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

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Abstract

Many fluid inclusion studies have been carried out in the Irish Midlands basin ore field (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 to 28 wt percent NaCl equiv but with the majority falling in the moderate-salinity range between 8 and 19 wt percent. 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 farther 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 ore field, range from 70° to 280°C but with the majority falling between 130° and 240°C. There is no evidence for systematic stretching or leakage of inclusions related to the postentrapment 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 Mississippi Valley-type (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 that hydrothermal fluid activity occurred over an extremely large area (>30,000 km²) 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 that 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 and/or 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 hanging-wall depressions where they ponded within permeable sediments and became enriched in H₂S via bacteriogenic sulfate reduction. The coincidence of structurally controlled, hightemperature reaction zones, brine-producing footwalls, and hanging-wall 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 ore field 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.

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Introduction

THE CARBONIFEROUS Irish Midlands basin hosts a remarkable concentration of base metals (~17 Mt known) in a prospective area of approximately 200×150 km. In addition to the known prospects, operating mines at Navan, Lisheen, and Galmoy, and the historic 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 hostrock sequences (Blakeman, pers. commun.). Such extensive mineralization implies the operation of a giant hydrothermal system of significant academic as well as economic interest. Indeed, the ore field 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 historic review of fluid inclusion studies carried out in the Irish ore field, including investigations of individual mineralized systems (deposits and prospects) as well as regional studies in the hostrock 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.

Geologic 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 nonargillaceous 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 volcano-sedimentary 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 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 initiated upon deposition of the carbonate sediments, with significant cementation occurring within a few tens of meters of the sea floor (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 subeconomic mineralization, a variety of massive, disseminated, breccia- and veinfilling 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 strata bound and occur as single or multiple lenses hosted by favorable horizons within the host-rock 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 to 7 imply temperatures of 300° to >550°C.



FIG. 1. Simplified geologic 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 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 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).

Any reequilibration 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 reequilibration (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 reequilibration 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 reequilibration 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 and/or 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

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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 gray 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 gray field indicates the approximate timing of late, conventional stylolites (variable orientations).

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 reequilibration 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 postentrapment 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 postentrapment 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).



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 (unpub.).

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 postentrapment reequilibration 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



overgrown by red CL zoned, inclusion-rich bands. Late, inclusion-free, dull to nonluminescent dolomite.



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 relationship to crystal growth zones. (A). Fine-grained replacement dolomite hosting LP₁ fluids displaying decreasing salinity and increasing T_h during growth. (B). Medium- to coarse-grained dolomite with core hosting B₃ brines and overgrowth hosting B₂ brines. Arrows indicate growth direction; dashed lines depict growth zones. Brackets indicate anomalous T_h, possibly due to leakage.

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 to 7 compared with values of 5 to 5.5 in normal limestones from the same drill hole 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 drill hole (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.

Historic Review of Fluid Inclusion Studies

Fluid inclusion studies in the Irish ore field 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 and/or 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-sea floor 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 subsea-floor environment (Anderson et al., 1998; Blakeman et al., 2002; Lee and Wilkinson, 2002; Wilkinson et al., 2003, 2005a, b) 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 ($T_{m(hydrate)}$), 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 (USGS unpub. 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 \pm 0.5 and -8.0 \pm 0.2°C

 $\begin{array}{c} 1 \ inclusion \ -6.0 \ \pm \ 0.1^{\circ}C \\ Filling \ [homogenization] \ temperature: \\ 3 \ inclusions \ 176 \ \pm \ 5^{\circ}C \\ 5 \ inclusions \ 185 \ \pm \ 3^{\circ}C \end{array}$

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.

Early results were also reported by Greig et al. (1971) from Silvermines. Only three data points (possibly averages of individual samples) were presented on a plot of T_h vs. distance from the Silvermines fault zone; these indicated T_h values of 190° to 280°C for inclusions hosted by quartz, sphalerite, and barite. Further reconnaissance results were presented by Probert (1983; cited in Andrew, 1993) from locations in the northern Midlands including the Navan deposit and the Keel, Moyvoughly, and Tatestown prospects (Fig. 1). The absence of paragenetic or spatial control makes interpretation of these results risky, but some comparisons with subsequent studies can be made (Table 1). More recent and carefully constrained results from Navan (this study) do not replicate these early measurements although it should be noted that the high-grade core of the deposit was mined out in the 1980s to 1990s.

Silvermines: The first detailed fluid inclusion study was carried out principally on the lower (epigenetic) orebodies and Old Red Sandstone-hosted footwall veins from the Silvermines deposit (Samson, 1983; Samson and Russell, 1983). Homogenization temperature and salinity data (modeled in the NaCl-H₂O system) were reported from inferred primary and pseudosecondary liquid-vapor fluid inclusions in quartz, sphalerite, calcite, and dolomite, and salinity data from the predominantly monophase liquid inclusions in barite. Extended results, including the addition of the first bulk analytical (crush-leach) chemical and isotopic (decrepitation, crushing) data and the observation and identification of trapped phases (calcite) in some inclusions were presented in a comprehensive, benchmark study by Samson and Russell (1987).

Wide ranges in microthermometric properties were observed (Table 1) and the occurrence of some vapor-rich inclusions in quartz was taken as evidence for episodic boiling; similar inclusions in carbonate and barite were discounted. Since then, vapor-rich inclusions have not been reported from the ore field (apart from in one lower Paleozoic basement-hosted vein sample; Everett et al., 1999a) so it is likely that boiling was not a common process in the district (Wilkinson et al., 2003). A broad negative correlation between T_h and salinity was interpreted as the first direct evidence for fluid mixing in the Irish deposits, previously suggested based on sulfur isotope data and the chemical conditions of sulfide deposition (Boast et al., 1981). An important detail within this correlation is that samples from different geographic locations and paleodepths within the system tend to fall in different parts of the array, consistent with a relatively stable mixing zone between higher temperature, less saline fluids at depth (and possibly also on the fringes of the system), and more saline, cooler fluids higher up and in the center, proximal to the main ore zones.

