson et al., 2009). The more calcic compositions could be indicative of greater degrees of fluid-rock interaction (see below). Alternatively, it may be that fluid compositions were shifted toward more calcic compositions during ore deposition. Sphalerite precipitation as a result of fluid mixing generates acid that can result in carbonate dissolution and consequent Ca (+Mg) enrichment in the fluid according to reactions such as:

$$2\ ZnCl_4^{2-} + 2\ H_2S + CaMg(CO_3)_2 = 2\ ZnS + 8\ Cl^- + Ca^{2+} + Mg^{2+} + 2\ H_2CO_3$$

This type of reaction is supported by abundant textural evidence for delicate replacement of different carbonate grain types by sulfides, as has been described from Lisheen (Wilkinson et al., 2005b). A third possibility is that ore formation resulted from mixing between fluids of LP_1 type and

696 the calcic B_3 brines (Fig. 5). However, this is thought to be unlikely given the young (probably post-
697 ore) age of the B_3 brines identified to date.
698
699 *Major element chemistry*
700 Bulk fluid inclusion analyses on quartz from basement-hosted vein samples (Everett et al., 1999a)
701 showed that LP_1 fluids had Na>Ca≥K and were Mg-poor. These compositions are comparable with
702 experimental data on fluids equilibrated with greywackes at temperatures of 200-350 °C, consistent
703 with derivation of mineralizing fluids from a Lower Paleozoic-equilibrated fluid reservoir. Na# were in
704 the range 0.88-0.94, consistent with the microthermometry-derived values reported here. Na-K-Ca
705 (Fournier & Truesdell, 1973) and K-Na and K-Mg alkali thermometers (Giggenbach, 1988) can be
706 applied because the mineralogy of the Lower Paleozoic succession (quartz, albite, K-feldspar,
707 muscovite, chlorite, illite, minor carbonate, trace sulfides) is similar to that in the geothermal
708 reservoirs from which the thermometers are calibrated. These geothermometers gave equilibration
709 temperatures (158-219 °C) not significantly different to T_h values suggesting that the inclusions were
710 trapped under pressures only slightly above saturated vapor pressure, indicating a relatively shallow
711 depth of vein formation. In terms of the detail of flow patterns and the relationship between these
712 feeder vein localities and the deposits, it may be important that these temperatures are lower than
713 many of the estimates for fluid temperatures in the ore deposits (Table 1).
714
715 *Halogen geochemistry*
716 The first halogen analyses of Irish fluids were presented by Everett (1999), Everett et al. (1999b)
717 and Gleeson et al. (1999), and were further expanded by Banks et al. (2002), Wilkinson et al. (2005a)
718 and Johnson et al. (2009). Although the uncertainty in these measurements is difficult to constrain,
719 different fluid types can be identified based on significant differences in halogen and major element
720 ratios and/or the restriction of particular signatures to specific paragenetic stages or geographic
721 locations.
722 Lower Paleozoic-hosted vein samples contain fluids that fall into two groups: Type LP_{1a} have Cl/Br
723 molar ratios (559-825) that are similar to seawater, interpreted as being produced by partial
724 evaporation of seawater to an evaporation ratio of ~4x to ~7x (evaporation ratio = mass of water in
725 seawater/mass of water in evaporated brine) prior to circulation into the basement (Wilkinson et al.,
726 2005a). Type LP_{1b} fluids are slightly less saline but have Cl/Br values below seawater (375-553); these
727 were interpreted to represent strongly evaporated bitterns (evaporation ratio up to 25x), relatively
728 enriched in Br, that had subsequently been diluted by either seawater, evaporated seawater or
729 meteoric water (Fig. 6A). Mixing curves show that the data are consistent with mixtures containing
730 ~5-20% brine (by mass) and ~80-95% evaporated seawater although other possibilities cannot be

731 excluded at present. The relatively narrow salinity range displayed by the LP_{1b} fluids (Everett et al.,
732 1999a) implies homogenization of these putative mixtures prior to trapping but it is uncertain when
733 this mixing occurred: prior to recharge, during flow within basement rocks, or close to the
734 paleosurface around the time of mineralization. Hydrogen and oxygen isotope data (see below) are
735 consistent with a model involving mixing of uninteracted brines (relatively near to the paleosurface)
736 with strongly interacted LP_1-type fluids to form the LP_{1b} fluids.
737 Results from deposit-hosted samples show that ore fluids from Silvermines are similar to LP_{1a}
738 whereas those from Tynagh are shifted to slightly more Br-rich compositions, closer to LP_{1b}. Tentative
739 modeling indicates that mixing between Br-enriched brines (<20%) and LP_1 fluids (evolved partially
740 evaporated seawater; >80%) can produce most of the range in Cl-Br compositions observed in the
741 Irish ore fluids (Fig. 6A) although it is possible that some of the spread is an artefact due to analysis of
742 inhomogeneous inclusion populations. Nonetheless, the data are consistent with trapping of
743 mixtures of high temperature fluids and brines at the ore depositional site, a process that has been
744 invoked as a key ore-forming mechanism (e.g. Anderson et al., 1998; Blakeman et al., 2002; Hitzman
745 et al., 2003; Wilkinson et al., 2005a, 2005b).
746 Combining exchangeable cation data with the conservative halogens allows processes undergone
747 by these seawater-derived fluids during crustal interaction to be explored. A plot of Cl/Br vs. Na/Br
748 (Fig. 6B) shows that all deposit and Lower Paleozoic basement-hosted vein data lie close to or above
749 the seawater evaporation trajectory (SET), best explained by loss of Na from fluids initially lying at
750 various points along the SET. Fluids from Silvermines appear to be more exchanged than those from
751 Tynagh, possibly accounted for by a greater degree of water-rock interaction, which could explain
752 the greater metal endowment of the Silvermines system. Both deposits appear to have formed from
753 more exchanged fluids (subsequently referred to as LP_2) than the Lower Paleozoic-hosted veins,
754 suggesting that the feeder veins (sampled lateral to the deposits) represent different, less basement-
755 interacted, parts of the flow system. The samples from Birdhill and Latteragh (closer to Silvermines;
756 Fig. 1) generally display greater degrees of Na loss than those from Fantane and Ballycar (Fig. 6B),
757 consistent with a convective type of flow pattern.
758 An equivalent plot but involving Ca (Fig. 6C) shows that there is very strong enrichment in Ca in
759 the Lower Paleozoic-hosted vein fluids relative to evaporated seawater. Unfortunately, no
760 comparable data for deposit-hosted inclusions exist. The exchange of Ca^{2+} for $2Na^{+}$, most commonly
761 mediated by reactions involving plagioclase, is a common process in crustal fluid-rock interactions
762 and is related to temperature and fluid salinity (Yardley, 2005). Ca is most enriched in samples from
763 the Birdhill and Latteragh localities supporting greater degrees of exchange in the genesis of these
764 fluids, consistent with the Na data. However, consideration of the cation balance shows that the Ca
765 gain in the LP_1 fluids is not matched by twice as great a loss (in molar terms) in Na so that an

766 additional source of Ca is required. One possibility is that Ca was acquired from the Carboniferous
767 sequence as a result of Mg-Ca exchange dolomitization in downflow zones:
768
769 $$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}$$
770
771 Some of the pre-mineralization, seawater-related dolomitization observed (D_{1a}) could have been
772 formed in this way and the process may also have been responsible for some of the Mg depletion
773 noted in the LP_1 fluids, although this can also be attributed to Mg-smectite and chlorite formation in
774 the basement rocks (see below).
775 Microthermometric data suggest that deposit sphalerite-hosted ore fluids (LP_2) are even more Ca-
776 rich than LP_1 fluids (Fig. 5) and this is supported by recent LA-ICP-MS analyses (Wilkinson et al.,
777 2009). This is consistent with greater degrees of basement exchange in their production although, as
778 noted earlier, the possibility of local Ca increase due to carbonate dissolution at the site of ore
779 formation cannot be excluded.
780
781 *Minor and trace element chemistry*
782 Plotting the minor and trace element chemistry of the LP_1 fluids normalized to their inferred
783 evaporated seawater precursor illustrates the Li enrichment, strong Mg depletion, and broad
784 increase in the transition metals and lithophile elements (Sr, Ba, Pb), that has occurred during crustal
785 interaction (Fig. 7). Similar changes are observed in modern seawater-dominated submarine
786 hydrothermal fluids interacting with ocean basalts, but with a lack of such strong enrichment in
787 elements concentrated in felsic crust such as Ba or Pb.
788 Lithium concentrations in LP_1 fluids are in the range 55-164 ppm (Everett et al., unpublished;
789 Wilkinson et al., 2005a), overlapping with, but generally lower than, the 86-503 ppm obtained by
790 crush-leach analysis from Silvermines and Tynagh ore-stage samples (Banks et al., 2002). All these
791 values are elevated significantly above evaporated seawater concentrations. Enrichment is most
792 likely due to interaction with basement rocks that typically contain 30-60 ppm Li (Crowther, 2007).
793 Magnesium concentrations in LP_1 fluids are in the range 30-310 ppm and are very depleted (Fig.
794 7), typical of seawater-derived fluids that have undergone low temperature exchange with silicate
795 rocks and/or have been involved in dolomitization. Thus, the Mg data, like Na, can be explained by
796 exchange for Ca during fluid infiltration.
797 Barium is strongly enriched in LP_1 fluids, such as at Fantane (mean 930 ppm; Wilkinson et al.,
798 2005a), even in the absence of significant base metals. It could be acquired by fluids from trace
799 barite or barian feldspar during basement interaction, but only once fluids were depleted in sulfate
800 either by anhydrite precipitation or reduction.

Bulk data suggest that ore metal concentrations are low in LP_1 fluids (2-33 ppm Zn, 11-68 ppm Pb; Everett et al., unpublished; Wilkinson et al., 2005a) and are highest in the most interacted fluids (based on Na/Br systematics) at Birdhill and Latteragh. This contrasts markedly with recent analyses of sphalerite-hosted inclusions from Silvermines that display one to two orders of magnitude higher Pb concentrations (Wilkinson et al., 2009). Such high metal contents appear to suggest that unusually efficient metal extraction was responsible for production of the LP_2 fluids that went on to form ore, potentially linked to the greater degrees of water-rock interaction suggested above.

