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Diagenetic evidence for an epigenetic origin of the Courtbrown Zn–Pb deposit, Ireland

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Abstract Mineralisation at the Courtbrown deposit in south-western Ireland is concentrated in the basal section of the Chadian Waulsortian Limestone, immediately above the Courceyan Ballysteen Limestone. Two episodes of sulphide deposition have been identified: an early stage of minor pyrite precipitation, and a later base-metal-rich mineralisation event. Sphalerite, galena and pyrite of the later mineralisation event occur predominantly as replacement phases along stylolites, dissolution seams, and within the micritic matrix of the host limestone. These sulphide minerals also occur as cements within late stage fractures.

The following diagenetic phases are present in the Waulsortian and Ballysteen Limestones in the Courtbrown area (from oldest to youngest): non-luminescent syndimentary calcite cements, non-luminescent equant calcite cements, bright luminescent calcite cement, dull luminescent calcite cement, planar dolomite cement and replacement dolomite (regional dolomite), saddle dolomite cement, and fibrous dull luminescent calcite cement filling pressure-shadows around the sulphide minerals.

Homogenisation temperatures for primary fluid inclusions within dull luminescent calcite cements (precipitated penecontemporaneously with base-metal mineralisation) range from 160 to 200 °C, with a mode at 170–180 °C. These values are unlikely to be representative of mineralisation temperatures as the fluid inclusions may have been significantly affected by heating and/or deformation during late burial (maximum paleotemperatures from Ro and CAI data around 310 °C).

The observed paragenetic sequence indicates that mineralisation is completely epigenetic. As the earliest

mineralisation is hosted by macro-stylolites, the sequence must have obtained a minimum burial depth of around 800 m prior to the onset of mineralisation. A burial depth of 800 m would correspond to an approximate early Chadian age for the Courtbrown area. Pressure-shadows around sphalerite further indicate that mineralisation preceded the major phase of Variscan deformation. Therefore, the base-metal mineralisation at Courtbrown is epigenetic, and the age of mineralisation is in the range of 350 to 307 Ma.

Introduction

The Lower Carboniferous carbonate succession of Ireland is host to a large number of base-metal deposits, ranging in size from small uneconomic prospects to world-class Zn–Pb deposits such as Navan, Galmoy, and Lisheen (Fig. 1). With a delineated resource of 1 Mt at 3.5% Zn, 2% Pb and 14 g/t Ag (Grennan 1986), the Courtbrown deposit is currently uneconomic. However, the deposit is of interest because it has previously been documented as being epigenetic in origin (Grennan 1986), whereas the majority of carbonate-hosted base-metal deposits in Ireland are classified as partly syngenetic-partly early diagenetic ‘Irish-type’ deposits (e.g. Derry et al. 1965; Boyce et al. 1983; Andrew 1986). In addition, most diagenetic events have been preserved at Courtbrown as the deposit was not subjected to pervasive dolomitisation.

The Courtbrown deposit is located on the southern edge of the River Shannon, County Limerick, in south-western Ireland (Figs. 1 and 2). It was discovered by Consolidated Mogul in 1961, but was abandoned in 1962 following the company’s discovery of the Silvermines deposit (Grennan 1986). Although it has been mentioned briefly in several broad reviews of Irish base-metal mineralisation (Schultz 1971; Hitzman and Large 1986; Hitzman and Beaty 1996; Johnston 1999), the deposit has received little attention in the literature. The

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Fig. 1 Map of Ireland showing the location of the Shannon Trough and Porcupine Basin (Croker 1995) the Limerick Syncline (Strogen 1988), the Rathdowney Trend including the Lisheen and Galmoy deposits (Shearley et al. 1996), the Kildare District including the Harberton Bridge deposit (Emo 1986), and the Navan, Tynagh and Silvermines deposits (Hitzman and Beaty 1996). The borders of Co. Limerick and Co. Clare are from State Mining and Prospecting Areas: 1st May 1998 map (Department of the Marine and Natural Resources Exploration and Mining Division)

only significant description of the Courtbrown deposit is by Grennan (1986), who detailed the general deposit stratigraphy and ore mineralogy.

This paper aims to build upon the earlier work of Grennan (1986) by providing a detailed petrologic study of the relationship between carbonate diagenesis and mineralisation in the Courtbrown area. The approach of this paper is (1) to provide a detailed description of the style of mineralisation and the diagenesis observed at the Courtbrown deposit; and (2) to provide a maximum and minimum age for the mineralisation through the application of basin subsidence analysis together with paragenetic and diagenetic observations.

Geological setting

Shallow marine conditions were established across the Irish Midlands during the Early Carboniferous, with marine sedimentation thickening within the newly formed Shannon Trough (Fig. 1). The Shannon Trough is believed to represent a half-graben bounded by faults to the south and sloping gently upwards to the north (Strogen 1988; Sleeman and Pracht 1999). To the west, the trough is thought to extend off the present shoreline where the younger Porcupine Basin truncates it along its western margin (Croker 1995; Sleeman and Pracht 1999; Fig. 1).

In the Courtbrown area, the Courceyan Lower Limestone Shales (Mellon House, Ringmoylan, and Ballyvergin formations) mark the beginning of sedimentation within the Shannon Trough (Fig. 2). These are overlain by the Ballysteen Limestone and Waulsortian Limestone of late Courceyan to early Chadian age (Sleeman and Pracht 1999; Fig. 2). In the Courtbrown area, the Waulsortian Limestone has been divided into the basal Transition Reef, and the Mudbank Reef (Grennan 1986). For this study however, these two sub-units will be described collectively as the Waulsortian Limestone.

The post-Waulsortian stratigraphy is not preserved in the Courtbrown area. However, Viséan limestones in the surrounding area (Fig. 2) record the development a carbonate ramp (the Limerick Ramp), prior to a return to deeper water conditions towards the end of the Viséan (Strogen 1988; Somerville and Strogen 1992; Sleeman and Pracht 1999). Late Dinantian to lower Namurian basin inversion marks a hiatus in sedimentation in the eastern Shannon Trough, whereas marine sedimentation continued to the west (Strogen 1988). Marine sedimentation then continued across the entire basin during the Upper Carboniferous, depositing a thick sequence of shales, siltstones, mudstones and sandstones prior to basin inversion during the Late Carboniferous/Permian Variscan Orogeny (Strogen 1988; Sleeman and Pracht 1999).

In addition to the carbonate sequence, Lower Carboniferous volcanic rocks are known to the east of the Courtbrown deposit within the Limerick Syncline (Figs. 1 and 2). Although the volcanic rocks have not been observed at Courtbrown, an aeromagnetic anomaly terminating to the south-east of the deposit has been attributed to an extension of the rocks eastward from the Limerick Syncline (Grennan 1986). Within the Limerick Syncline, two volcanic formations can be identified: (1) the Chadian to Arundian Knockroe Formation that consists of alkali basalt–trachyte suite volcanoclastic rocks, lavas and intrusions (Strogen 1988); and (2) the Asbian Knockseefin Formation that is dominated by ankaramite and limburgite lavas (Strogen 1988; 1995).

On a local scale, the Courtbrown deposit is located on the southern flank of a large east–north-east-trending regional anticline (Figs. 2 and 3). The ore-stage sulphide minerals are concentrated within the basal section of the Waulsortian Limestone (Fig. 3) along the northern margin of a smaller, shallow amplitude east–north-east-trending asymmetric fold (Grennan 1986). In addition, minor disseminated sulphide minerals are also observed in the underlying Ballysteen Limestone. Mineralisation is paragenetically associated with a dull luminescent burial calcite cement discussed below.