Tynagh: Tynagh, the first Zn-Pb deposit to be discovered in the lower Carboniferous of the Midlands basin, was the subject of a fluid inclusion study by Banks and Russell (1992). Primary and secondary inclusion data were reported from limestone-hosted vein sphalerite from epigenetic 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 Old Red Sandstone 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

TABLE 1. Summary of Microthermometric

					Homo	genization '	Г (°С)		Salinity (wt % NaCl equiv)
	Location	Ref.	Minerals	n	Mode(s)	Min	Max	Spread	Mode(s)
	Deposits								
Z	Abbertown	1	s n	3	100-110	105	193	18	10-11
	Abbeytown	1	sp	18	130-140	88	180	92	19-13 24-25
	Navan	2	-	6	180-190	-	100	52	24
	ivavali	3	dol sn	40	130-140 160-170	90	175	85	-
		4	sn	98	100-110 , 100-170 100-110 , 140-150	75	176*1	101	5-6 14-15 24-25
		4	ce dol ba	85	120-130	73	171*2	98	7-8 20-21
	Tymagh	5	-	303	150-160	80	280	200	8 17
	Tynagn	6	sn	60	230-240	181	200	62	12-13
		6	$\frac{3P}{\alpha z (\alpha/\sigma)}$ ha	150	150-160	101	202†	96	10-11 16-17 20-21
	Galmov	4 7	sn	78	160-170	129	179	50	11-12 13-14
	Gannoy	7	dol co	75	180-190	111	228	117	13_14
	Lishaan	8	uoi, ce	10	100-150	87	240	153	-
İ	Lisiteen	8	dol	_	-	145	240	115	14-16
		47	sp	282	170-180 200-210	139*1	210*2	71	4.5 11.12 13.14 17.18
		7	sp ce dol az	101	150-160, 200-210	100	210	154	19-13 16-17
	Silvermines	4	ee, uoi, qz	52	180-100, 200-210	148	208	60	12-13, 17-18
	Suvernines	9 10	sp	35	170-180 190-200	155	194	30	14-15
		11	az en ha	00	170-100, 100-200	100	280	90	-
		11	qz, sp, ba	-	-	100	200	50	-
s		9, 10	qz, cb, ba	331	170-180, 190-200	72* ²	248^{*1}	176	15-16, 18-19
	Prospects								
z	Tatestown	2	_	26	180-190	90	210	120	10-12
	Keel	2	_	48	140-150	130	180	50	11 18
	1001	12	SD	11	180-190	176	185	9	11-12
		13	sp	-	110-120	117	123	6	-
		4	sp	47	120-130	107	192	85	14-15 9-10
		14	3P 07	8	180-190	98	196	98	5-6
	Keel fault Garrycam	15	sn sn	25	~130	110	187	77	-
	Reef lault, Garrycan	15	dol	6	~140	136	159	23	
	Carrycam	15	dol ba	-		146	286	140	~17
	Mowoughly	2	-	229	190-200	120	240	120	9
	Harberton Bridge	16	_		~100	120	240	120	-
	nuberton bridge	17	00	29	60-70	48	70	22	15-16
		11	ce	20	00-10	0F	10	22	10-10
	Kinnitty	18	сс	36	50-60	44	76	32	20-21
	Cooleen	19	sp	6	170-180	171	212	41	14-15
		19	dol	39	180-190	129	225	96	13-14
		19	сс	34	150-160	95	177	82	11-12, 13-14
	Rathdownev	7	dol	67	180-190, 210-220 ,	155	267	112	11-12, 13-14
	prospects				250-260				,
	Holveross	7	sp	23	170-180	156	184^{*4}	28	10-11, 16-17
	Derrykearn	20	sp	-	-	185	228	43	-
		20	dol	-	-	157	189	32	~14
	Courtbrown	21	сс	40	170-180	160	190^{*2}	30	-
	D.II. C.			2		1.41	150	01	10.17
	Pallas Green	4	sp	3	- 150 160 120 140	141	172	31	16-17
		ZZ	ee	18	150-100 , 130-140	94	181	87	10-12
	Regional Carbonates								
	Newcastle West	23	qz	-	-	160	190	30	-
	Newcastle West	23	dol	-	-	160	200	40	-
	Midlands	24	dol, ee	-	250-260	164	271	107	11-12 , 16-17¥
	Midlands	24	dol, ee	-	120-130 , 140-150§	55	209	154	2-3 [¥] , 8-9 , 9-10 [§]
	Midlands	24	dol, ee	-	90-100 , 140-150§	59	170^{*3}	111	25-26
	Midlands	4	dol	46	140-150, 190-200	135	236	101	12-13
	Midlands	4	dol	43	180-190, 220-230	175	257	82	12-13