Oxygen and hydrogen isotopes

Fluid δD (obtained by direct measurement of fluid inclusions) and calculated fluid $\delta^{18}O$ values (based on mineral compositions and mineral-water fractionation factors) from ore-stage samples at Silvermines were interpreted to reflect equilibration of seawater-derived fluids with the Lower Paleozoic sequence (Samson and Russell, 1987). Similar data from Lower Paleozoic-hosted feeder veins (Everett et al., 1999b) suggested mineralizing solutions with $\delta^{18}O_{H2O}$= 2.4-9.0‰ and δD= -24 to -55‰, overlapping with the Silvermines orefluids. This is supporting evidence for Lower Paleozoic flow of the ore-forming solutions, although the generally lower δD of the Silvermines fluids is noteworthy.

Modeling of these data using the new constraints on fluid origins discussed above shows that the measured compositions cannot be produced by equilibration of seawater or evaporated seawater with inferred Lower Paleozoic rock compositions, even at low water/rock ratios (Fig. 8). Utilising a possibly depleted Carboniferous seawater precursor ($\delta^{18}O$ = -3‰; Veizer et al., 1999) has negligible effect because fully-equilibrated fluids at low water/rock ratios are essentially buffered by the rock composition. The discrepancy requires involvement of an unexchanged fluid with much lower δD, lower fluid-rock fractionation factors for hydrogen and/or lower δD of the rocks involved. The observation that low temperature brine inclusions trapped in barite at Silvermines are characterized by low δD values (-41.4 to -54.6 ‰; Samson and Russell, 1987) suggests that a D-depleted shallow brine may have existed and mixing between this and exchanged evaporated seawater could explain the relatively D-depleted LP_1 fluid data and some of the ore fluid compositions (Fig. 8). A possible explanation for the depleted brine signature is bacterial fractionation of hydrogen isotopes at the seafloor (Samson and Russell, 1987); however, it can also be reproduced by shifting the seawater evaporation trajectory to lower $\delta^{18}O$ and δD values and assuming a depleted Carboniferous seawater precursor (Fig. 8). Thus, the low δD signature could be merely a product of evaporation past halite precipitation (cf. Knauth and Beeunas, 1985).

834 The isotopic compositions of the bulk of the Silvermines ore fluids (which tend to have higher T_h
835 values and lower salinities than most LP_1 fluids) cannot be explained by brine-LP_1 mixing in the ore-
836 forming environment (Fig. 8) and appear to require a greater hydrogen isotope shift during fluid-rock
837 interaction. The involvement of D-depleted lithologies at greater depth cannot be tested although
838 this would be consistent with the higher fluid temperatures suggested by higher $\delta^{18}O$ values and
839 generally higher T_h values. Interaction with mafic rocks (δD -70 to -105 ‰; Agrinier et al., 1995),
840 Caledonian granite or the Precambrian crystalline basement that may have undergone earlier
841 deuteric alteration are all possibilities.
842
843 **Discussion and Implications**
844
845 *Regional fluid evolution*
846 Fluid inclusion data, coupled with stable and radiogenic isotope systematics, describe a basinal
847 system in which widespread mobilization of hydrothermal fluids led to progressive overprinting of
848 normal, early diagenetic processes and localized convergence of a number of factors toward ore-
849 forming conditions. Fluid chemistry suggests that some of the early dolomitization (D_{1a}; Fig. 2) could
850 have formed from "normal" evaporated seawater that subsequently penetrated the basement and
851 evolved into interacted but unfertile solutions. Regionally-developed, coarse white dolomite cements
852 (D_{1b}) then formed above fault-focused plumes of these evolved solutions, as they became thermally
853 buoyant and migrated back toward the surface. The coarse white dolomite is thus interpreted to
854 reflect a slightly lower temperature and spatially more extensive manifestation of the hydrothermal
855 system that was ultimately responsible for the formation of the ore deposits (Wilkinson, 2003).
856 Increased focusing and greater penetration depth are inferred to have led to the local generation
857 of higher temperature, more exchanged, highly metalliferous fluids. It was only where these LP_2
858 fluids returned to the near seafloor environment and mixed with sulfidic brines that economic
859 mineralization was formed, accompanied by hydrothermal dolomite (D_2, D_3). Continued flow of these
860 fluids after the main mineralizing event(s), with brines excluded from the ore systems perhaps by the
861 deposition of impermeable capping sequences (e.g., Calp Limestone over the Waulsortian; Upper
862 Dark Limestones over the Navan Group), led to overprinting of ore by late stage veins in some of the
863 deposits (D_4, C_4).
864 The late pink dolomite (D_5) is a distinct, post-ore marker that has been interpreted in terms of a
865 post-ore brine migration, probably related to the onset of Variscan compressional tectonism in the
866 mid- to late Carboniferous (Andrew, 1986; Wilkinson, 2003; Wilkinson et al., 2003). Thus, the onset
867 of compression in the Midlands Basin is considered to have been the principal tectonic control that
868 switched off convective fluid circulation.

Regional variations in fluid properties

The compilation of microthermometric data presented resolves some trends not previously recognized. Plotting principal modal T_h and salinity data from each locality (Fig. 9) shows that there is a regional pattern, with lower T_h and/or lower salinity fluids predominant in the north and western Midlands and higher T_h, higher salinity fluids in the south and east. This division corresponds broadly to the position of the Iapetus Suture Zone (Fig. 1) and it is proposed that this marks a major discontinuity between flow systems operating in the two halves of the Midlands Basin. Evidence for a contrast in the chemical composition of fluids in the northern Midlands compared with the south was previously suggested by Wilkinson et al. (2007) based on a preliminary regional LA-ICP-MS study of fluid inclusions in feeder veins. This showed that Zn:Pb ratios and Zn contents were significantly higher in the northern Midlands localities investigated, possibly related to a greater volcanic contribution in the Lower Paleozoic basement to the north of the Iapetus Suture. The generally lower T_h values in the northern domain is presumed to reflect a shallower circulation system, possibly limited by a thinner Lower Paleozoic sequence underlain by relatively impermeable Dalradian or Lewisian metamorphic rocks. Nonetheless, some interaction with the crystalline basement in the north has been suggested based on Nd isotope analyses of hydrothermal carbonates (Walshaw et al., 2006).

Higher temperatures, particularly in the southwest, are consistent with the lower Zn:Pb ratios in these fluids and higher $\delta^{18}O$ values. At Tynagh and Silvermines, there is evidence that submarine warm springs developed (Banks, 1985; Boyce et al., 2003; Wilkinson et al., 2003, 2005a) perhaps because these rising fluids were more buoyant due to their higher temperatures and lower salinities and were consequently able to punch through cool, dense porewater bodies resident in the shallow sediments to reach the seafloor. Elsewhere (e.g. Lisheen, Galmoy, Navan), dense shallow brines may have impeded venting with possible late stage exhalation at Navan linked to unroofing of the deposit due to major tectonic instability and submarine gravity sliding during development of the Boulder Conglomerate (Ashton et al., 1986).

In terms of their T_h-salinity properties, the fluids associated with the MVT deposits are distinct and do not clearly fit the broader regional pattern (Fig. 9). It is noteworthy that the principal area in which these deposits are observed is spatially associated with a low in the regional vitrinite/CAI maturity data. This relationship suggests that this region has not undergone the same subsidence and higher temperature fluid flow history as much of the rest of the Midlands and is consequently suggested to be not prospective for true Irish-type deposits (*sensu* Wilkinson, 2003).

Brine origins

Seawater evaporation to varying degrees played a key role in the generation of orefluids for the Irish Zn-Pb deposits. The principal orefluids were produced from partially evaporated seawater; there is no evidence for the involvement of brines produced by halite dissolution as would probably be required in the lateral flow models driven by Variscan topographic relief (e.g., Hitzman and Beaty, 1996). An interesting question is why only these partially evaporated fluids appear to have circulated to depth. It could be due to the paleogeography, with recharge areas only tapping marine waters from partially restricted sub-basins and not from areas of high evaporation (Fig. 10). A complex paleogeographic control on brine evolution has been recognized in studies of recent intracratonic marine basins such as the Dead Sea (Klein-BenDavid et al., 2004). Alternatively, more strongly evaporated brines may also have circulated into the basement but were too dense to undergo return buoyant flow to the near-surface.

More strongly evaporated brines were widespread, but these are only recognized in the Lower Carboniferous succession, with the exception of the small component inferred to be present in the LP_{1b} fluids. Three brine types have been identified, all enriched in Ca: (B_1) relatively high Na# (~0.8) brines associated with pink dolomite; (B_2) more saline brines with elevated Ca (Na# ~0.5) associated with pervasive dolomitization; and more calcic brines (Na# ~0.6-0.2), associated with dolomitization of shelf limestones. Evaporation of modern seawater only produces very low Ca brines due to the precipitation of gypsum and an excess of SO_4^{2-} over Ca^{2+}. The observed variable enrichments in Ca are therefore most likely due to Ca gain, possibly via gypsum dissolution and, probably more likely, Ca-Mg exchange dolomitization. Mole-for-mole replacement of Ca by Mg results in net volume reduction (ΔV = -9.74 cm^3 mol^{-1}; -13%), consistent with the observation of increasing porosity and development of coarse, euhedral saddle dolomite during progressive dolomitization. Similar fluid-rock interactions have been suggested for the origin of Ca chloride brines in the Dead Sea Rift (e.g. Stein et al., 2000).