Methods of study

The Waulsortian and Ballysteen Limestones were sampled from core drilled at exploration prospects 2872 and 3489 and the

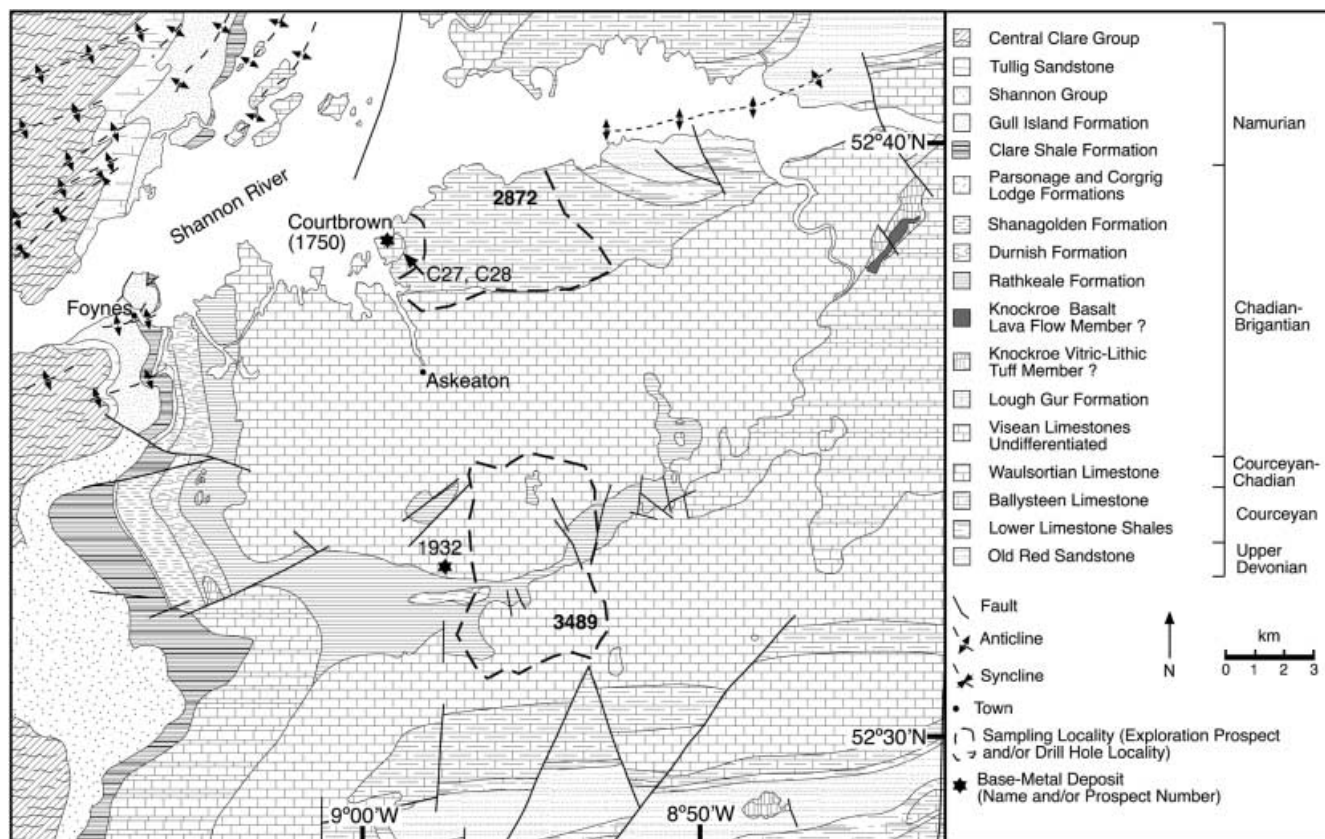


Fig. 2 Regional geology of the Shannon Estuary, based on the geological map of Sleeman et al. (1999). Exploration lease boundaries are from the State Mining and Prospecting Areas: 1 May 1998 map (Department of the Marine and Natural Resources Exploration and Mining Division) and the Geological Society of Ireland core shed database

Courtbrown deposit (holes C27 and C28) (Fig. 2). Sample numbers used throughout the paper are formatted as drill hole name–drill hole number–depth in drill hole. The drill core was sampled from the Geological Society of Ireland core shed (holes C27 and C28) and the Tara Mines core shed (holes 2872-3 and 3489-4). As the earlier work of Grennan (1986) provides a detailed description of the deposit geology and ore mineralogy, this study has focused on poorly mineralised samples that have preserved the relationship between the sulphide minerals and burial cements. This approach allows an accurate determination of the paragenesis to be made. Petrographic analyses were carried out on polished thin sections, which were examined under cathodoluminescence using a Nuclide ELM-2B Luminoscope (operating conditions were 8 kV beam energy and approximately 0.6 mA beam current).

Microprobe analyses were carried out with a Cameca SX50 electron microprobe fitted with both a wavelength dispersive spectrometer (for quantitative analysis) and an energy dispersive spectrometer (for qualitative analysis). The investigation was conducted with the electron gun operating at 14.94 eV and 25.08 nA. The energy dispersive spectrometer used LIF, PET and TAP crystals for analysis. Counting times were 150 s for iron and strontium, 50 s for magnesium and calcium, and 100 s for manganese.

For fluid inclusion analysis, doubly polished blocks were used on a Zeiss microscope fitted with a 40× Nikon ELWD objective, a Fluid Inc. USGS-type microthermometry stage, and a Wavetek Doric 410A gas-flow heating and freezing system. Homogenisation temperatures were constrained to between 2–3 °C using the methods of Goldstein and Reynolds (1994). Criteria used for the

recognition of primary fluid inclusions were those of Goldstein and Reynolds (1994).

The burial history of the Courtbrown area was reconstructed using lithological thicknesses from Grennan (1986), Fitzgerald et al. (1994) and Sleeman and Pracht (1999). The ages for the Carboniferous are from Harland et al. (1990). Burial depths, including a correction for compaction, were generated using the method of Sclater and Christie (1980).

Results

Diagenetic and textural observations in this study were made from the Waulsortian and Ballysteen Limestones in the Courtbrown area. Both syndimentary and burial calcite cements are preserved in these carbonates, occluding primary intra-skeletal, stromatolitic, intergranular and secondary dissolution porosity, as well as fractures.

Synsedimentary cements

Where present, marine calcite cements are the first cavity-filling phases, occurring predominantly as radial fibrous cements. The presence of abundant inclusions gives the cement a dull, cloudy appearance under plane-polarised light. Under cathodoluminescence, the cement is non-luminescent with some patchy or blotchy dull luminescence in the younger generations. Non-luminescent scalenohedral calcite cements generally follow the fibrous