Data from the Irish Ore Field

Salinity (wt % NaCl equiv)					
Min	Mari	Connord	Thud	$\delta^{34}S$	Notes
Min	Max	Spread	1 _m nya	(%0, V-CD1)	Notes
10	11	1.0	-		
10	25	15.0	-		Postore calcite-py breccia: 139°-174°C, 10-13 wt %
20	25	5.0	-		
-	-	-	-		Authors concluded T _h values >150°C due to stretching
5.4	26.2	20.8	-23.5		Primary low T _h brine inclusions in late sphalerite
5.6	25.2	19.6	-22.9		Monophase inclusions occur
5	23	18.0	-		
8.1	13.5	5.4	-		Secondary low T _h brine inclusions common
6.4	23.2	16.8	-		Higher salinity modes and monophase brine inclusions in barite
10.8	16.6	5.8	-22.4		
8.8^{*2}	20.9	12.1	-		
7	20	13.0	-		
14	16	2.0			
4.0	18.1	14.1	-22.6*4		Secondary low T _h brine inclusions common in sphalerite
5.4	24.6*1	19.2	-22.7		Abundant secondary low T _h brine inclusions, rare low salinity inclusions
12.1	19.3*1	6.8	-23.1	0.0 (sp), 7.5 (sp)	
9.6	16.6*3	7.0	-		Inclusions with T_h in 79-130 range interred to be secondary
-	-	-	-		Only 3 data (averages?) actually presented; temperature range in original ref.
0.0*/	~~~~	10.0			includes salinity isotope geothermometry
8.3*4	27.5	19.2	-		Monophase brine inclusions predominant in barite
10	10	0			(1007)
10	12	2	-		Salinity range cited by Hitzman (1995); not given by Andrew (1993)
-	- 11.7	- 0 =	-		
9.2	11.7	2.5	-	05	
17	22 16 5*4	5.0 10 F	-	-0.0	Pale to two groups and alorite has T and calinity at low and of you go
6.0	10.5**	10.5	-23.9		Pale to transparent sphalerite has 1_h and samity at low end of range
4.4	9.1	4.1 E 0	-		Pala to transmort enhalerite has T at law and of range
10.4	24.2	5.0	-		rate to transparent sphaterine has T_h at low end of range
-	-	-	-		No evidence of clathrates observed
-	-	-	-		No evidence of clamfates observed
-	-	-	-		
9.8	20.1	10.3	-991-347		Abundant monophase inclusions, possible two modes in hydrate melting
0.0	20.1	10.0	-22.1, -04.7		temperature
87	22.5	13.8	-21.3		temperature
13.9	14.9	10.0	-21.0	51(m)	Reworked enhalerite clast has low Ty population of 93-193 °C
10.5	17.6	6.8		8.5(sn) - 9.2(nv)	Reworked sphalerite clast has low 1 _h population of 55-125 C
4.8	14.2	9.4	_	0.0(3p), 0.2(py)	
1.0	22.4	21.0	-22.7		High T. population at Durrow (DUB1-686)
					ingi il population a Dation (Deni 666)
10.4	17.9	7.5	-22.7		Four inclusions with T _b in range 205°-244°C
13	18	5.0	-		Only ranges given
-	-	-	-		Only ranges given
-	-	-	-		Interpreted by authors to be "almost certainly not representative of
					mineralization temperatures"
13	16.1	3.1	-24.0	11.0(sp)	Drillhole sample: MN3268.9/174.1 m
-	-	_	_	10.5(sp), 11.5(gn)	Drillhole samples: MN3268.4/148.7 m, MN3268.4/115.8 m.
				· I // · · · · · · · · · · · · · · · · ·	MN3268.15/155.7 m
-	-	-	-		
~24	-	-	-		
1.4	18.9	17.5	-		Fluid type 1; not observed in supra-Waulsortian
0	16.2	16.2	-		Fluid type 2
17.9	35.9	18.0	-		Fluid type 3
9.2	14.7	5.5	-		Coarse white dolomite
10.5	14.2	3.7	-		White dolomite cemented breccia (white matrix breccia-type);
					clathrate occasionally observed

								TABLE 1.	
				Home	ogenization T	Γ (°C)		Salinity (wt % NaCl equiv)	
Location	Ref.	Minerals	n	Mode(s)	Min	Max	Spread	Mode(s)	
Midlands	4	dol	90	130-140	81	159^{*2}	78	30-31#	
Midlands	4	pink dol	49	90-100 , 120-130	89	137^{*4}	48	23-25	
<u>Basement</u> SW Midlands area SW Midlands area	4, 25 4, 25	sp qz, cc, dol, ba	71 585	150-160, 210-220 170-180	135*3 101*12	224 238	89 137	11-12, 13-14, 16-17 10-11, 13-14 , 17-18	

*n = number of outliers excluded

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

t - 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-CaCl2 modeling

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 "postore" 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 equiv; T_{m(hydrate)} -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 postore pink dolomite and later calcite widely developed in the Midlands basin (the D₅ and C₆ 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 ground waters 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 ore field (Fig. 1) and its genetic relationship to it remains enigmatic. A small number of two-phase fluid inclusions were analyzed 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 to 13 wt percent NaCl equiv, salinities that are typical of ore-related inclusions throughout the Midlands basin. The T_h values varied from 85° to 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 host-rock 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 liquidvapor 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-CaCl₂-H₂O system. Fluid inclusions in sphalerite showing permissive evidence for a primary origin displayed T_{m(hydrate)} of $-22.6^{\circ} \pm$ 0.3° C, indicating the dominance of NaCl (e.g., see Bodnar, 2003b). These yielded salinities mostly in the range 10.2 to 18.0 wt percent NaCl equiv. 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° to 210°C (up to 241°C) with the highest mode observed for samples

Salinity (wt % NaCl equiv)			equiv)		504G					
	Min	Max	Spread	T _m hyd	0 ³⁴ S (‰, V-CDT)	Notes				
	24.1#	32.8#	8.7	-1.7		Calcic brines in replacive dolomite: drill holes 97-3459-10, 97-2091-9, 99-2512-10, 99-2512-16, 00-2512-2				
	23.0	28.7	5.7	-17.9		Pink dolomite; drill hole samples 97-3476-01				
	11.2*3 8.4*4	18.1 20.6*11	6.9 12.2	-23.2 -22.7		Three low T_h , low S inclusions in one sample (KEL-20) Low T_h , high S primary population in one qz sample (LAT-1); correlation between TmI and Tmhyd				

- not available

(Cont.

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 (unpub.), 15 = Thompson (1992) cited in Slowey et al. (1995), 16 = Finlow-Bates, pers. commun. in Emo (1986), 17 = Trude and Wilkinson (2001), 18 = Strongman (unpub.), 19 = Lee (2002), 20 = unknown, cited in Hitzman and Beaty (1996), 21 = Reed and Wallace (2001), 22 = Crowther and Wilkinson (unpub.), 23 = Mulhall (2003), 24 = Johnson et al. (2009), 25 = Everett et al. (1999a)

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- 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" (drill hole 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 postore-stage pink dolomite (D₅) 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 to 16.3 wt percent NaCl equiv and a relatively narrow range of homogenization temperatures between 129° and 179°C (Table 1), notably lower than at Lisheen. Hydrate melting was recorded in one sample at $-22.4^{\circ} \pm 0.2^{\circ}$ C, indicating predominance of NaCl over CaCl₂. 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 synore-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 $T_h (111^\circ - 228^\circ C)$ and salinity but are consistent with the possible mixing trend defined at Lisheen.