Role of fluid mixing

In Ireland, ore formed at the interface between deeply-circulating and shallow, diagenetic flow systems (e.g. Wilkinson et al., 2005a) within carbonate host rocks, with mixing being an important process that allowed low-sulfur, metal-rich fluids to saturate with sulfides and at the same time generate porosity for sulfide deposition. However, fluid inclusion data suggest that mixing also occurred in other parts of the flow system that, in combination with the variety of fluid types potentially involved (seawater, variably evaporated seawater, exchanged variably evaporated seawater, bittern brines), resulted in significant complexity in fluid chemistry. In the Lower Paleozoic basement there is evidence for mixing of Br-enriched brine with partially evaporated, extensively exchanged seawater as the latter fluids ascended toward the paleoseafloor. The rare occurrence of

939 barite in Lower Paleozoic-hosted veins with a Carboniferous seawater sulfate signature (Everett,
940 1999), pyrite with low (ore-like) $\delta^{34}S$ values, and variations in Na# in fluid inclusions are consistent
941 with minor LP_1-brine mixing within at least the upper parts of the basement sequence.
942 Mixing of LP_2 fluids with brines in the ore-forming environment appears to have been an
943 important depositional mechanism and the halogen data suggest that Br-enriched bittern brines
944 were involved. These brines must have become enriched in reduced sulfur by bacteriogenic
945 reduction (e.g. Boyce et al., 1983; Caulfield et al., 1986) prior to mixing. It is suggested that the
946 development of submarine hot springs and/or seeps above major hydrothermal plumes resulted in
947 the local development of chemosynthetic faunal communities including abundant sulfate-reducing
948 bacteria. These bacterial blooms could have concentrated H_2S in brines trapped in seafloor
949 depressions and in underlying lithologies proximal to hydrothermal upflow zones. In the Waulsortian-
950 hosted deposits, these sulfidic brines could have been resident within permeable Waulsortian that
951 had been previously dolomitized (e.g. Lisheen, Galmoy; Wilkinson et al., 2005b) or in sedimentary
952 slump breccias in undolomitized Waulsortian (e.g. Silvermines; Lee and Wilkinson, 2002), perched on
953 the relatively impermeable underlying argillaceous limestones. Mixing along the interface between
954 such brine lenses and upwelling LP_2 fluids is consistent with the observation that the base of massive
955 sulfide is often planar, horizontal and commonly transgresses stratigraphy. Furthermore, the contact
956 between hydrothermal black dolomite cemented breccias (formed at the mixing interface) and
957 overlying white matrix breccias (cement precipitated from largely unmodified LP_2 fluids) is
958 subhorizontal and sharp to gradational over a few meters (Hitzman et al., 2002; Lee and Wilkinson,
959 2002; Fusciardi et al., 2003).
960 Fluid inclusion data show that, generally, hydrothermal dolomite was precipitated at the highest
961 temperatures, probably during the first increments of fluid mixing. The lack of Mg in the LP fluids
962 indicates that mixing with unexchanged, Mg-rich brines is likely to be essential for extensive dolomite
963 development in areas where pre-existing diagenetic dolomite was not abundant (e.g., Silvermines:
964 Lee and Wilkinson, 2002). In the south and east Midlands, where early pervasive dolomitization of
965 the Waulsortian had occurred (Hitzman, 1995), local recrystallization could have supplied some of
966 the required Mg.
967 Across the orefield, sphalerite-hosted inclusions tend to form relatively tight clusters of data from
968 individual samples and be polymodal in terms of salinity. The reason for this is uncertain although it
969 is suggested that the more crystalline sphalerite samples amenable to inclusion analysis may
970 represent pockets of mixed fluid that precipitated sphalerite during cooling in the waning stages of
971 individual pulses of hydrothermal fluid ingress. Finer-grained sphalerite types probably precipitated
972 over a greater part of any mixing interval but the fluid inclusion record of this is only (partly)
973 preserved in the coexisting gangue. The salinity modes observed may reflect different degrees of

974 mixing but the occurrence of comparable modes in different deposits as well as in basement-hosted
975 veins (Table 1; Wilkinson et al., 2009) suggests that infiltration of LP fluids of varying salinity and
976 composition occurred at different times as well as in space. The majority of sphalerite in the
977 Waulsortian-hosted systems appears to be associated with the more saline mode(s), suggesting that
978 this (presumably more highly evaporated) interacted seawater was particularly important for ore
979 formation (Wilkinson et al., 2009).
980 Calcite appears to have been more commonly precipitated during extensive mixing and at lower
981 temperatures, although some high temperature, unmixed, fluids are responsible for the formation of
982 calcite feeder veins in some of the deposit footwalls (e.g., Silvermines: Lee and Wilkinson, 2002).
983 At Lisheen, Galmoy, Silvermines (Cooleen Zone), Castlegarde and Keel, a trend toward more
984 dilute, lower T_h inclusions has been recognized, consistent with mixing between LP fluids and low
985 temperature seawater. It is perhaps not suprising that this is observed given the inferred near-
986 seafloor environment of ore-formation. Evidence from Silvermines suggests that such mixing tends
987 to be restricted to the margins of the system, outside the region of brine influence. It is suggested
988 that upwelling orefluids may have been deflected around a dense brine lens, mixing along the
989 interface with brine and then being diluted by normal seawater along the margins (Fig. 10). Although
990 seawater mixing does appear to be capable of driving fluids to sulfide saturation (presumably via
991 cooling and decreased ligand concentration), it is not thought to be favourable for extensive sulfide
992 deposition due to the limited sulfur supply in the LP fluids. The predominance of deep, hydrothermal
993 sulfur in these zones is confirmed by the high (>0) $\delta^{34}S$ values observed in the subeconomic Cooleen
994 Zone at Silvermines (Lee, 2002).
995 The subeconomic prospects generally appear to show a restricted salinity range, being dominated
996 by LP fluids that vary widely in temperature between localities. At present, it is not known if the
997 prospects formed from LP fluids with less (LP_1) or more (LP_2) exchanged character. Dilution trends
998 are observed in some of the prospects (e.g., Castlegarde, Cooleen, Keel), but the brine mixing trends
999 that appear to be consistently observed in the ore deposits are weak or absent. Thus, LP-brine mixing
1000 is one of the key factors that appears to be missing from the subeconomic systems. The low
1001 temperature, possibly slightly younger, MVT deposits show some evidence of mixing but lack the
1002 elevated temperatures that may be required for significant metal solubilization and show little
1003 evidence of the bacteriogenic sulfide trap, being typified by positive $\delta^{34}S$ values (Dixon, 1990).
1004 Cooling, neutralization due to extensive retrograde carbonate dissolution, and inorganic sulfate
1005 reduction are suggested as the controls of sulfide deposition from these late, cool, LP-type fluids that
1006 are interpreted to reflect the waning phase of the convective flow system.
1007 The formation of economic mineralization in Ireland appears to reflect the coincidence of high
1008 temperature reaction zones in the basement, brine-producing footwalls, and hangingwall structural-

stratigraphic traps, with bacterial blooms linked to upwelling plumes of hydrothermal fluids. The ore deposits can therefore be viewed as products of self-organizing systems – with a first-order structural control – that locally converged on ore-forming conditions. Understanding the basement structural architecture will therefore be critical for predicting new deposits.

Wider implications

The Irish hydrothermal system shares much of the variety and complexity observed in other intracratonic basin-hosted Zn-Pb(-Ba) ore districts. This includes the coexistence of contrasting styles of mineralization that are typically observed in the more distal and platform-marginal parts of the basinal environment (Sangster, 1990). In Ireland, true Irish-type (carbonate-hosted, stratiform-stratabound, massive sulfide replacement ore deposits) and MVT deposits are linked by the same type of fluids, but the MVT deposits display distinct morphologies and chemical characteristics that are related to their likely younger age, lower temperature of formation, and lack of a bacteriogenic sulfide trap. Specific characteristics include: non-stratiform breccia geometry, crustiform clast coatings, high Zn/Pb, dendritic galena, presence of melnikovite, abundance of marcasite-calcite, finely banded colloform sphalerite, and pale crystalline sphalerite. Higher temperature (Irish-type) indicators include: stratiform sulfide and (where present) breccia body geometry, massive sulfide texture, high Ni and Cd, low Zn/Pb, dark crystalline sphalerite, chalcopyrite, tennantite and other sulfosalts.

The Irish-type ore deposits can be viewed as intermediate between classic shale-hosted, deeper water Sedex deposits and platform carbonate-hosted MVT deposits in that they formed in a ramp environment beneath water depths of up to several hundred meters; they formed at around the time of host rock deposition to up to ~10 My later; and they are hosted by carbonates within a carbonate-shale sequence. The deposits were probably produced by convective flow systems that developed many of the geological features more commonly associated with Sedex than with MVT deposits, including higher fluid temperatures and lower salinities, footwall (classic epigenetic) feeder vein and breccia zones, and strong zoning on the deposit scale in terms of metals and alteration patterns (e.g., Ashton et al., 1992; Fusciardi et al., 2003; Lowther et al., 2003). The recognition of significant heterogeneity in fluid chemistry in Ireland (and in the metal tenor of resulting deposits) may reflect an intrinsic character of convective flow systems that might be anticipated in other Sedex provinces.

The derivation of a range of components from the underlying low-grade metamorphic basement can be convincingly demonstrated (Pb, Sr) or inferred (Li, Ca, Ba, Mn, Fe, Co, Ni, Cu, Zn, As). Fluids flowing within extensive fracture permeability in this metal-fertile, arc-derived greywacke-shale (±volcanic) succession are clearly capable of efficiently extracting metals. This implies that basement

involvement could be important in other sediment-hosted systems, and the common assumption that fluids and metals are solely derived from basinal clastic successions (e.g., Goodfellow et al., 1993; Leach et al., 2005) should be tested critically. The potential for surficial recharge of fluids, as documented in Ireland, means that the system is not intrinsically fluid volume-limited enabling potentially greater metal mobilization. Such deep crustal circulation is probably a requirement in basin environments where subsidence has been limited and basin successions are consequently thin; however, it may not be required in long-lived intracratonic basins (typified by many Proterozoic systems), where basin sequences may be in excess of 10 km.