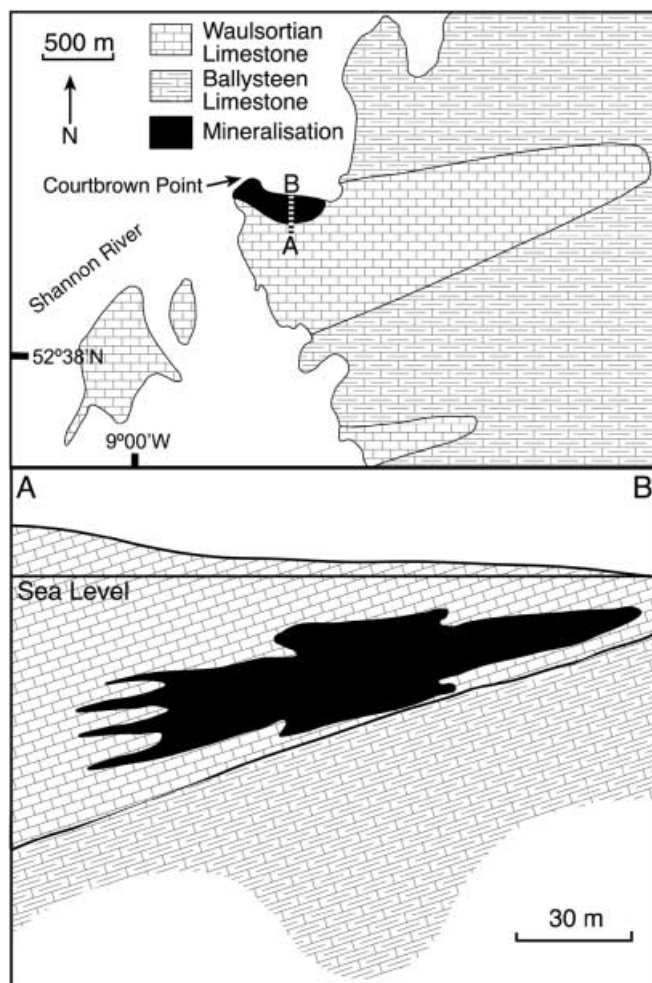


Fig. 3 Plan map of the Courtbrown deposit (*top*) with a N-S section through the Courtbrown mineralisation (*bottom*) (modified from Grennan 1986)

marine calcites. Where the inclusion-rich fibrous cements are not present, the scalenohedral cements may be attached directly to the substrate. They are inclusion-free and have a straight extinction under cross-polarised light.

Equant calcite cements

Clear equant calcite cements directly overgrow the syndimentary cements, and the host rock (where there are no syndimentary cements). Cathodoluminescence microscopy reveals the presence of three major luminescent zones within the equant calcite cements (from oldest to youngest): non-luminescent cement, bright luminescent cement, and dull luminescent cement (Fig. 4A, B).

The non-luminescent equant calcite cements directly overgrow the syndimentary cements or depositional components. They are typically equigranular, and may have either a cloudy or clear appearance. Under cathodoluminescence, they are uniformly non-luminescent and commonly exhibit thin bright luminescent bands

within the younger cement generations. A microprobe traverse (Fig. 5) across a section of uniformly non-luminescent cement shows the concentrations of manganese and iron to be below the reliable detection limit (< 100 ppm) of the machine.

Bright luminescent calcite cements directly overgrow the non-luminescent cements and are only rarely observed in direct contact with skeletal components. Physical compaction and grain breakage commonly predate the precipitation of the bright luminescent cements, indicating they were precipitated in a burial diagenetic environment (Fig. 4C). They have a similar appearance to the non-luminescent variety under plane-polarised light, but, under cathodoluminescence, they are readily identifiable by their bright luminescent character. The thickness of the bright luminescent band is highly variable, ranging from a few micrometres to hundreds of micrometres. The microprobe traverse (Fig. 5) reveals a sudden increase in the concentration of manganese, and to a lesser extent iron, corresponding to the bright luminescent cements. The concentration of manganese increases from ~100 ppm to more than 8,800 ppm, whereas iron increases from < 100 to ~500 ppm. The concentration of manganese decreases markedly towards the end of the bright luminescent cements.

Dull luminescent calcite cements follow the bright luminescent cements and fill virtually all the remaining primary porosity. They are commonly coarser-grained than the preceding cement types and have an equigranular, clear appearance. Under cathodoluminescence, they have an overall dull luminescent character. Closer inspection shows these cements to be finely-banded, with some bright and/or non-luminescent zones. Across the dull luminescent cements, the concentration of the manganese remains relatively constant, generally ranging from ~100 to 450 ppm (Fig. 5). Similarly, the concentration of iron remains between ~100 and 500 ppm, although it increases locally to 2,500 ppm.

Fluid inclusion analyses were conducted on the dull luminescent calcite cement that is associated with the mineralisation. It is commonly inclusion-rich and may contain small inclusions (< 4 μm) of sphalerite and/or galena. Seventy fluid inclusions were examined from mineralised samples collected from drill hole 2872-3. Homogenisation temperatures for primary fluid inclusions within the dull luminescent calcite cements range from 160 to 200 $^{\circ}\text{C}$, with a mode at 170 to 180 $^{\circ}\text{C}$ (Fig. 6A). Pseudosecondary and secondary fluid inclusions from the same calcites give slightly lower homogenisation temperatures, in the range 140 to 185 $^{\circ}\text{C}$, with a mode at 150 to 160 $^{\circ}\text{C}$ (Fig. 6A).

Dolomitisation and dolomite cements

Dolomite occurs as both a replacement phase and cement within the Waulsortian and Ballysteen limestones. Neither stratigraphic unit has been extensively dolomitised. Replacement dolomite generally occurs as isolated