Subeconomic prospects

Studies of the subeconomic prospects in the ore field have been important in order to constrain relative timing of mineralization in less intensely altered environments and to compare geologic 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 strata-bound 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° to 187°C and salinities of 11 to 24 wt percent NaCl equiv 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 metalgold epithermal deposits (Čorbett, 2004). Post-sphalerite quartz contains the most dilute inclusions (4.4-9.1 wt % NaCl equiv; Collins, unpub. M.Sc. dissertation, Imperial College London, 2005; this study), suggesting that dilution eventually quenched mineralization. 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 MVT sulfide- and carbonate-cemented breccia deposits (Holdstock, 1982). The Kildare district has been widely cited as hosting an end member of the spectrum of styles of deposit in the ore field (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 marcasitecalcite, 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 drill hole, 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° to 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 percent NaCl equiv, 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° to 80°C and modal salinity of 20 to 21 wt percent with a total range of 8 to 22 wt percent NaCl equiv (Table 1). Hydrate was commonly observed with a modal melting temperature of -21.3°C, indicating dominance of Na over Ca (Strongman, unpub. M.Sc. 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 that 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 1990s before being abandoned as uneconomic. Mineralization is replacive and is focused within partially and wholly dolomitized sedimentary breccias. It comprises stratiform massive, semimassive, 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 are 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 $T_h = 180^\circ - 190^\circ C$; salinity = 10.8-17.6 wt % NaCl equiv) and calcite (modal T_h = 150°-160°C; 4.8-14.2 wt % NaCl equiv) 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° to 180°C with salinity modes at 10 to 11 and 16 to 17 wt percent NaCl equiv (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° to 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 sphaleritehosted 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° to 100° and 80° to 90°C respectively). Secondary, low $T_{\rm h}$ brine inclusions (28-29 wt % NaCl equiv), 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° to 190°C (Reed and Wallace, 2001). Freezing data were not reported. Although these results are within the most common range for fluids in the ore field (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 postentrapment modification based on inferred overheating to \sim 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 ore field. Mineralization at Castlegarde comprises a variety of breccias, and replacement and cavity-fill styles. Early marcasite and pyrite, which may form massive intervals in drill core, have partly replaced early calcite cements, and Waulsortian host-rock clasts. Sphalerite is often very finely color banded, partly replaces earlier Fe sulfides, and contains later euhedral and dendritic galena (Crowther and Wilkinson, unpub. report to the Noranda-Minco joint venture, 2002).

Two-phase fluid inclusions were analyzed in calcite that fills sulfide-lined vugs and is sometimes replaced by sulfides. The majority of T_h values ranged from 132° to 181°C with a mode of 150° to 160°C. Salinities varied from 16.1 to 4.3 wt percent 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 1990s. 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 drill core through the late 1990s (Wilkinson, unpub. 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 (preore) 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-vapor inclusions in coarse white "regional" dolomite (Fig. 2) in the 1990s (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, nonplanar replacement dolomite yielded rare data from twophase aqueous inclusions with T_h values of 170° to 200°C and salinities of ~2 to 15 wt percent NaCl equiv (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 liquidvapor fluid inclusions, distributed along growth zones, in Waulsortian-hosted samples of coarse white dolomite from throughout the Midlands (Wilkinson, 2003; unpub. data). T_h data are in the range 140° to 240°C with salinities of 10 to 15 wt percent NaCl equiv, identical to the majority of hydrothermal fluids observed in the deposits (Table 1).

White dolomite-cemented breccias: Breccias cemented by planar to nonplanar 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 liquidvapor 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 CO₂, 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, nonplanar 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 CaCl₂. 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° to 204°C, salinities of 13.5 to 19.9 wt percent NaCl equiv, and $T_{m(hydrate)}$ 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 ($\sim 12 \text{ wt } \%$), 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 twophase inclusions with T_h values of 144° to 203°C and salinities of 10.3 to 13.5 wt percent NaCl equiv, similar to coarse white dolomite elsewhere.

Pink dolomite: Paragenetically late, coarse-grained, cream to pink dolomite (Fig. 2) is widely observed in the Midlands as a replacement, vug- and vein-filling cement phase (e.g., Boast et al., 1981; Andrew, 1986; Eyre, 1998) and has also been described cutting mineralized veins in the lower Paleozoic basement (Everett et al., 1999a). It displays a well-developed saddle morphology and shows pronounced compositional zoning in CL (Wilkinson, 2003). It commonly occurs as an overgrowth of earlier coarse white dolomite in vugs and, as a result, may be confused with this earlier dolomite. Minor sulfides (mainly pyrite, chalcopyrite, and sphalerite) are occasionally observed encrusting pink dolomite crystals which may explain why this dolomite has been interpreted as preore (Wright et al., 2000). However, where observed in the deposits, it is always postore and is associated with extensive dissolution of sulfides (Boast et al., 1981; Eyre, 1998).

The pink dolomite contains two-phase liquid-vapor inclusions with very consistent properties (Table 1). Homogenization temperatures are mostly in the range 91° to 137°C and salinities are 23.7 to 24.7 wt percent NaCl equiv. First melting is normally observed below -50°C indicating significant CaCl₂, but combined ice and hydrate melting temperatures (avg -17.9°C) indicate that these brines have Na > Ca.

Other dolomite data: Gregg et al. (2001), Mulhall (2003), and Johnson et al. (2001, 2009) identified three main types of fluid in the Midlands based on inclusions hosted by "late diagenetic" saddle dolomite cements, but the relative timing of the hosting dolomites was not fully resolved. Based on analogy with known fluids elsewhere in the Midlands it is considered probable that the saddle dolomite that hosts inclusions homogenizing in the range 100° to 270°C and with salinities of 0 to 17 wt percent NaCl equiv ("type 2" and "type 3" fluids, Gregg et al., 2001) is correlatable with coarse white and/or white matrix breccia dolomite (Fig. 2), whereas the white to pink saddle dolomite cements hosting inclusions with T_h values of 70° to 120°C and salinities of 19 to >26 wt percent NaCl equiv are likely to be equivalent to the late (postore) pink dolomite described above. The difficulty in distinguishing between some of the dolomite types is probably due in part to the development of epitaxial overgrowths. For the late pink dolomite, its field distinction is largely based on a coloration that is not always developed. Significantly, the type 3 fluid, which has comparable properties to the ore-forming fluids (Table 1), was not observed in Supra-Waulsortian lithologic units (Johnson et al., 2001, 2009), consistent with a principal high-temperature hydrothermal event that predated their deposition (e.g., Lee and Wilkinson, 2002).

Footwall stratigraphy

The first study of fluid flow at greater paleodepths investigated the structural, mineralogical, and isotopic characteristics of vein systems hosted by lower Paleozoic rocks. This was coupled with fluid inclusion data to test whether mineralizing fluids had circulated in fracture permeability within this volcano-sedimentary succession (Everett et al., 1999a). Three main vein types were identified that cut dark grey-green Silurian graywackes, mudstones, and sandstones in the southwest Irish Midlands at locations up to 32 km west-southwest and 20 km east-southeast of Silvermines (Fig. 1): (1) early hematitic calcite-quartz \pm pyrite; (2) quartz-calcite \pm sphalerite, galena, chalcopyrite, pyrite, barite; and (3) ankeriteferroan dolomite-quartz \pm sphalerite, pyrite.