A complex evolution in pore fluid chemistry in the carbonate host rocks can be documented from early, seawater-related diagenetic fluids (based mainly on textures and marine carbon and oxygen isotope signatures) that were replaced by progressively hotter hydrothermal fluids (from textures and fluid inclusion, carbon, oxygen and strontium isotope data). Later brines then dolomitized younger sediments and overprinted the ore deposits. All these fluids were derived ultimately from seawater, and the ambient paleoclimate and paleotopography played a key role in controlling fluid heterogeneity and possibly fluid fertility, as well as recharge. The evolution of brine chemistry and the flow pathways utilized are likely to be a function of the detailed paleogeography/ geomorphology, distribution and diagenesis of sedimentary facies, and basin floor/margin permeability as is highlighted in studies of modern intracratonic basins (e.g. Stanislavsky and Gvirtzman, 1999; Stein et al., 2000; Klein-BenDavid et al., 2004). Consequently, significant complexity should be expected in fluid origins in intracratonic basin-hosted ore districts elsewhere, but these can be resolved with careful application of modern microchemical analyses of fluid inclusions.

Concluding remarks

The Irish orefield presents arguably the best database available on the thermal and chemical characteristics of hydrothermal fluids involved in sediment-hosted ore genesis and is an excellent example of a fossil, crustal scale hydrothermal system. As such, it provides a valuable laboratory that could be used for further understanding the dynamics of flow, the chemical exchange and the origin, transport and deposition of metals during seawater-crust interaction. Outcrop access to various parts of the stratigraphic record in Ireland, coupled with mine exposures and extensive drillcore has allowed a three dimensional understanding of the hydrothermal system to be developed. Fluid inclusion measurements, together with careful paragenetic studies that require the use of detailed textural analytical tools such as cathodoluminescence, have allowed the system to be examined as a function of relative time. Future geochronology is desirable, although the interpretation of increasingly precise geochonological ages will remain problematic in the absence of finely resolved stratigraphic dating in the Lower Carboniferous. Regional-scale sampling has identified large-scale

heterogeneity in fluid properties and the data indicate complex fluid-fluid and fluid-rock interaction processes at the local scale. Although a start has been made, further work comparing and interpreting thermal, chemical and isotopic tracers in the ore systems with those in weakly mineralized prospects is needed to better understand the processes controlling the localization of economic mineralization.

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Table 1. Summary of microthermometric data from the Irish Orefield.

	Location	Ref.	Minerals	n	Homogenization T (°C)				Salinity (wt% NaCl equivalent)				$T_m$hyd	$\delta^{34}S$	Notes
					Mode(s)	Min	Max	Spread	Mode(s)	Min	Max	Spread			
	DEPOSITS														
N	Abbeytown	1	sp	3	**100-110**	105	123	18	**10-11**	10	11	1.0	-		
		1	cc	18	**130-140**	88	180	92	**12-13**, 24-25	10	25	15.0	-		Post-ore calcite-py breccia: 139-174°C, 10-13 wt%
	Navan	2	-	6	**180-190**	-	-	-	**24**	20	25	5.0	-		
		3	dol, sp	40	**130-140**, 160-170	90	175	85	**-**	-	-	-	-		Authors concluded T_h values >150°C due to stretching
		4	sp	98	**100-110**, 140-150	75	176*[1]	101	**5-6**, 14-15, 24-25	5.4	26.2	20.8	-23.5		Primary low T_h brine inclusions in late sphalerite
		4	cc, dol, ba	85	**120-130**	73	171*[2]	98	7-8, **20-21**	5.6	25.2	19.6	-22.9		Monophase inclusions occur
	Tynagh	5	-	303	**150-160**	80	280	200	**8**, 17	5	23	18.0	-		
		6	sp	60	**230-240**	181	243	62	**12-13**	8.1	13.5	5.4	-		Secondary low T_h brine inclusions common
		6	qz (o/g), ba	150	**150-160**	106	202†	96	**10-11**, 16-17, 20-21	6.4	23.2	16.8	-		Higher S modes and monophase brine inclusions in barite
	Galmoy	4, 7	sp	78	**160-170**	129	179	50	11-12, **13-14**	10.8	16.6	5.8	-22.4		
		7	dol, cc	75	**180-190**	111	228	117	**13-14**	8.8*[2]	20.9	12.1	-		
	Lisheen	8	sp	-	**-**	87	240	153	**-**	7	20	13.0	-		
		8	dol	-	**-**	145	260	115	**14-16**	14	16	2.0	-		
		4, 7	sp	282	**170-180**, 200-210	139*[1]	210*[2]	71	4-5, 11-12, 13-14, **17-18**	4.0	18.1	14.1	-22.6*[4]		Secondary low T_h brine inclusions common in sphalerite
		7	cc, dol, qz	101	150-160, **200-210**	123	277	154	12-13, **16-17**	5.4	24.6*[1]	19.2	-22.7		Abundant secondary low T_h brine inclusions, rare low S inclusions
S	Silvermines	4	sp	52	**180-190**	148	208	60	12-13, **17-18**	12.1	19.3*[1]	6.8	-23.1	0.0 (sp), 7.5 (sp)	
		9, 10	sp	35	**170-180**, 190-200	155	194	39	**14-15**	9.6	16.6*[3]	7.0	-		Inclusions with T_h in 79-130 range inferred to be secondary
		11	qz, sp, ba	-	-	190	280	90	**-**	-	-	-	-		Only 3 data (averages?) actually presented; T range in original ref. includes S isotope geothermometry
		9, 10	qz, cb, ba	331	170-180, **190-200**	72*[2]	248*[1]	176	15-16, **18-19**	8.3*[4]	27.5	19.2	-		Monophase brine inclusions predominant in barite
	PROSPECTS														
N	Tatestown	2	-	26	**180-190**	90	210	120	**10-12**	10	12	2	-		Salinity range cited by Hitzman (1995); not given by Andrew (1993)
		2	-	48	**140-150**	130	180	50	**11**, 18	-	-	-	-		
		12	sp	11	**180-190**	176	185	9	**11-12**	9.2	11.7	2.5	-		
	Keel	13	sp	-	**110-120**	117	123	6	-	17	22	5.0	-	-6.5	
		4	sp	47	**120-130**	107	192	85	**14-15**, 9-10	6.0	16.5*[4]	10.5	-23.9		Pale to transparent sp has T_h and salinity at low end of range
		14	qz	8	**180-190**	98	196	98	**5-6**	4.4	9.1	4.7	-		Quartz post-sphalerite
	Keel fault, Garrycam	15	sp	25	**~130**	110	187	77	**-**	18.4	24.2	5.8	-		Pale to transparent sp has T_h at low end of range
		15	dol	6	**~140**	136	159	23	-	-	-	-	-		No evidence of clathrates observed
	Garrycam	15	dol, ba	-	**-**	146	286	140	**~17**	-	-	-	-		No evidence of clathrates observed
	Moyvoughly	2	-	229	**190-200**	120	240	120	**9**	-	-	-	-		
	Harberton Bridge	16	-	-	**~100**	-	-	-	**-**	-	-	-	-		
		17	cc	29	**60-70**	48	70	22	**15-16**	9.8	20.1	10.3	-22.1, -34.7		Abundant monophase inclusions; possible two modes in hydrate melting temperature
	Kinnitty	18	cc	36	**50-60**	44	76	32	**20-21**	8.7	22.5	13.8	-21.3		
		19	sp	6	**170-180**	171	212	41	**14-15**	13.9	14.9	1.0	-	5.1(sp)	Reworked sp clast has low T_h population of 93-123 °C
	Cooleen	19	dol	39	**180-190**	129	225	96	**13-14**	10.8	17.6	6.8	-	8.5(sp), 9.2(py)	
		19	cc	34	**150-160**	95	177	82	11-12, **13-14**	4.8	14.2	9.4	-		
	Rathdowney prospects	7	dol	67	180-190, **210-220**, 250-260	155	267	112	11-12, **13-14**	1.4	22.4	21.0	-22.7		High T_h population at Durrow (DUR1-686)
	Holycross	7	sp	23	**170-180**	156	184*[4]	28	10-11, **16-17**	10.4	17.9	7.5	-22.7		Four inclusions with T_h in range 205-244°C
	Derrykearn	20	sp	-	-	185	228	43	-	13	18	5.0	-		Only ranges given
		20	dol	-	-	157	189	32	**~14**	-	-	-	-		Only ranges given
	Courtbrown	21	cc	40	**170-180**	160	190*[2]	30	-	-	-	-	-		Interpreted by authors to be "almost certainly not represenatative of mineralization temperatures"
S	Pallas Green	4	sp	3	**-**	141	172	31	**16-17**	13	16.1	3.1	-24.0	11.0(sp)	Drillhole sample: MN3268.9/174.1 m
		22	cc	18	**150-160**, 130-140	94	181	87	**10-12**	-	-	-	-	10.5(sp), 11.5(gn)	Drillhole samples: MN3268.4/148.7 m, MN3268.4/115.8 m, MN3268.15/155.7 m
	REGIONAL CARBONATES														
	Newcastle West	23	qz	-	-	160	190	30	-	-	-	-	-		
	Newcastle West	23	dol	-	-	160	200	40	-	~24	-	-	-		
	Midlands	24	dol, cc	-	**250-260**	164	271	107	**11-12**, 16-17¥	1.4	18.9	17.5	-		Fluid Type 1; not observed in supra-Waulsortian
	Midlands	24	dol, cc	-	**120-130**, 140-150§	55	209	154	2-3¥, **8-9**, 9-10§	0	16.2	16.2	-		Fluid Type 2
	Midlands	24	dol, cc	-	**90-100**, 140-150§	59	170*[3]	111	**25-26**	17.9	35.9	18.0	-		Fluid Type 3
	Midlands	4	dol	46	140-150, **190-200**	135	236	101	**12-13**	9.2	14.7	5.5	-		Coarse white dolomite
	Midlands	4	dol	43	180-190, **220-230**	175	257	82	**12-13**	10.5	14.2	3.7	-		White dolomite cemented breccia (white matrix breccia-type); clathrate occasionally observed
	Midlands	4	dol	90	**130-140**	81	159*[2]	78	**30-31**#	24.1#	32.8#	8.7	-1.7		Calcic brines in replacive dolomite: drillholes 97-3459-10, 97-2091-9, 99-2512-10, 99-2512-16, 00-2512-2
	Midlands	4	pink dol	49	**90-100**, 120-130	89	137*[4]	48	**23-25**	23.0	28.7	5.7	-17.9		Pink dolomite; drillhole samples 97-3476-01
	BASEMENT														
	SW Midlands area	4, 25	sp	71	150-160, **210-220**	135*[3]	224	89	11-12, 13-14, **16-17**	11.2*[3]	18.1	6.9	-23.2		Three low T_h, low S inclusions in one sample (KEL-20)
	SW Midlands area	4, 25	qz, cc, dol, ba	585	**170-180**	101*[12]	238	137	10-11, **13-14**, 17-18	8.4*[4]	20.6*[11]	12.2	-22.7		Low T_h, high S primary population in one qz sample (LAT-1); correlation between Tml and Tmhyd

*?Numbers of outliers unknown (incomplete bivariate plot)

n - Number of inclusions measured for Th; in most cases the number of salinity estimates will be less

† - Th values in euhedral ore-stage quartz at Tynagh extend up to 314°C with salinities of 7.0-24.8 wt%; high Th values in barite ignored

‡ - Modes unavailable; only ranges given

¥ - From sub-Waulsortian samples

§ - From supra-Waulsortian samples

- Salinities estimated from final ice melting temperatures using metastable extension of ice liquidus; these are underestimated by <8 % relative to NaCl-$CaCl_2$ modelling.