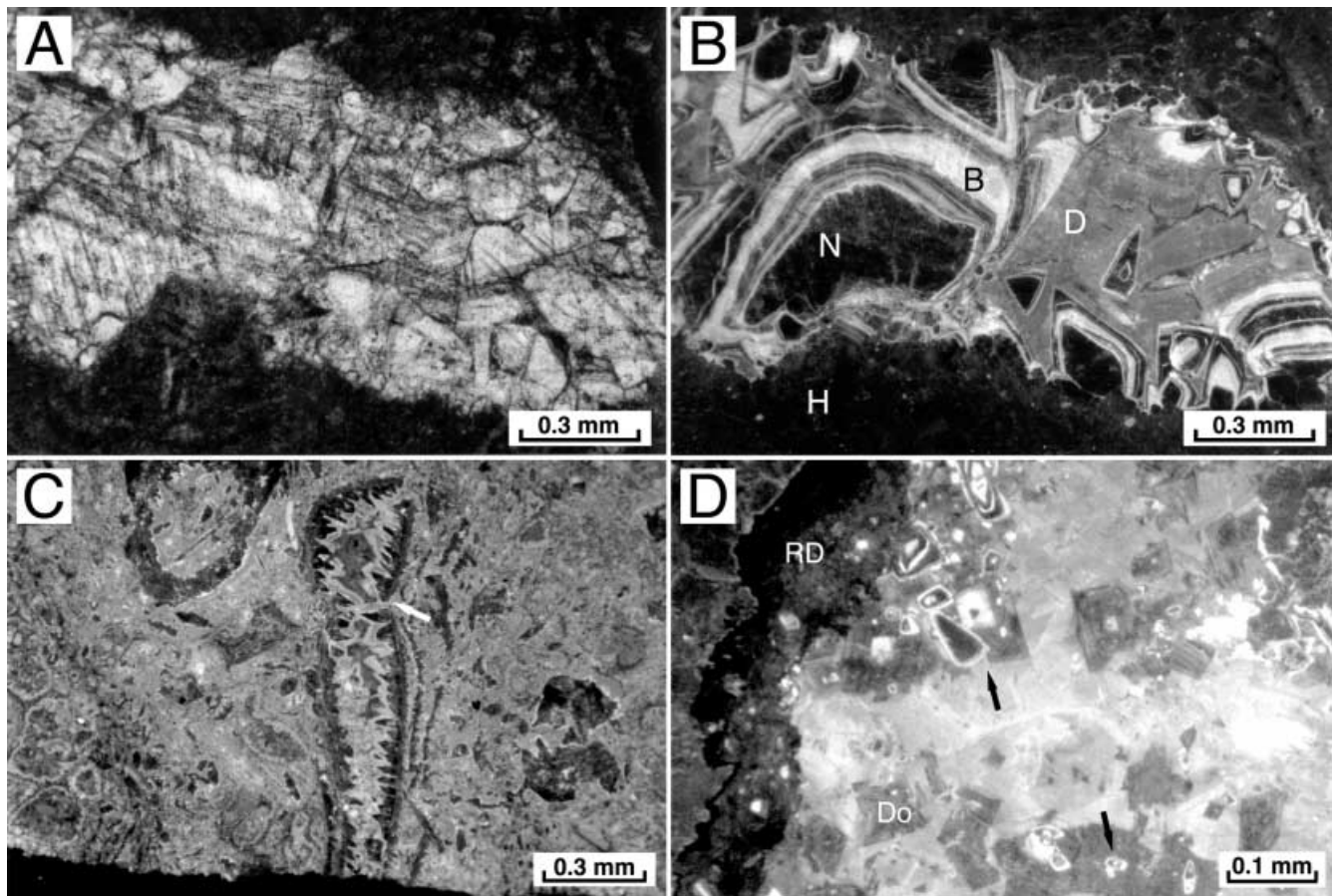


Fig. 4 Plane-light and cathodoluminescence photomicrographs of diagenetic phases at Courtbrown. **A** Plane-light photomicrograph of a primary pore filled by equant calcite cement. Sample 3489-4-240.3. **B** Same area as **A**, in cathodoluminescence, showing non-luminescent (*N*), bright luminescent (*B*) and dull luminescent (*D*) cements. Host rock (*H*) is micrite. Sample 3489-4-240.3. **C** Cathodoluminescence view of a broken molluscan (*arrow*). Molluscan is filled by non-bright dull luminescent calcite cements. Molluscan has broken prior to bright luminescent calcite cement (i.e. break is lined by bright luminescent calcite). Sample C28-13'. **D** Cathodoluminescence view of a primary pore filled by equant calcite cements and planar-dolomite cement (*Do*). Dolomite cement directly overgrows bright luminescent calcite cement (*arrows*). Dolomite with same luminescence has replaced a stylolite (*RD*). Sample 3489-4-240.3

crystals or crystal clusters (80–100 μm crystal diameter) that have straight extinction and an euhedral or subhedral crystal shape (Fig. 7A). It has a restricted distribution, in most cases constituting less than 1% of the matrix. Seen under cathodoluminescence, the replacement dolomite generally has a uniform or weakly zoned dull red luminescence. Many dolomite crystals exhibit a bright red luminescent core.

Replacement dolomite is also observed within stylolites and dissolution seams (Fig. 4D). It is of a similar appearance (i.e. has the same luminescent zonation) to the replacement dolomites within the matrix, but is coarser grained, commonly reaching 0.4 mm in diameter.

Planar dolomite cement occurs as a cavity-filling phase within both primary and secondary porosity.

Individual dolomite crystals may be as large as 1.4 mm in diameter (Fig. 7C), however, most of the grains measure between 0.7 and 1 mm in diameter. Under cathodoluminescence, the dolomites have a similar luminescence to the replacement dolomites observed in the matrix. In some dolomite cements, an early bright red luminescent zone is visible (Fig. 4D). When associated with sulphide minerals (particularly galena), a late stage of non-luminescent dolomite is commonly present (Fig. 7C, D). This late stage dolomite is commonly dedolomitised to dull luminescent calcite (Fig. 7C, D). Replacement dolomite and planar dolomite cements post-date the bright luminescent calcite cement (Fig. 4D) and pre-date the precipitation of galena and sphalerite (Fig. 7A, C, D).

Saddle dolomite cements are present in some large stromatactis cavities. These cements are inclusion-rich, coarsely crystalline (1–2 mm) and non-luminescent, with the exception of a late stage bright red luminescent zone that rims the crystals. The saddle dolomite cements both pre- and post-date the dull luminescent calcite cements (Fig. 7B).

Mineralisation

The drill programs of the early 1960s by Consolidated Mogul delineated a resource of approximately

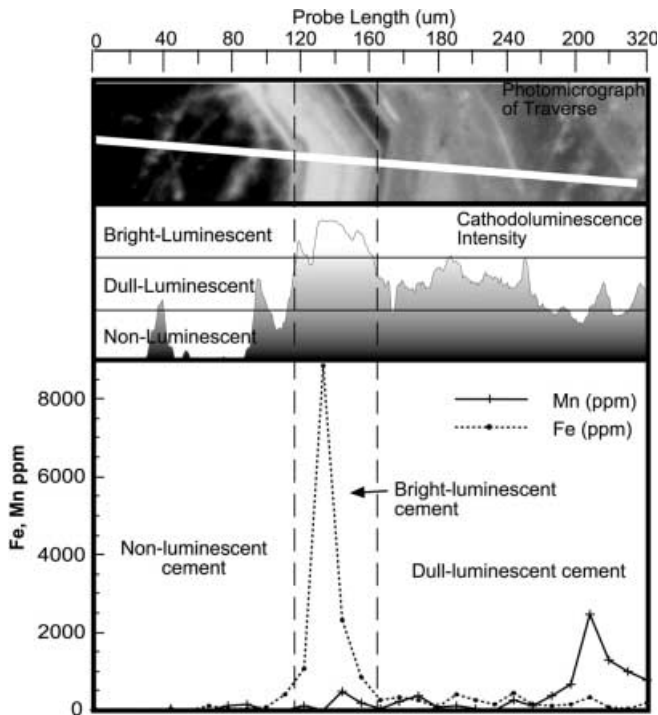


Fig. 5 Electron microprobe traverse of the non- to bright to dull luminescent calcite cement sequence. Cathodoluminescence photomicrograph shows position of traverse. Relative intensity of cathodoluminescence along traverse is shown in *middle plot*. *Lowermost plot* shows the concentration of iron and manganese

250,000 tonnes at a grade of 6.5% Pb + Zn. This value was later increased to 1,000,000 t at 3.5% Zn, 2% Pb, and 14 g/t Ag following a drill program carried out by Irish Base Metals and Dresser Minerals (Grennan 1986). The deposit varies from 1 to 8 m in thickness, and extends for 425 m along strike and 100 m down-dip (Grennan 1986). Sphalerite, galena and pyrite are the main sulphide minerals with minor amounts of chalcopyrite, tennantite and arsenopyrite (Grennan 1986).

Grennan (1986) divided the style of mineralisation at the Courtbrown deposit into six categories: (1) stylolitic, (2) modified stylolites, (3) disseminated, (4) semi-massive sulphides, (5) vein-type and (6) mineralisation within the Ballysteen Limestone. In addition, observations from the present study have highlighted the presence of mineralisation within primary porosity as a seventh distinct style. For consistency, the following section utilises the original divisions of Grennan (1986) with additional observations from the present study.

1. Stylolitic: the bulk of the mineralisation observed during the present study occurred as coarsely crystalline sphalerite, galena and pyrite along micro- and macro-stylolites (Fig. 8B). The sulphide minerals mainly replace the insoluble residue along stylolites and may replace the surrounding host carbonate. Stylolites are better developed within the Waulsortian facies.