Vein types 2 and 3 are associated with weak to locally intense sericite-chlorite-carbonate alteration, and disseminated pyrite(-carbonate) is observed in the vicinity of well-developed vein systems. Clots of a distinctive fine-grained pistachio green mineral are commonly observed within type 2 veins and along vein margins and more rarely in type 3 veins. In some cases it is associated with pink dolomite that cuts both vein types. Microprobe analyses indicate that these comprise phengitic K mica, sometimes intimately intergrown with chlorite.

The majority of the fluid inclusions observed were of liquid-vapor aqueous type with a minority of secondary monophase, liquid-only inclusions. Inclusions within quartz which showed a highly variable degree of fill from 5 to 75 percent liquid were recorded in one sample—possible evidence for boiling. Some liquid-vapor and liquid-only inclusions contained trapped solid phases that showed no change upon heating; these were interpreted to be calcite and K mica.

Inclusions considered to represent the primary vein-forming fluids in type 1 veins had low to moderate salinities (0.2–10.8 wt % NaCl equiv) and T_h values from 150° to 250°C. Lower temperature (109°–189.9°C), moderate- to high-salinity (12.2–23.8) secondary inclusions were also recorded. The origin of the type 1 veins is uncertain, although structural relationships are consistent with a lower Carboniferous age, and the occurrence of hematite, chlorite, and calcite is similar to the early (presulfide) ironstones and associated hematitebearing veins reported at several Irish base metal deposits (Hitzman et al., 1995). However, the fluid properties are also comparable with inclusions commonly associated with the Caledonian granites in Ireland, interpreted to represent widespread meteoric circulation subsequent to their emplacement and crystallization (O'Reilly et al., 1997a, b).

Primary fluid inclusion data from vein types 2 and 3 show T_h-salinity characteristics ($123^{\circ}-238^{\circ}C$, 9.7-20.6 wt % NaCl equiv) that are comparable with data from Carboniferous-hosted mineralization (Table 1). In addition, the highest T_h inclusions hosted by quartz and sphalerite commonly contain CO₂ as noted elsewhere. These fluids are believed to represent ore fluids trapped enroute 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-CaCl₂-H₂O 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 ore field 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 no.: NaCl/[NaCl + CaCl₂]) greater than 0.5. Based on crush-leach data, Samson and Russell (1987) suggested that the moderate-salinity ore fluids had high Na numbers and that two brine types existed, one with high Na numbers and one with low Na numbers.

Here, new data are presented from basement-hosted veins, regional carbonates, deposits (Silvermines), and prospects (Keel and Castlegarde). Excluding three outliers below $-30^{\circ}C$ (probably erroneous observation), $T_{m(hydrate)}$ ranges from to -29.0° to $+1.1^{\circ}$ C but is mostly between -22° and -24°C (Table 1). Modeling ice and hydrate melting in the NaCl-CaCl₂-H₂O system (Naden, 1996) gives Na numbers mostly in the range of 0.66 to 0.95 for basement-hosted veins, 0.42 to 0.88 for regional carbonates, and 0.61 to 0.92 for deposits and prospects. The uncertainty for careful measurement of $T_{m(hvdrate)}$ is ±0.2°C and for ice melting ±0.1°C which translates into a modeled uncertainty of +0.03/-0.01 in Na numbers and ±0.1 wt percent in total salinity (wt % NaCl + CaCl₂ equiv). The degree of uncertainty due to the presence of other cations or anions in the fluids cannot be assessed. Plotting Na numbers 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 number of ~0.75 (25 wt % salinity; type B_1) and Na number ~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 B₂ 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-CaCl₂-H₂O phase diagram indicates variably Ca-rich fluid compositions with Na numbers 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) postmineralization.

Results for moderate-salinity fluids in basement-hosted veins (LP_1) indicate relatively high Na numbers (0.7-0.9), typical for ore fluids from Silvermines (Samson and Russell, 1987). Basement-hosted sphalerite typically displays average Na numbers ~0.75 at the lower end of this range. The variation in Na number as a function of total salinity could reflect LP_1-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,



FIG. 5. Plot of Na number (NaCl/[NaCl + CaCl₂]) vs. total salinity (wt % NaCl + CaCl₂ equiv) based on ice and hydrate melting temperatures in fluid inclusions. Fields for lower Paleozoic vein-hosted fluids (LP₁), deposit sphalerite-hosted ore fluids (LP₂), 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). Abbreviations: SWET = seawater evaporation trajectory, cc = calcite, qz = quartz, sp = sphalerite.

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 LP₁ fluids. It is therefore possible that the actual oreforming 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:

$$2ZnCl_4^{2-} + 2H_2S + CaMg(CO_3)_2 = 2ZnS + 8Cl^- + Ca^{2+} + Mg^{2+} + 2H_2CO_3.$$
(1)

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 LP₁ type and the calcic B_3 brines (Fig. 5). However, this is thought to be unlikely given the young (probably postore) age of the B_3 brines identified to date.

Major element chemistry

Bulk fluid inclusion analyses on quartz from basementhosted vein samples (Everett et al., 1999a) showed that LP₁ fluids had Na > Ca \geq K and were Mg poor. These compositions are comparable with experimental data on fluids equilibrated with graywackes at temperatures of 200° to 350°C, consistent with derivation of mineralizing fluids from a lower Paleozoic-equilibrated fluid reservoir. Na numbers were in the range 0.88 to 0.94, consistent with the microthermometry-derived values reported here. Na-K-Ca (Fournier and Truesdell, 1973) and K-Na and K-Mg alkali thermometers (Giggenbach, 1988) can be applied because the mineralogy of the lower Paleozoic succession (quartz, albite, K-feldspar, muscovite, chlorite, illite, minor carbonate, trace sulfides) is similar to that in the geothermal reservoirs from which the thermometers are calibrated. These geothermometers gave equilibration temperatures (158°-219°C) not significantly different from T_h values, suggesting that the inclusions were trapped under pressures only slightly above saturated vapor pressure, indicating a relatively shallow depth of vein formation (Everett et al., 1991a). In terms of the detail of flow patterns and the relationship between these feeder vein localities and the deposits, it may be important that these temperatures are lower than many of the estimates for fluid temperatures in the ore deposits (Table 1).