- not available

References: 1. Hitzman (1986); 2. Probert (1983); 3. Peace et al. (2003); 4. This study; 5. Unknown, erroneously referenced as Boast (1981) in Andrew (1993); 6. Banks and Russell (1992); 7. Eyre (1998); 8. Thompson et al. (1992); 9. Samson and Russell (1983); 10. Samson and Russell (1987); 11. Greig et al. (1971); 12. Roedder (1976); 13. Caulfield et al. (1986); 14. Collins (unpublished); 15. Thompson (1992) cited in Slowey et al. (1995); 16. Finlow-Bates, pers. comm. in Emo (1986); 17. Trude and Wilkinson (2001); 18. Strongman (unpublished); 19. Lee (2002); 20. Unknown, cited in Hitzman and Beaty (1996); 21. Reed and Wallace (2001); 22. Crowther and Wilkinson (unpublished); 23. Mulhall (2003); 24. Johnson et al. (2009); 25. Everett et al. (1999a).

Figure Captions

Fig. 1. Simplified geological map of Ireland showing localities mentioned in the text (numbered). 1. Abbeytown; 2. Tatestown; 3. Navan; 4. Keel; 5. Garrycam; 6. Moyvoughly; 7. Ballinasloe; 8. Tynagh; 9. Newcastle West; 10. Harberton Bridge; 11. Stradbally; 12. Kinnitty; 13. Derrykearn; 14. Durrow; 15. Ballyragget No. 1 borehole; 16. Rathdowney East; 17. Lisheen; 18. Galmoy; 19. Holycross; 20. Fantane; 21. Latteragh; 22. Silvermines; 23. Birdhill; 24. Ballycar; 25. Tobermalug; 26. Castlegarde; 27. Caherconlish South; 28. Srahane West; 29. Courtbrown; 30. Meelin No. 1 borehole; 31. Rocky Island. Modified after the Mineral Deposits of Ireland map (CSA Ltd and the Geological Survey of Ireland, 1994) and Everett et al. (2003).

Fig. 2. Summary of cementation and mineralization paragenesis in the Irish Midlands Basin. Modified from Wilkinson et al. (2003) and incorporating observations from Eyre (1998), Wilkinson and Earls (2000), Gregg et al. (2001), Reed and Wallace (2001), Lee and Wilkinson (2002) and Wilkinson et al. (2005b). The area filled with the breccia symbol indicates the range of paragenetic stages that are observed incorporated as clasts in synsedimentary breccias; the light grey field indicates the approximate timing of formation of undulose, subhorizontal solution seams (broadly synchronous with the onset of main hydrothermal activity); the hatched field indicates the main period of hydrothermal activity; and the dark grey field indicates the approximate timing of late, conventional stylolites (variable orientations).

Fig. 3. Plots of homogenization temperature as a function of maximum inclusion dimension for: (A) Lower Paleozoic-hosted feeder veins; (B) Regional Lower Carboniferous carbonate cements; (C) Mineral deposits. Data from Everett et al. (1999a) and Wilkinson (unpublished).

Fig. 4. Sketches of fluid inclusion assemblages from carbonate cements illustrating consistent microthermometric properties (homogenization temperatures and final ice melting temperatures), and systematic changes in relation to crystal growth zones. (A) Fine-grained replacement dolomite hosting LP_1 fluids displaying decreasing salinity and increasing T_h during growth. (B) Medium- to coarse-grained dolomite with core hosting B_3 brines and overgrowth hosting B_2 brines. Arrows indicate growth direction; dashed lines depict growth zones. Brackets indicate anomalous T_h, possibly due to leakage.

Fig. 5. Plot of Na# ($NaCl/[NaCl+CaCl_2]$) versus total salinity (wt% $NaCl+CaCl_2$ equivalent) based on ice and hydrate melting temperatures in fluid inclusions. Fields for Lower Paleozoic vein-hosted fluids (LP_1), deposit sphalerite-hosted ore fluids (LP_2) and inferred brine compositions are shown. Possible processes controlling variations in composition are indicated (see text for details). Data from one Silvermines sphalerite sample (BH K22/188') containing brine inclusions (Samson and Russell, 1987) and average data for barite and

Group 2 and 3 inclusions from Tynagh (Banks and Russell, 1992) are also shown. Comparative Southwest England brine data are from Stoffell et al. (2004) and Dead Sea brines from Klein-BenDavid et al. (2004).

Fig. 6. Halogen systematics of Irish fluids. (A) log Br versus log Cl plot; (B) Cl/Br versus Na/Br; (C) Cl/Br versus Ca/Br. Possible mixing and exchange trajectories are shown. Dashed lines in (B) represent 25 and 50% Na loss from evaporated seawater precursors. Seawater evaporation trajectory from McCaffrey et al. (1987). Compositions of modern seawater and seawater-derived brine with an evaporation ratio of 25x are shown for reference (stars).

Fig. 7. Range of major, minor and trace element compositions of LP_1 fluids (mean values from Fantane, Latteragh, Birdhill and Ballycar; Wilkinson et al., 2005a and unpublished) normalized to an evaporated seawater precursor (prior to gypsum precipitation). This illustrates the element gains/losses undergone by partially evaporated seawater during basement circulation. A range of ocean ridge vent fluid compositions are shown for comparison, normalized to a normal seawater precursor (data from TAG, MARK-1, MARK-2 and 21°N OBS; Von Damm, 1990).

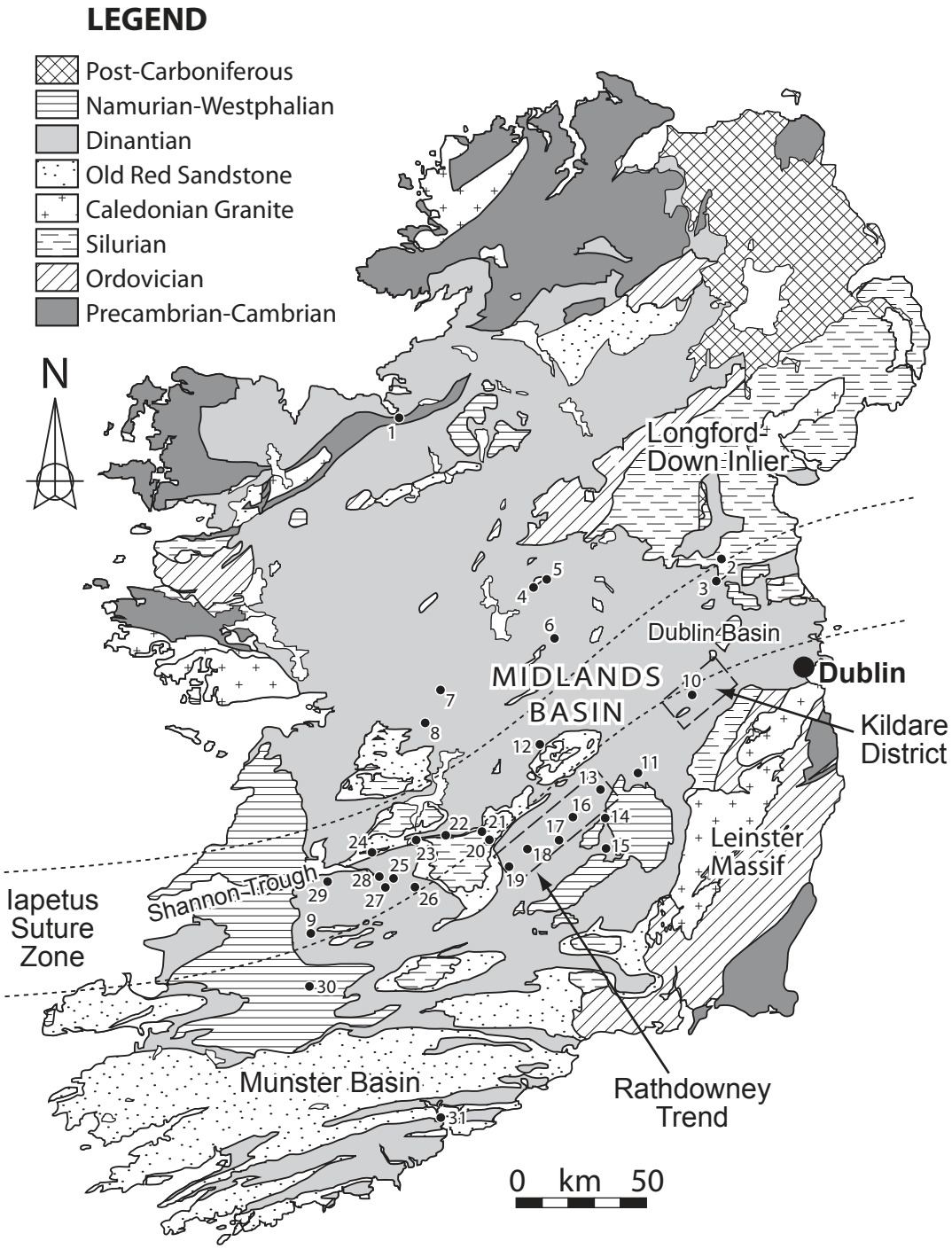
Fig. 8. Calculated $\delta^{18}O$ and measured δD compositions of water trapped in quartz-hosted fluid inclusions from Lower Paleozoic-hosted veins compared with results from Silvermines (Samson and Russell, 1987). Possible Lower Carboniferous seawater composition derived from data in Veizer et al. (1999) and assuming consistent relationship between seawater oxygen and hydrogen isotope compositions and a constant global meteoric water line. Seawater evaporation trajectory from Knauth and Beeunas (1985) and shown for both modern seawater (green) and possible Lower Carboniferous seawater (blue) starting points. Solid sausage-shaped fields indicate compositions for seawater partially evaporated to the degree inferred for the LP_1 fluids. Dashed curves illustrate modeled exchange trajectories for the extremes of the two fields, calculated at 200 and 300 °C. Range and mean Lower Paleozoic wholerock compositions from Thomas et al. (1985). Rock-fluid fractionation factors ($\Delta^{O}_{r\text{-}w}$ = 7.0, 3.4 at 200 and 300 °C respectively; $\Delta^{H}_{r\text{-}w}$ = -32.6, -33.2 at 200 and 300 °C respectively) estimated using the approach outlined in Samson and Russell (1987). Most of the LP_1 fluid compositions can be explained by small degrees of mixing between fully basement-equilibrated fluids with low δD brines, possibly produced by strong evaporation (25x evaporation ratio) of ^{18}O- and D-depleted Lower Carboniferous seawater. The higher temperature Silvermines orefluids (LP_2) do not fit the modeling implying use of inappropriate fractionation factors or, potentially, exchange with unusually low δD basement rocks.