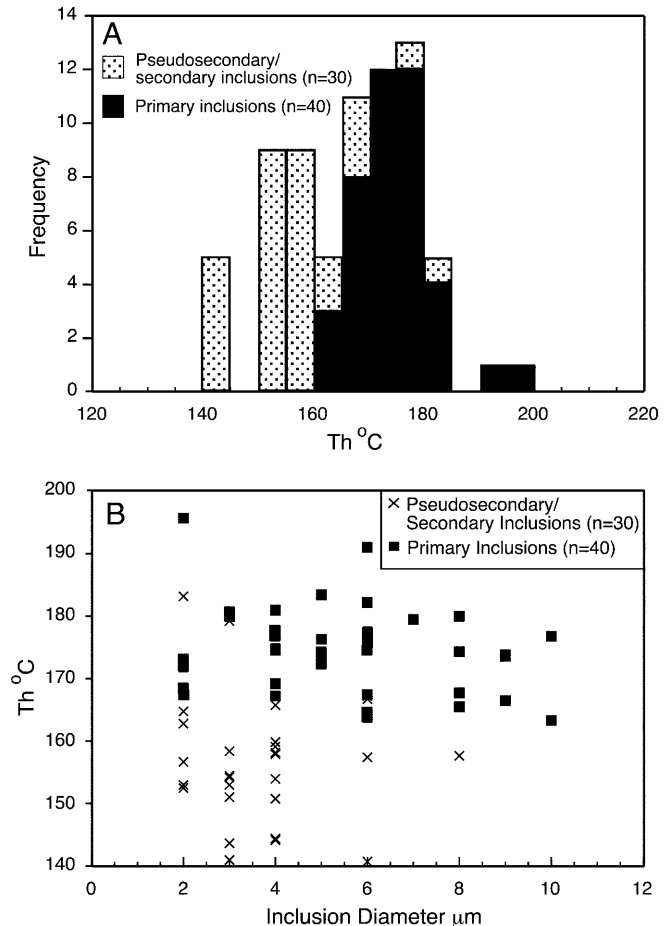


Fig. 6 **A** Histogram of homogenisation temperatures for primary and secondary/pseudosecondary fluid inclusions in dull luminescent ore-stage calcite cements. **B** Inclusion size vs homogenisation temperature for primary and secondary/pseudosecondary inclusions

2. Modified stylolites: where stylolites are well developed, they may grade laterally into cavities (< 5 mm wide). The cavities have irregular morphologies and appear to be produced by fracturing and dissolution. Dull luminescent equant calcite cements generally fill the dissolution cavities, and where mineralised, coarsely crystalline sphalerite and massive galena and pyrite are also observed.
3. Disseminated mineralisation: disseminated mineralisation occurs in both the Ballysteen and the Waulsortian Limestones. It occurs predominantly as fine-grained replacement pyrite within the micrite matrix of the host limestone and may also be seen replacing syndepositional calcite cements and the micritic walls of skeletal remains. Rarely, disseminated sphalerite and euhedral galena are also observed.
4. Semi-massive sulphide minerals: bands of massive pyrite or mixtures of galena and sphalerite occur over narrow widths (< 30 cm). The galena and sphalerite

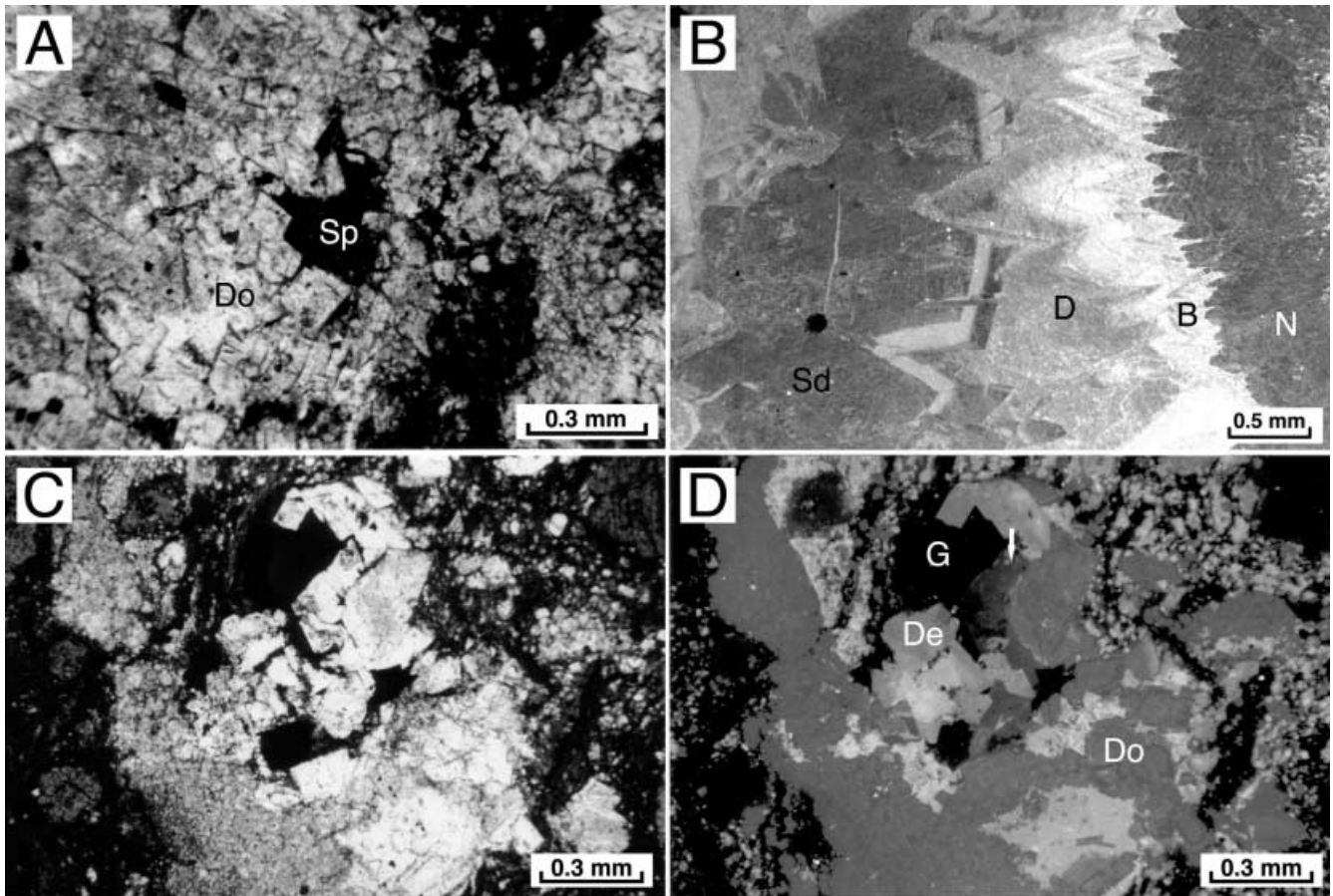


Fig. 7 Plane-light and cathodoluminescence photomicrographs of dolomite and sulphides. **A** Sphaerite (*Sp*) has overgrown planar dolomite (*Do*). Sample C28-13'. **B** Cathodoluminescence view of primary stromatactis cavity filled by, from oldest to youngest, non-luminescent calcite cement (*N*), bright luminescent calcite (*B*), dull luminescent calcite (*D*), saddle dolomite (*Sd*), and more dull luminescent calcite cement. Sample 3489-4-250.9. **C** Plane-light photomicrograph of galena and dolomite. Sample C28-13'. **D** Same area as in **C**, in cathodoluminescence, showing planar-dolomite cement (*Do*) overgrown by galena (*G*). Final phase of dolomite is non-luminescent (*arrow*) and is partially dedolomitised (*De*). Sample C28-13'

6. Mineralisation within the Ballysteen Limestone: within the Ballysteen Limestone, mineralisation is prevalent within well-developed dissolution seams (i.e. between 5 mm and 2 cm thick). Coarsely crystalline sphaerite, euhedral galena and acicular pyrite are the main ore-minerals present.
7. Mineralisation within primary porosity: although uncommon, early pyrite is observed within primary porosity. It occurs as fine irregular crystals within both the bright and dull luminescent calcite cements. Galena and sphaerite are notably absent.

are commonly coarse-grained and crystalline, whereas the pyrite is fine-grained. Some of the bands appear to parallel bedding planes (Grennan 1986).