Halogen geochemistry

The first halogen analyses of Irish fluids were presented by Everett (1999), Everett et al. (1999b), and Gleeson et al. (1999) and were further expanded by Banks et al. (2002), Wilkinson et al. (2005a), and Johnson et al. (2009). Although the uncertainty in these measurements is difficult to constrain, different fluid types can be identified based on significant differences in halogen and major element ratios and/or the restriction of particular signatures to specific paragenetic stages or geographic locations.

Lower Paleozoic-hosted vein samples contain fluids that fall into two groups: type LP1a have Cl/Br molar ratios (559-825) that are similar to seawater, interpreted as being produced by partial evaporation of seawater to an evaporation ratio of $\sim 4 \times$ to $\sim 7 \times$ (evaporation ratio = mass of water in seawater/mass of water in evaporated brine) prior to circulation into the basement (Wilkinson et al., 2005a). Type LP_{1b} fluids are slightly less saline but have Cl/Br values below seawater (375-553); these were interpreted to represent strongly evaporated bitterns (evaporation ratio up to $25 \times$), relatively enriched in Br, that had subsequently been diluted by either seawater, evaporated seawater, or meteoric water (Fig. 6A). Mixing curves show that the data are consistent with mixtures containing ~5 to 20 percent brine (by mass) and ~80 to 95 percent evaporated seawater although other possibilities cannot be excluded at present. The relatively narrow salinity range displayed by the LP_{1b} fluids (Everett et al., 1999a) implies homogenization of these putative mixtures prior to trapping but it is uncertain when this mixing occurred: prior to recharge, during flow within basement rocks, or close to the paleosurface around the time of mineralization. Hydrogen and oxygen isotope data (see below) are consistent with a model involving mixing of uninteracted brines (relatively near to the paleosurface) with strongly interacted LP₁-type fluids to form the LP_{1b} fluids.

Results from deposit-hosted samples show that ore fluids from Silvermines are similar to LP_{1a} , whereas those from Tynagh are shifted to slightly more Br-rich compositions, closer to LP_{1b} . Tentative modeling indicates that mixing between Br-enriched brines (<20%) and LP_1 fluids (evolved partially evaporated seawater; >80%) can produce most of the range in Cl-Br compositions observed in the Irish ore fluids (Fig. 6A), although it is possible that some of the spread is an artefact due to analysis of inhomogeneous inclusion populations. Nonetheless, the data are consistent with trapping of mixtures of high-temperature fluids and brines at the ore depositional site, a process that has been invoked as a key ore-forming mechanism (e.g., Anderson et al., 1998; Blakeman et al., 2002; Hitzman et al., 2003; Wilkinson et al., 2005a, b).

Combining exchangeable cation data with the conservative halogens allows processes undergone by these seawater-derived fluids during crustal interaction to be explored. A plot of Cl/Br versus Na/Br (Fig. 6B) shows that all deposit and lower Paleozoic basement-hosted vein data lie close to or above the seawater evaporation trajectory, best explained by loss of Na from fluids initially lying at various points along the seawater evaporation trajectory. Fluids from Silvermines appear to be more exchanged than those from Tynagh, possibly accounted for by a greater degree of water-rock interaction, which could explain the greater metal endowment of the Silvermines system. Both deposits appear to have formed from more exchanged fluids (subsequently referred to as LP₂) than the lower Paleozoic-hosted veins, suggesting that the feeder veins (sampled lateral to the deposits) represent different, less



FIG. 6. Halogen systematics of Irish fluids. (A). log Br vs. log Cl plot. (B). Cl/Br vs. Na/Br. (C). Cl/Br vs. Ca/Br. Possible mixing and exchange trajectories are shown. Dashed lines in (B) represent 25 and 50% Na loss from evaporated seawater precursors. Shaded-dashed fields indicate different feeder vein localities. Seawater evaporation trajectory from McCaffrey et al. (1987). Compositions of modern seawater and seawater-derived brine with an evaporation ratio of $25 \times$ are shown for reference (stars).

basement-interacted, parts of the flow system. The samples from Birdhill and Latteragh (closer to Silvermines; Fig. 1) generally display greater degrees of Na loss than those from Fantane and Ballycar (Fig. 6B), consistent with a convective type of flow pattern.

An equivalent plot but involving Ca (Fig. 6C) shows that there is very strong enrichment in Ca in the lower Paleozoichosted vein fluids relative to evaporated seawater. Unfortunately, no comparable data for deposit-hosted inclusions exist. The exchange of Ca²⁺ for 2Na⁺, most commonly mediated by reactions involving plagioclase, is a common process in crustal fluid-rock interactions and is related to temperature and fluid salinity (Yardley, 2005). Ca is most enriched in samples from the Birdhill and Latteragh localities supporting greater degrees of exchange in the genesis of these fluids, consistent with the Na data. However, consideration of the cation balance shows that the Ca gain in the LP_1 fluids is not matched by twice as great a loss (in molar terms) in Na so that an additional source of Ca is required. One possibility is that Ca was acquired from the Carboniferous sequence as a result of Mg-Ca exchange dolomitization in downflow zones:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}.$$
 (2)

Some of the premineralization, seawater-related dolomitization observed (D_{1a}) could have been formed in this way and the process may also have been responsible for some of the Mg depletion noted in the LP₁ fluids, although this can also be attributed to Mg smectite and chlorite formation in the basement rocks (see below).

Microthermometric data suggest that deposit sphaleritehosted ore fluids (LP_2) are even more Ca rich than LP₁ fluids (Fig. 5) and this is supported by recent LA-ICP-MS analyses (Wilkinson et al., 2009). This is consistent with greater degrees of basement exchange in their production although, as noted earlier, the possibility of local Ca increase due to carbonate dissolution at the site of ore formation cannot be excluded.

Minor and trace element chemistry

Plotting the minor and trace element chemistry of the LP_1 fluids normalized to their inferred evaporated seawater precursor illustrates the Li enrichment, strong Mg depletion, and broad increase in the transition metals and lithophile elements (Sr, Ba, Pb) that has occurred during crustal interaction (Fig. 7). Similar changes are observed in modern seawater-dominated submarine hydrothermal fluids interacting with ocean basalts but with a lack of such strong enrichment in elements concentrated in felsic crust such as Ba or Pb.