Fig. 9. Modal homogenization temperature-salinity plot for all localities in the Irish Midlands based on the data compiled in Table 1. With a few exceptions, localities north and west of the Iapetus Suture plot in the lower left of the diagram and those from the south and east plot in the upper right suggesting a broad

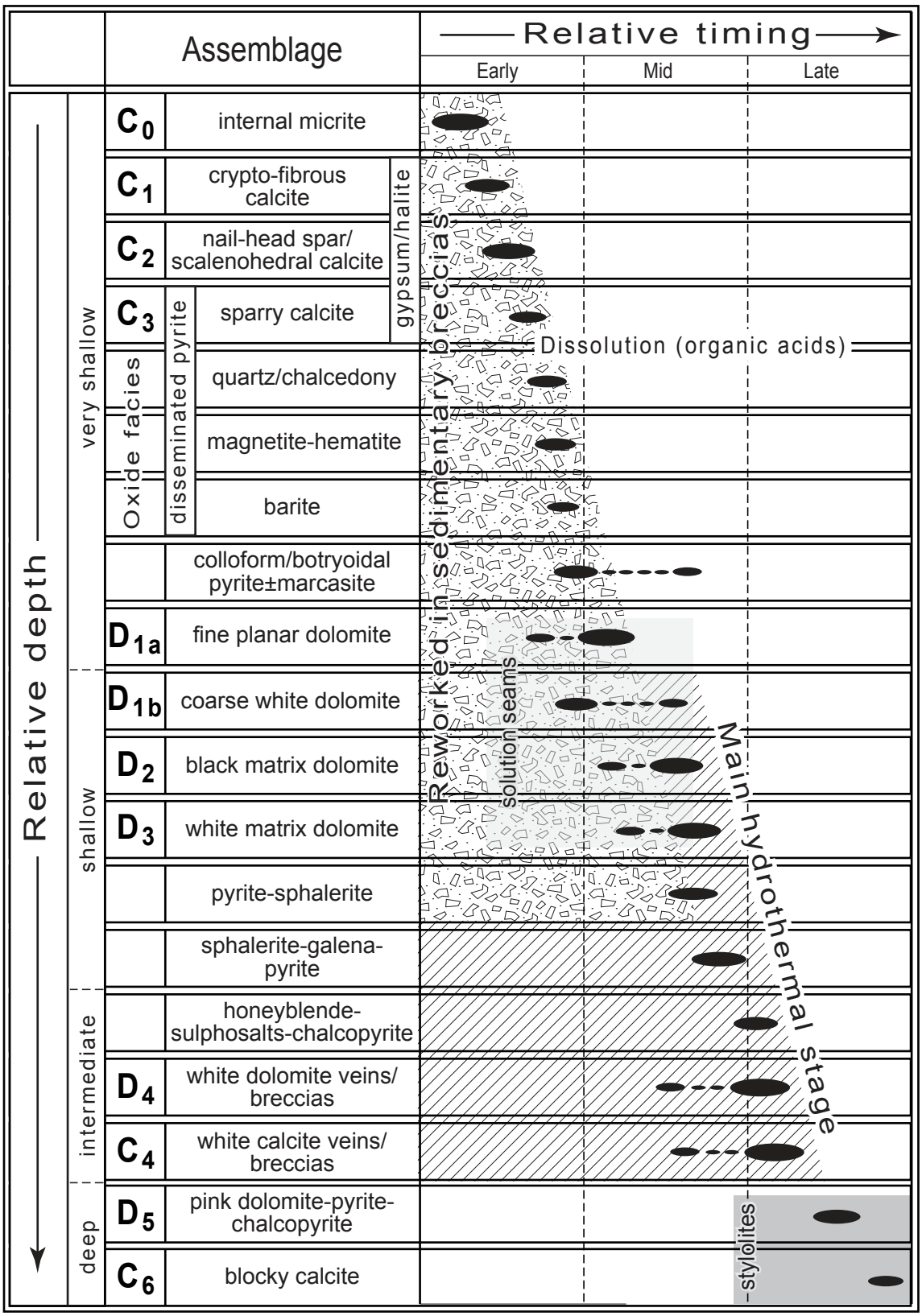
division into two main flow compartments. Exceptions are: low temperature brines at Navan that are at least partly post-ore because they occur in late stage vug-filling cements and in veins that extend far into the hanging wall stratigraphy; and high temperature, sphalerite-hosted inclusions at Tynagh (Banks and Russell, 1992).

Fig. 10. Diagrams illustrating fluid processes and controls on mineralization. A. Schematic cross-section illustrating processes responsible for generation of fluid types and chemical exchange during crustal circulation. Note approximate 2x vertical exaggeration; B. Three-dimensional cartoon representation of fault arrays, seafloor topography and mixing processes operating in the ore-forming environment. White arrows indicate possible brine migration pathways from uplifted footwall into hanging wall depressions via relay ramps; C. Representation of paleogeography in the Irish Midlands showing localization of deposits (red areas represent projection of massive sulfide lenses to the paleoseafloor) on the basinward side of fault-controlled shelves/islands where strongly evaporated bittern brines were generated.