5. Vein type: Grennan (1986) noted the presence of apparently near-vertical calcite veins, which occur in the basal section of the Wausortian Limestone. They typically contain brecciated fragments of finer-grained pyrite, galena and sphaerite, within coarser crystalline white calcite. In addition, the present study has also highlighted the occurrence of mineralised fractures within both the Wausortian and Ballysteen Limestones. Individual fractures may be as wide as 1 cm and contain coarsely crystalline sphaerite, galena and bladed pyrite, with any remaining fracture porosity occluded by coarsely crystalline dull luminescent calcite and minor planar dolomite cement.

Paragenesis of carbonate and sulphide minerals

Optical petrology and cathodoluminescence were used to determine the paragenesis of the cement sequence. Using the principles of superposition and cross cutting relationships, a paragenetic diagram was constructed (Fig. 9). The order of paragenesis for the major phases is as follows, from oldest to youngest:

1. Non-luminescent syndepositional marine cements.
2. Non-luminescent equant calcite cement followed by bright luminescent calcite cement.
3. Early pyrite, replacement dolomite and planar dolomite cement.
4. Dull luminescent equant calcite cement, and ore-stage sphaerite, galena and pyrite.

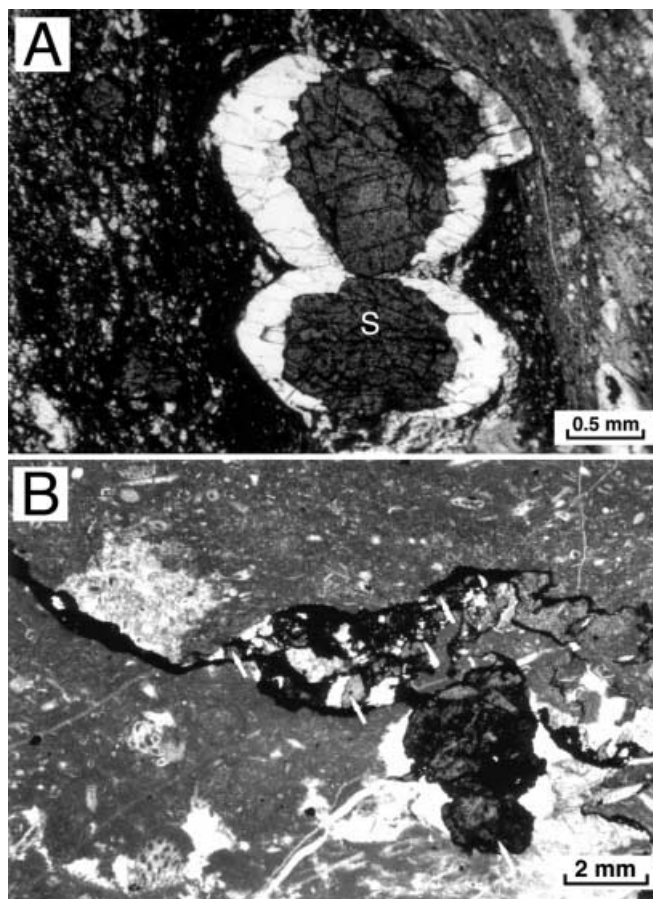


Fig. 8 **A** Plane-light photomicrograph of replacement sphalerite (S) within a solution-seam. Well-developed pressure-shadows are present around the sphalerite and have been cemented by fibrous dull luminescent calcite. Sample C28-13'. **B** Plane-light photomicrograph of replacement sphalerite within stylolite (arrows). Sample 2872-3-31.35

5. Saddle dolomite cement.
6. Dull luminescent calcite cement
7. Variscan deformation and the formation of pressure-shadows cemented by fibrous dull luminescent calcite.

Unlike many other Zn–Pb deposits (e.g. McManus and Wallace 1992), the main ore-phases (i.e. sphalerite and galena) are generally absent from within primary porosity. Where sulphide minerals are present in primary porosity, they are predominantly irregular fine grains of early pyrite. This observation is consistent with a relatively late diagenetic origin for the base-metal sulphide minerals, following near-complete loss of primary porosity by burial cementation. Similarly, the common observation of ore-stage sulphide minerals and dolomite replacing macro-stylolites indicates a burial origin for the sulphides. Therefore, the observed paragenesis suggests that the main phase of mineralisation at Courtbrown occurred relatively late in the paragenetic sequence and is epigenetic in origin. Importantly, there is no evidence of any sulphide minerals being interla-

minated with synsedimentary cements, ruling out any synsedimentary component to the mineralisation.

Discussion

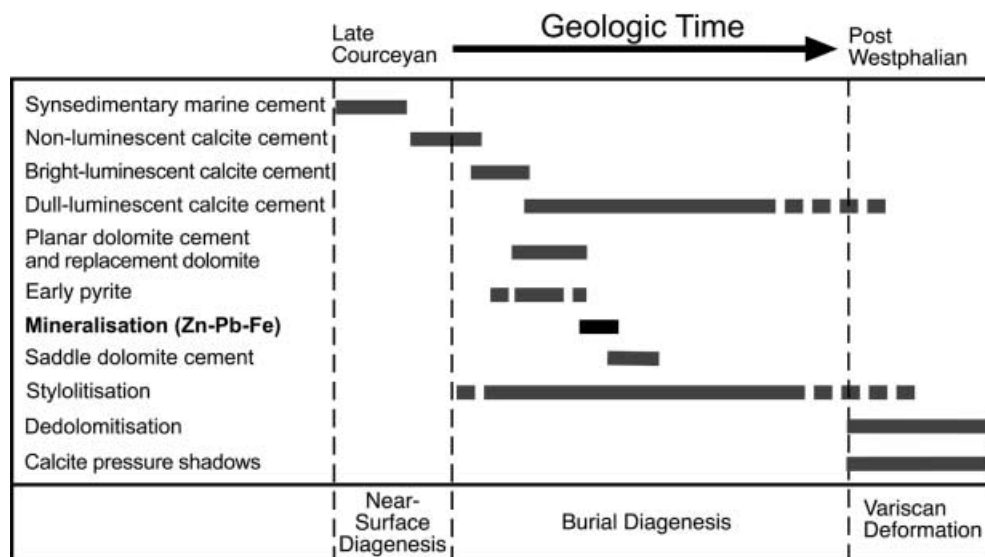
Classification of the mineralisation style

The style of mineralisation at Courtbrown shares many similarities with Mississippi Valley-type (MVT) deposits. Whereas MVT deposits themselves vary considerably in their style and host rocks, most authors agree on the basic features of these deposits: the deposits are epigenetic, carbonate-hosted and have a simple mineralogy. Furthermore, there is a common association with diagenetic dolomites, mineralisation temperatures are in the range of 75 to 200 °C and there is generally no association with igneous intrusions (Ohle 1959; 1980; Jackson and Beales 1967; Anderson and Macqueen 1982; Leach and Sangster 1993). The Courtbrown mineralisation has the characteristics that are typical of MVT deposits.

In addition, the Courtbrown deposit has had a diagenetic history similar to those noted in many MVT provinces (e.g. the Viburnum Trend; Voss and Hagni 1985), with the precipitation of sulphide minerals preceded by the formation of replacement dolomite and planar dolomite cements. These pre-mineralisation dolomites at Courtbrown are probably equivalent to the regional dolomites that pre-date mineralisation elsewhere in the Irish Midlands (Hitzman et al. 1998; Sevastopulo and Redmond 1999). Similarly, the saddle dolomite cement which is associated with the Courtbrown mineralisation, is another phase that is common in many MVT deposits (e.g. Voss and Hagni 1985), including other Irish Zn–Pb deposits (e.g. Hitzman et al. 1998; Peace and Wallace 2000). Therefore, similar to the Harberton Bridge mineralisation (County Kildare, Ireland; Fig. 1), Courtbrown is a MVT-like deposit that is located within the Irish mineral field, a region well known as the type locality for ‘Irish-type’ deposits.