Lithium concentrations in LP₁ fluids are in the range 55 to 164 ppm (Everett et al., unpub. data; Wilkinson et al., 2005a), overlapping with, but generally lower than, the 86 to 503 ppm obtained by crush-leach analysis from Silvermines and Tynagh ore-stage samples (Banks et al., 2002). All these values are elevated significantly above evaporated seawater concentrations. Enrichment is most likely due to interaction with basement rocks that typically contain 30 to 60 ppm Li (Crowther, 2007).

Magnesium concentrations in LP₁ fluids are in the range 30 to 310 ppm and are very depleted (Fig. 7), typical of seawater-derived fluids that have undergone low-temperature exchange with silicate rocks and/or have been involved in dolomitization. Thus, the Mg data, like Na, can be explained by exchange for Ca during fluid infiltration.

Barium is strongly enriched in LP_1 fluids, such as at Fantane (mean 930 ppm; Wilkinson et al., 2005a), even in the absence



FIG. 7. Range of major, minor, and trace element compositions of LP₁ fluids (mean values from Fantane, Latteragh, Birdhill, and Ballycar; Wilkinson et al., 2005a and unpub.) normalized to an evaporated seawater precursor (prior to gypsum precipitation). This illustrates the element gains and/or 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).

of significant base metals. It could be acquired by fluids from trace barite or barian feldspar during basement interaction but only once fluids were depleted in sulfate 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., unpub. data; 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 LP₂ 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 $\delta^{18}O_{H_2O} = 2.4$ to 9.0 per mil and $\delta D = -24$ to -55 per mil, overlapping with the Silvermines ore fluids. This is supporting evidence for lower Paleozoic flow of the ore-forming solutions, although the generally lower δD values 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). Utilizing 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 $\delta \hat{D}$ values, lower fluid-rock fractionation factors for hydrogen, and/or lower δD values 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 LP₁ 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 sea floor (Samson and Russell, 1987); however, it can also be reproduced by shifting the seawater evaporation trajectory to lower δ^{18} O and δ D 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).

The isotopic compositions of the bulk of the Silvermines ore fluids (which tend to have higher T_h values and lower salinities than most LP₁ fluids) cannot be explained by brine-LP₁ mixing in the ore-forming environment (Fig. 8) and appear to require a greater hydrogen isotope shift during fluidrock interaction. The involvement of D-depleted lithologic units located beneath the known Lower Paleozoic sequence cannot be tested, although this would be consistent with the higher fluid temperatures suggested by higher δ^{18} O values and generally higher T_h values. Interaction with mafic rocks (δD -70 to -105%; Agrinier et al., 1995), Caledonian granite, or the Precambrian crystalline basement that may have undergone earlier deuteric alteration are all possibilities.



FIG. 8. Calculated δ^{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 LP₁ 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 whole-rock compositions from Thomas et al. (1985). Rock-fluid fractionation factors ($\Delta^{O}_{rw} = 7.0, 3.4 at 200^{\circ}$ and 300° C, respectively; $\Delta^{H}_{rw} = -32.6, -33.2 at 200^{\circ}$ and 300° C, respectively) estimated using the approach outlined in Samson and Russell (1987). Most of the LP₁ fluid compositions can be explained by small degrees of mixing between fully basement-equilibrated fluids with low δD brines, possibly produced by strong evaporation ($25 \times$ evaporation ratio) of ¹⁸O- and D-depleted lower Carboniferous seawater. The higher temperature Silvermines ore fluids δD basement rocks.

Discussion and Implications

Regional fluid evolution

Fluid inclusion data, coupled with stable and radiogenic isotope systematics, describe a basinal system in which widespread mobilization of hydrothermal fluids led to progressive overprinting of normal, early diagenetic processes and localized convergence of a number of factors toward ore-forming conditions. Fluid chemistry suggests that some of the early dolomitization (D_{1a}; Fig. 2) could have formed from "normal" evaporated seawater that subsequently penetrated the basement and evolved into interacted but unfertile solutions. Regionally developed, coarse white dolomite cements (D_{1b}) then formed above fault-focused plumes of these evolved solutions, as they became thermally buoyant and migrated back toward the surface. The coarse white dolomite is thus interpreted to reflect a slightly lower temperature and spatially more extensive manifestation of the hydrothermal system that was ultimately responsible for the formation of the ore deposits (Wilkinson, 2003).

Increased focusing and greater penetration depth are inferred to have led to the local generation of higher temperature, more exchanged, highly metalliferous fluids. It was only where these LP_2 fluids returned to the near-sea-floor environment and mixed with sulfidic brines that economic mineralization was formed, accompanied by hydrothermal dolomite (D_2, D_3) . Continued flow of these fluids after the main mineralizing event(s), with brines excluded from the ore systems perhaps by the deposition of impermeable capping sequences (e.g., Calp Limestone over the Waulsortian; Upper Dark Limestones over the Navan Group), led to overprinting of ore by late-stage veins in some of the deposits (D_4, C_4) .

The late pink dolomite (D_5) is a distinct, postore marker that has been interpreted in terms of a postore brine migration, probably related to the onset of Variscan compressional tectonism in the mid- to late Carboniferous (Andrew et al., 1986; Wilkinson, 2003; Wilkinson et al., 2003). Thus, the onset of compression in the Midlands basin is considered to have been the principal tectonic control that 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



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 postore 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).

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 δ^{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 pore water bodies resident in the shallow sediments to reach the sea floor. 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 and/or 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 Irishtype deposits (as in the sense of, Wilkinson, 2003).

Brine origins

Seawater evaporation to varying degrees played a key role in the generation of ore fluids for the Irish Zn-Pb deposits. The principal ore fluids 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



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 2× vertical exaggeration. B. Three-dimensional cartoon representation of fault arrays, sea-floor 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 paleosea floor) on the basinward side of fault-controlled shelves and/or islands where strongly evaporated bittern brines were generated.

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:(B1) relatively high Na number (~ 0.8) brines associated with pink dolomite; (B_2) more saline brines with elevated Ca (Na no. ~ 0.5) associated with pervasive dolomitization; and more calcic brines (Na no. $\sim 0.6-0.2$), 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 Ca²⁺. 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 ($\Delta V = -9.74 \text{ cm}^3 \text{ mol}^{-1}$; -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 paleosea floor. The rare occurrence of barite in lower Paleozoichosted veins with a Carboniferous seawater sulfate signature (Everett, 1999), pyrite with low (ore-like) δ^{34} S values, and variations in Na number in fluid inclusions are consistent with minor LP₁-brine mixing within at least the upper parts of the basement sequence.