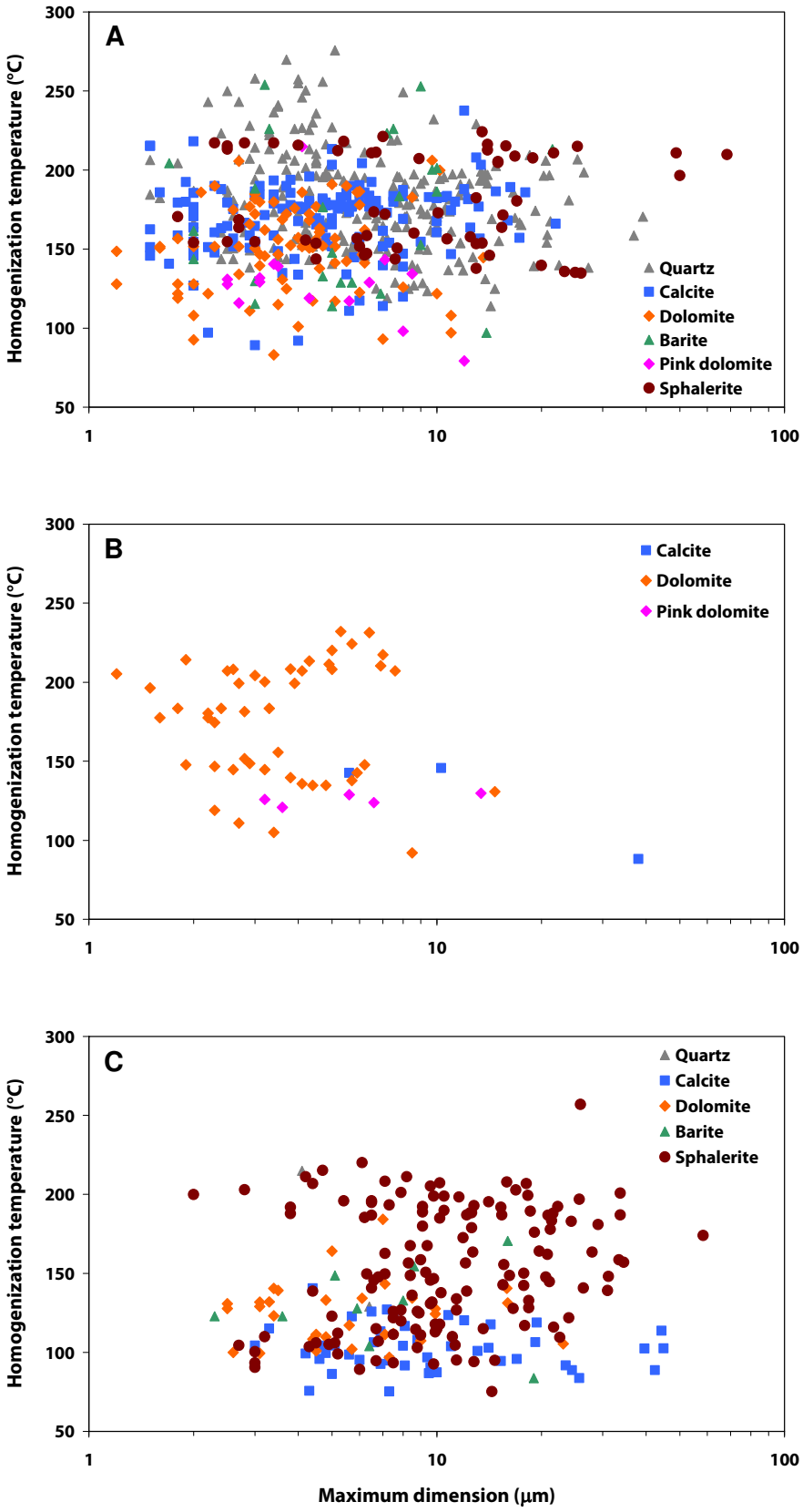
Wilkinson_Fig. 1



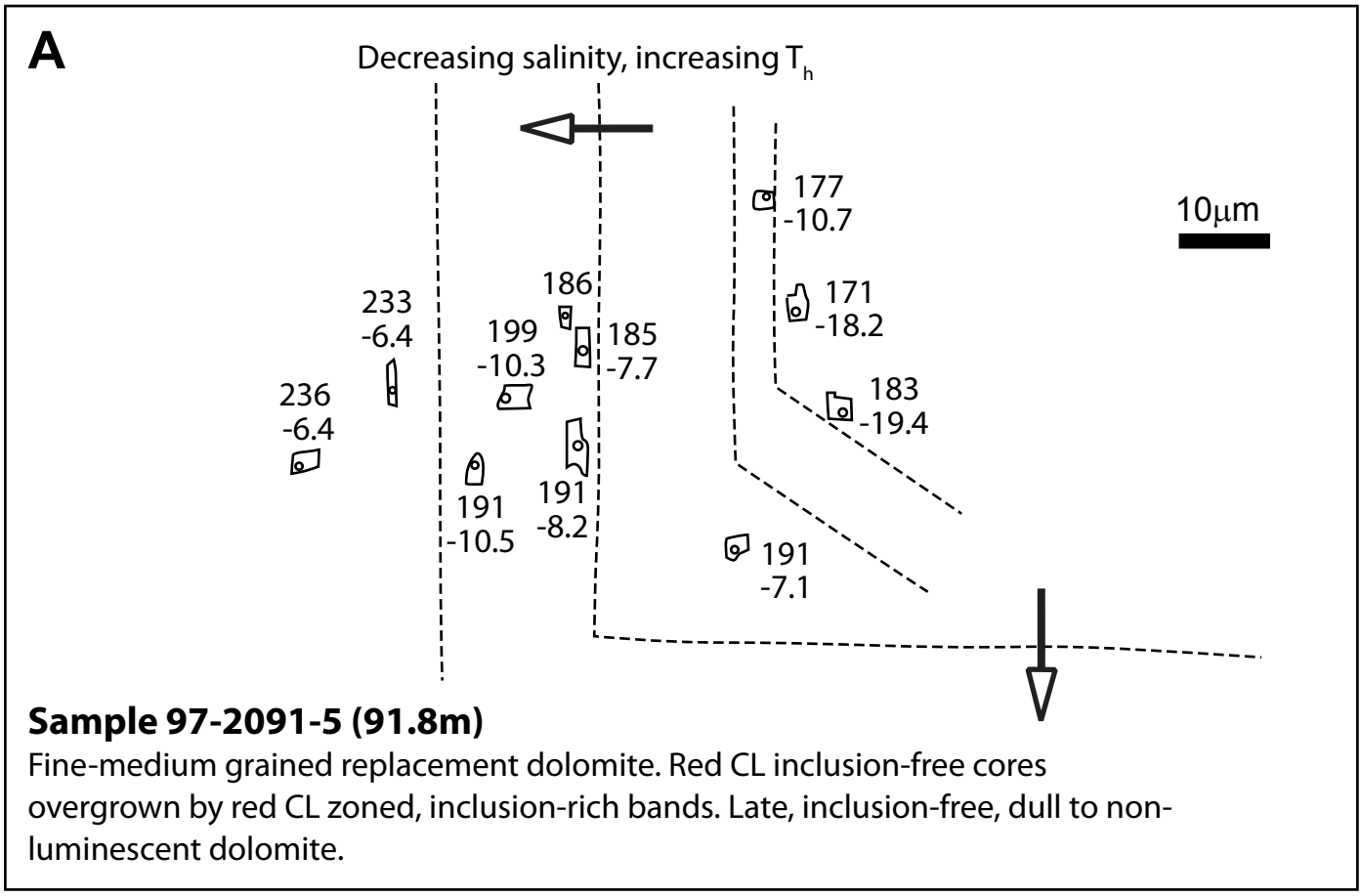
Wilkinson_Fig. 2



Wilkinson_Fig.3



Wilkinson_Fig. 4



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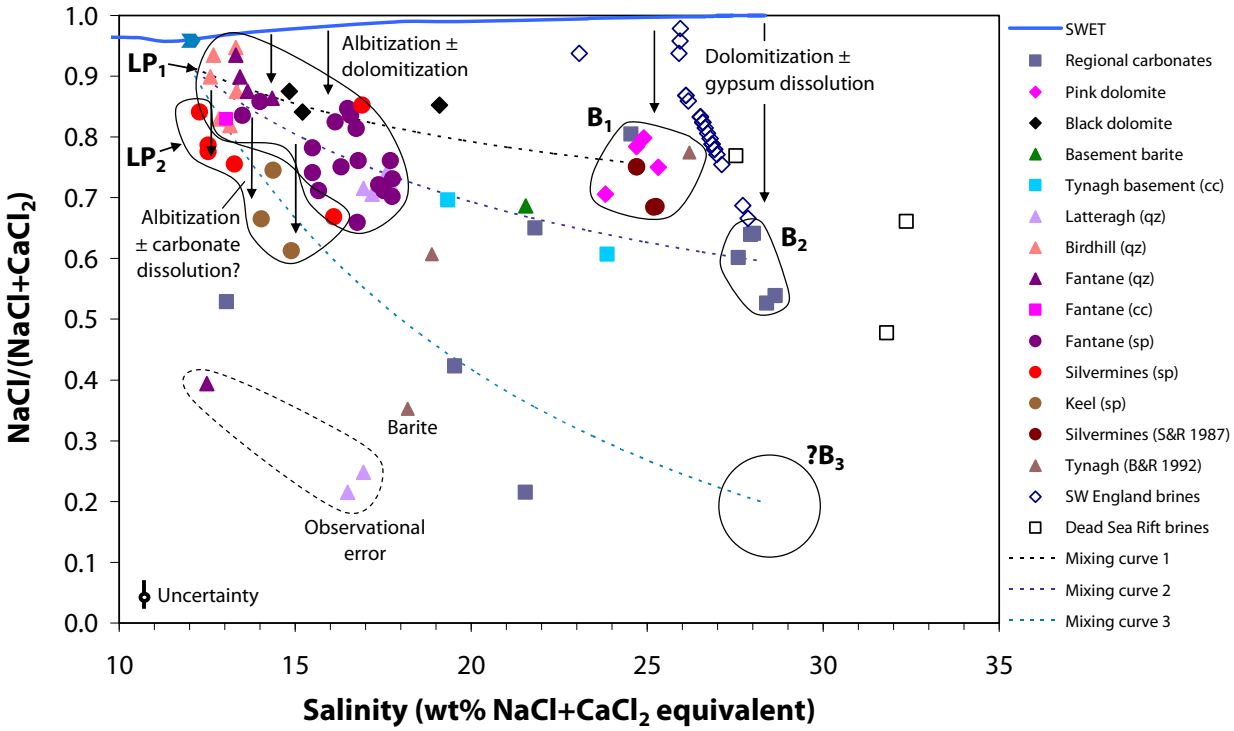
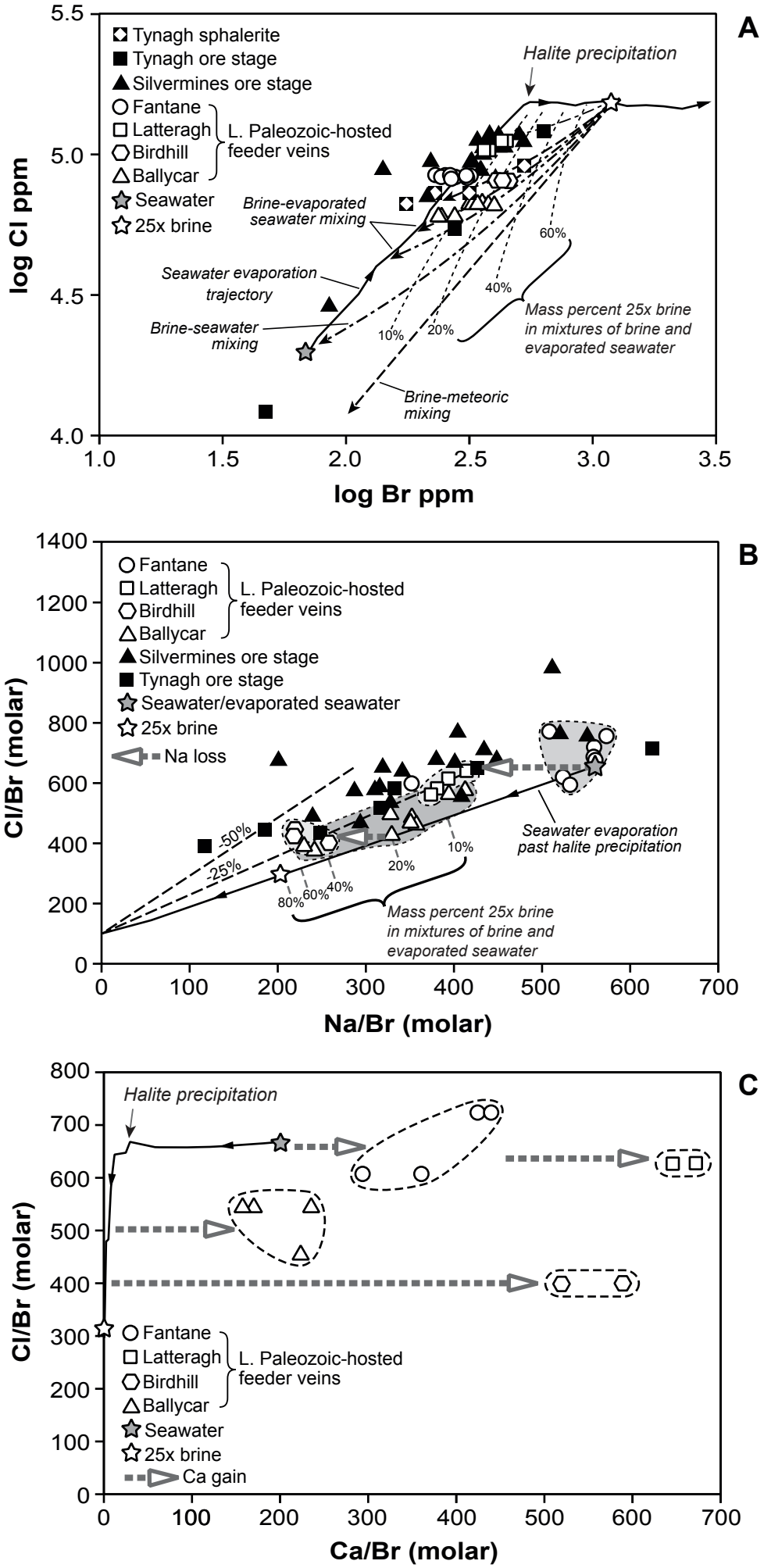
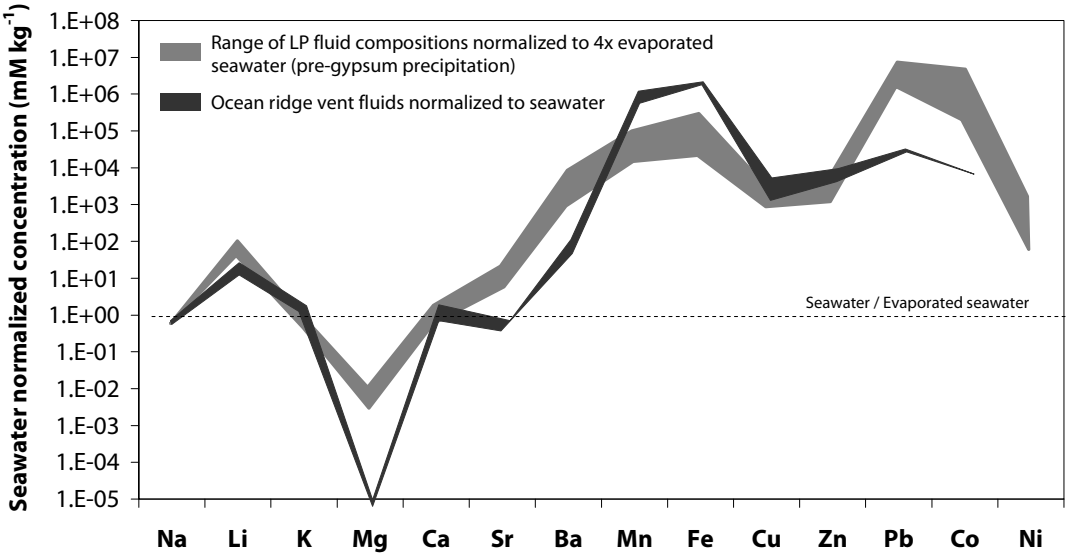