Strogen (1995) suggested a possible link between the Lower Carboniferous volcanic succession in the Limerick Syncline (Fig. 1) and the formation of base-metal deposits in the surrounding area. Indeed, Grennan (1986) has used the inferred position of the Lower Carboniferous volcanic rocks in the Courtbrown area, to support a hypothesis that fluids related to the Asbian volcanic rocks were responsible for the mineralisation. However, except for the aeromagnetic anomaly suggesting such rocks may be locally present in the subsurface (Grennan 1986), there is little evidence to support an igneous source for the ore-fluids. Importantly, (1) the Courtbrown deposit shares the same stratigraphic position and style of mineralisation as other Zn–Pb deposits in Ireland, which show no volcanic affiliation (e.g. Lisheen, Galmoy), (2) volcanic rocks have not been intersected during drilling at the Courtbrown deposit and (3) the mineral assemblage, zonation and paragenetic sequence expected in a deposit

Fig. 9 Paragenetic sequence. The relative timing of major diagenetic and mineralisation phases for the Courtbrown deposit



associated with an intrusive body (e.g. the Zeehan Pb–Zn ore field; Both and Williams 1968a, 1968b) are not observed. In addition, the absence of a vitrinite reflectance halo surrounding the deposit rules out a localised igneous heat source that may have aided the generation or circulation of ore fluids. It appears unlikely, therefore, that the mineralisation at Courtbrown is related to the Lower Carboniferous volcanic event.

Burial history of the Courtbrown region

Accepting that the formation of the epigenetic base-metal mineralisation at Courtbrown is related to diagenetic events, the application of burial history analysis in conjunction with paragenetic observations can help constrain the timing of mineralisation. An accurate understanding of the subsidence history of the Shannon Trough is, therefore, required. The following section summarises the general subsidence history of the Shannon Trough as outlined by Strogen (1988, 1995), Somerville and Strogen (1992), Croker (1995), Strogen et al. (1996) and Sleeman and Pracht (1999); Fig. 10 is a graphic representation of the interpreted burial history of the Courtbrown area constructed during this present study. Sediment thicknesses used for the construction of the burial diagram are in italics.

The subsidence history of the Shannon Trough has to a large degree controlled facies development across the basin. Sedimentation within the trough was initiated during the early Courceyan with the deposition of the Lower Limestone Shales (~50 m thick; Grennan 1986) followed by the Ballysteen Limestone (~250 m thick; Grennan 1986; Fig. 10).

The initiation of differential subsidence accompanying the deposition of the Waulsortian Limestone during the late Courceyan to early Chadian saw a marked change in the subsidence regime across the trough

(Strogen 1988; Somerville and Strogen 1992). Accelerated subsidence concentrated in the west Co. Limerick area and the Shannon Estuary resulted in the thickening of the Waulsortian Limestone from 150–400 m in east Limerick to ~1,200 m in the Shannon Estuary (Somerville and Strogen 1992; Fig. 10). However, by the end of Waulsortian times, carbonate production matched the subsidence rate, and differential water depths were eliminated by the early Chadian (Somerville and Strogen 1992). Somerville and Strogen (1992) suggest that it is this initial sag phase centred on the Shannon Estuary that led to the development of a north-west-dipping carbonate ramp, which would dominate facies development until the end of the Viséan. Volcanic activity commenced after the deposition of the Waulsortian Limestone in the east Co. Limerick area and continued until the late Asbian (Strogen 1988).

Although the post-Waulsortian stratigraphy has not been preserved in the Courtbrown area, for this present study, lithological thicknesses from the surrounding area have been used to estimate the amount of Viséan sediments removed from the Courtbrown deposit. From the late Chadian to early Arundian, outer ramp conditions (the Rathkeale Formation: ~460 m thick; Fig. 10) were established across the west Co. Limerick area, whereas middle and inner ramp facies were developed to the east (Somerville and Strogen 1992). From the late Arundian, the carbonate ramp prograded north-westwards as subsidence decelerated, bringing middle ramp conditions (the Durnish Formation: ~307 m thick; Fig. 10) to the west Co. Limerick area during the Holkerian (Somerville and Strogen 1992; Sleeman and Pracht 1999). The west Co. Limerick area returned to outer ramp conditions during the Asbian and Brigantian with the late Viséan sediments preserving a transition to deeper water facies (the Shanagolden Formation: ~77 m thick, and the Parsonage and Corrig Lodge Formations: ~50 m thick) (Sleeman and Pracht 1999; Fig. 10).

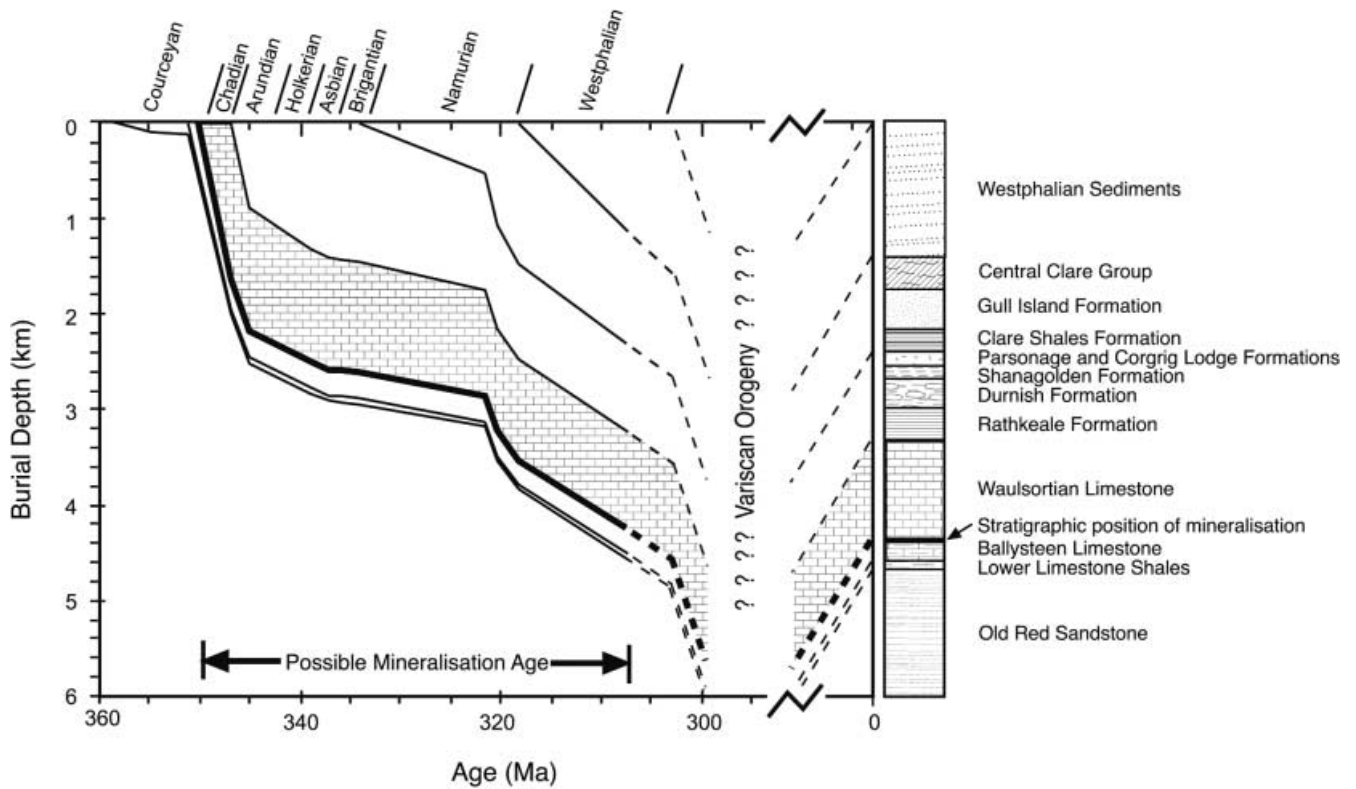


Fig. 10 Burial history diagram for the Courtbrown region. The post-Variscan uplift history is not shown. The column on the right shows the reconstructed stratigraphic section for the Courtbrown area, based on the regional stratigraphy and the Porcupine Basin to the west. The possible age of mineralisation is based on paragenetic considerations (discussed in text). The stratigraphic position of the ore-stage base-metal mineralisation is denoted by the solid black line