Mixing of LP₂ fluids with brines in the ore-forming environment appears to have been an important depositional mechanism and the halogen data suggest that Br-enriched bittern brines were involved. These brines must have become enriched in reduced sulfur by bacteriogenic reduction (e.g., Boyce et al., 1983; Caulfield et al., 1986) prior to mixing. It is suggested that the development of submarine warm springs and/or seeps above major hydrothermal plumes resulted in the local development of chemosynthetic faunal communities including abundant sulfate-reducing bacteria. These bacterial blooms could have concentrated H₂S in brines trapped in seafloor depressions and in underlying lithologic units proximal to hydrothermal upflow zones. In the Waulsortian-hosted deposits, these sulfidic brines could have been resident within permeable Waulsortian that had been previously dolomitized (e.g., Lisheen, Galmoy; Wilkinson et al., 2005b) or in sedimentary slump breccias in undolomitized Waulsortian (e.g., Silvermines; Lee and Wilkinson, 2002), perched on the relatively impermeable underlying argillaceous limestones. Mixing along the interface between such brine lenses and upwelling LP₂ fluids is consistent with the observation that the base of massive sulfide is often planar, horizontal, and commonly transgresses stratigraphy. Furthermore, the contact between hydrothermal black dolomite cemented breccias (formed at the mixing interface) and overlying white matrix breccias (cement precipitated from largely unmodified LP₂ fluids) is subhorizontal and sharp to gradational over a few meters (Hitzman et al., 2002; Lee and Wilkinson, 2002; Fusciardi et al., 2003).

Fluid inclusion data show that, generally, hydrothermal dolomite was precipitated at the highest temperatures, probably during the first increments of fluid mixing. The lack of Mg in the LP fluids indicates that mixing with unexchanged, Mg-rich brines is likely to be essential for extensive dolomite development in areas where preexisting diagenetic dolomite was not abundant (e.g., Silvermines: Lee and Wilkinson, 2002). In the south and east Midlands, where early pervasive dolomitization of the Waulsortian had occurred (Hitzman, 1995), local recrystallization could have supplied some of the required Mg.

Across the ore field, sphalerite-hosted inclusions tend to form relatively tight clusters of data from individual samples and be polymodal in terms of salinity. The reason for this is uncertain although it is suggested that the more crystalline sphalerite samples amenable to inclusion analysis may represent pockets of mixed fluid that precipitated sphalerite during cooling in the waning stages of individual pulses of hydrothermal fluid ingress. Finer grained sphalerite types probably precipitated over a greater part of any mixing interval but the fluid inclusion record of this is only (partly) preserved in the coexisting gangue. The salinity modes observed may reflect different degrees of mixing but the occurrence of comparable modes in different deposits as well as in basement-hosted veins (Table 1; Wilkinson et al., 2009) suggests that infiltration of LP fluids of varying salinity and composition occurred at different times as well as in space. The majority of sphalerite in the Waulsortian-hosted systems appears to be associated with the more saline mode(s), suggesting that this (presumably more highly evaporated) interacted seawater was particularly important for ore formation (Wilkinson et al., 2009).

Calcite appears to have been more commonly precipitated during extensive mixing and at lower temperatures, although some high-temperature, unmixed, fluids are responsible for the formation of calcite feeder veins in some of the deposit footwalls (e.g., Silvermines: Lee and Wilkinson, 2002).

At Lisheen, Galmoy, Silvermines (Cooleen zone), Castlegarde, and Keel, a trend toward more dilute, lower T_h inclusions has been recognized, consistent with mixing between LP fluids and low-temperature seawater. It is perhaps not suprising that this is observed given the inferred near seafloor environment of ore formation. Evidence from Silvermines suggests that such mixing tends to be restricted to the margins of the system, outside the region of brine influence. It is suggested that upwelling ore fluids may have been deflected around a dense brine lens, mixing along the interface with brine and then being diluted by normal seawater along the margins (Fig. 10). Although seawater mixing does appear to be capable of driving fluids to sulfide saturation (presumably via cooling and decreased ligand concentration), it is not thought to be favorable for extensive sulfide deposition due to the limited sulfur supply in the LP fluids. The predominance of deep, hydrothermal sulfur in these zones is confirmed by the high (>0) δ^{34} S values observed in the subeconomic Cooleen zone at Silvermines (Lee, 2002).

The subeconomic prospects generally appear to show a restricted salinity range, being dominated by LP fluids that vary widely in temperature between localities. At present, it is not known if the prospects formed from LP fluids with less (LP_1) or more (LP₂) exchanged character. Dilution trends are observed in some of the prospects (e.g., Castlegarde, Cooleen, Keel), but the brine mixing trends that appear to be consistently observed in the ore deposits are weak or absent. Thus, LP-brine mixing is one of the key factors that appears to be missing from the subeconomic systems. The low-temperature, possibly slightly younger, MVT deposits show some evidence of mixing but lack the elevated temperatures that may be required for significant metal solubilization and show little evidence of the bacteriogenic sulfide trap, being typified by positive δ^{34} S values (Dixon, 1990). Cooling, neutralization due to extensive retrograde carbonate dissolution and inorganic sulfate reduction are suggested as the controls of sulfide deposition from these late, cool, LP-type fluids that are interpreted to reflect the waning phase of the convective flow system.

The formation of economic mineralization in Ireland appears to reflect the coincidence of high-temperature reaction zones in the basement, brine-producing footwalls, and hanging-wall 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-strata-bound, 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: nonstratiform 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 m.y. 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 geologic 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 graywacke-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 volumelimited 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 and/or geomorphology, distribution and diagenesis of sedimentary facies, and basin floor and/or margin permeability as is highlighted in studies of modern intracratonic basins (e.g., Stanislavsky and Girtzman, 1999; Stein et al., 2000; Klein-BenDavid et al., 2004). Consequently, significant complexity should be expected in fluid origins in intracratonic basinhosted ore districts elsewhere, but these can be resolved with careful application of modern microchemical analyses of fluid inclusions.

Concluding Remarks

The Irish ore field 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 drill core 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. Regionalscale 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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