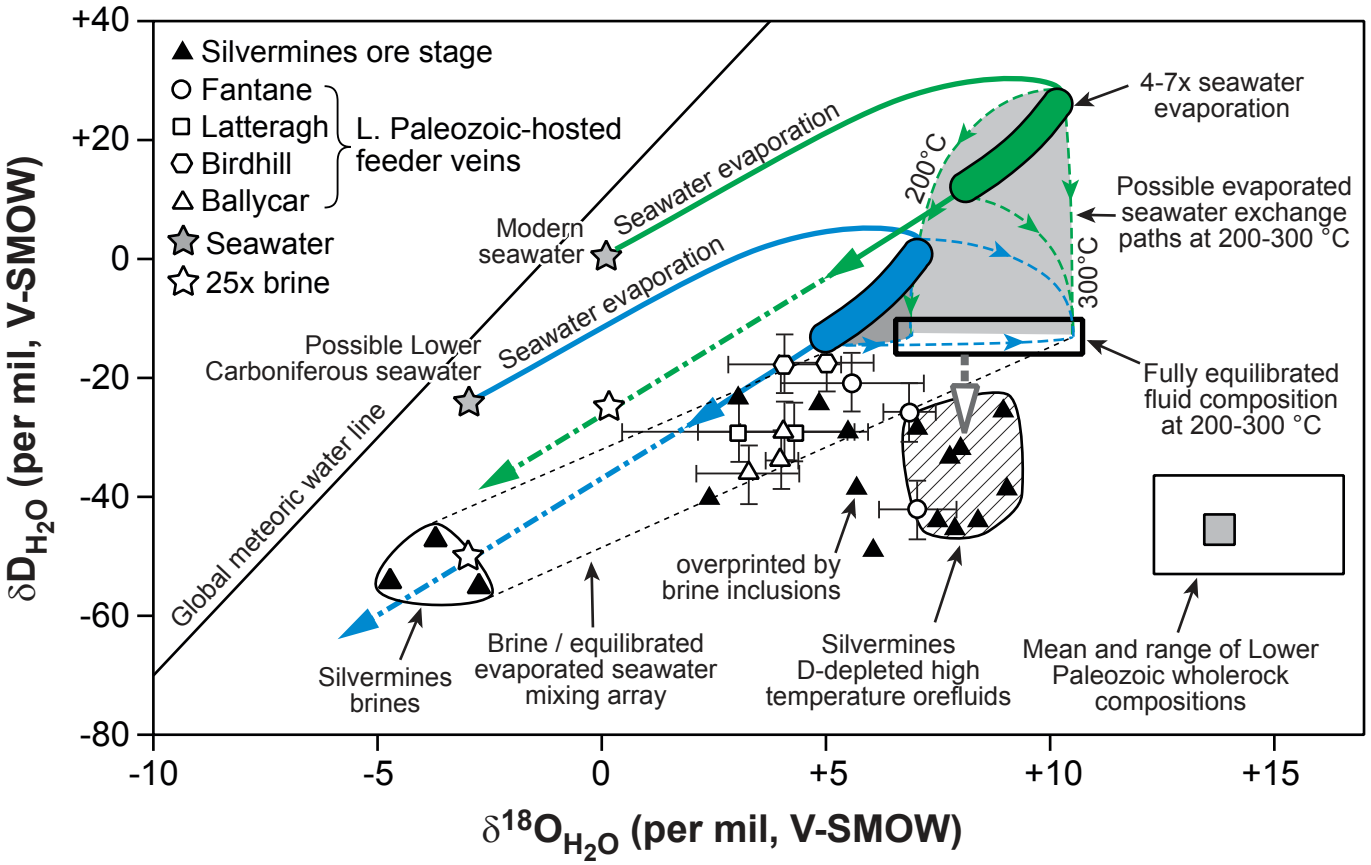
Wilkinson_Fig. 6



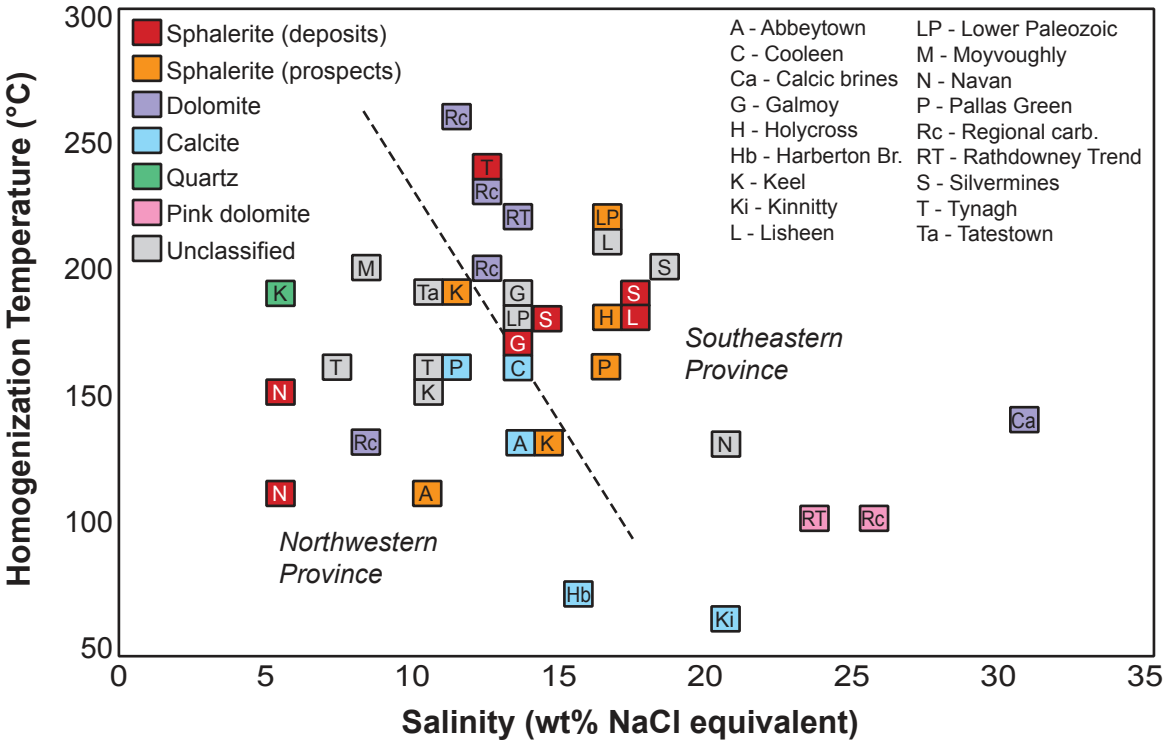
Wilkinson_Fig. 7



Wilkinson_Fig.8



Wilkinson_Fig.9



Wilkinson_Fig.10