The Namurian marks a significant change in the evolution of the Shannon Trough. During this time, deep-water siliciclastics dominated sedimentation and inversion occurred in the Limerick Syncline area, where an angular unconformity separates the Namurian rocks and the underlying Lower Carboniferous carbonate sequence (Strogen 1988). Similarly, Croker (1995) has identified a minor unconformity separating the Lower Carboniferous sequence and Namurian sedimentary rocks to the north-west in Co. Clare (Fig. 1). Strogen (1988) and Croker (1995) have attributed the unconformities to the possible first effects of the approaching Variscan deformation front along the southern boundary of the Shannon Trough.

While the Limerick Syncline underwent inversion during the early Namurian, marine deposition continued in the western portions of the Shannon Trough (Strogen 1988). The oldest Namurian sediments are the Clare Shales Formation (~280 m thick), which is a unit characterised by mud-dominated shales deposited in deep-water conditions (Sleeman and Pracht 1999). These are, in turn, overlain by the Gull Island Formation (~400 m thick), which is comprised of finer-grained siltstones and sandstones. A high subsidence

and deposition rate during sedimentation has been inferred for this formation by Sleeman and Pracht (1999). However, by the late Namurian, the sedimentation rate overtook subsidence, resulting in the seaward progradation of deltaic sediments of the Central Clare Group (~360 m thick; Sleeman and Pracht 1999; Fig. 10).

The depositional history of the Shannon Trough during the Westphalian and Stephanian is not preserved in the Courtbrown region. However, the offshore Porcupine Basin, to the west, has preserved a nearly complete pre-Variscan succession, which includes around 1,500 m of Westphalian and ~330 m of Stephanian/Autunian sediments (Fitzgerald et al. 1994). Furthermore, Fitzgerald et al. (1994) suggest that the pre-Variscan succession may have been significantly thicker onshore. Vitrinite reflectance data (Clayton et al. 1989) from the south of Ireland certainly support the idea that a pre-Variscan sequence, possibly as thick as 3 km (Croker, 1995), was deposited and has since been removed. Sedimentation ceased within the Shannon Trough following basin inversion during the Late Carboniferous/Permian Variscan Orogeny (Croker 1995; Sleeman and Pracht 1999; Fig. 10).

Thermal history of the Courtbrown region

Conodont colour alteration indices (CAI) for the Courtbrown region vary from 4.5 to 6, with most carbonate samples having a CAI value of 5 (Clayton et al. 1989). Similarly, vitrinite reflectance data from the

Courtbrown region indicate Ro values in the range of 4.5 to 5.2% for Carboniferous sedimentary rocks (Clayton et al. 1989), corresponding to a maximum temperature of approximately 310 °C using Barker's (1988) correlation between maximum temperature and Ro. However, fluid inclusion homogenisation temperatures (Th) in calcites, which precipitated contemporaneously with ore-stage sulphide minerals at Courtbrown, are in the range of 170–180 °C, significantly less than the regional maximum paleotemperatures indicated by the Ro and CAI data.

The measured fluid inclusion size shows no correlation with homogenisation temperature (Fig. 6B). Furthermore, the Th distribution is unimodal (Fig. 6A). Both of these have been used to suggest that the fluid inclusions have not been stretched during over-heating (Goldstein and Reynolds 1994) and, therefore, the Th values obtained are a good approximation to mineralisation temperatures. However, calcite is a relatively weak mineral and should not preserve trapping temperatures during significant over-heating (Goldstein and Reynolds 1994; Tobin and Claxton 2000). Tobin and Claxton (2000) have used variable-time hydrothermal experiments to demonstrate that the Th distribution can remain unimodal during over-heating. In addition, the Th values from stretched inclusions will be greater than the original Th values, but less than peak burial temperatures.

Given the maximum paleotemperature of approximately 310 °C for the Courtbrown region achieved prior to basin inversion during Variscan deformation, it appears likely that the fluid inclusion temperatures for the Courtbrown deposit have been significantly affected by post-entrapment heating. Furthermore, the lack of correlation between Th and inclusion size could simply mean that all fluid inclusions in the ore-stage calcite have stretched regardless of size.

Relative timing of formation of the sulphide and carbonate minerals

The timing of individual diagenetic phases (including formation of ore minerals) can be estimated by correlating the diagenetic and mineralisation history of the carbonates with their burial history (e.g. Wallace et al. 1991; McManus and Wallace 1992). Several constraints can be placed on the timing of the diagenetic and mineralisation events, including:

1. The paragenesis and luminescence stratigraphy of the diagenetic phases.
2. The minimum depth required for macro-stylolite formation.
3. The presence of Variscan deformation structures.

The luminescent stratigraphy observed in the burial calcite cements can be used to place constraints on the oxidation potential of the fluids responsible for their formation. These constraints may, in turn, be used to infer a formation depth for the calcite cements. Luminescence

within carbonates is largely controlled by the inclusion of trace elements in solid solution, particularly Mn^{2+} and Fe^{2+} which are considered the main activators and quenches respectively, of luminescence (Frank et al. 1982; Machel 1985; Barnaby and Rimstidt 1989). Microprobe results from this present study (Fig. 5) support this hypothesis, with bright luminescence in the calcite cements corresponding with elevated Mn concentrations (i.e. > 500 ppm), while dull luminescence coincides with lower Mn concentrations (i.e. < 500 ppm). The non-luminescent calcite cements contain negligible concentrations of Mn and Fe (i.e. < 100 ppm).

Work on the luminescence stratigraphy of the burial calcite cements has attempted to explain the luminescence pattern of non to bright to dull as the result of interaction with increasingly reduced fluids during burial (Frank et al. 1982; Machel 1985; Barnaby and Rimstidt 1989). The later parts of this cementation sequence are believed to represent a reduced subsurface burial environment (Frank et al. 1982; Machel 1985; Barnaby and Rimstidt 1989). Therefore, as base-metal mineralisation at the Courtbrown deposit occurs in the later half of the cementation sequence and is contemporaneous with the dull luminescent calcite cements, the most likely environment for the formation of the sulphide mineralisation is a burial environment.

A further constraint can be placed on the timing of diagenetic and mineralising events by assigning a minimum burial depth for the formation of pressure dissolution structures (i.e. stylolites and dissolution seams), which host ore-stage mineralisation. The observed paragenesis of the Courtbrown deposit (Fig. 9) supports a burial origin for the stylolites and dissolution seams, as stylolitisation began during the precipitation of the bright luminescent calcite cement, and continued until well after the occlusion of remaining primary porosity by dull luminescent calcite. Previous work by Nicolaides and Wallace (1997), Lind (1993) and Railsback (1993) suggest that a minimum burial depth of around 800 m is required for the formation macro-stylolites. Therefore, as mineralisation at the Courtbrown deposit is found to be predominantly hosted by well-developed macro-stylolites and thick dissolution seams, the carbonate sequence had presumably obtained a minimum burial depth of approximately 800 m prior to the onset of mineralisation.

Deformation structures resulting from the Variscan Orogenic event may be used to place a minimum age on the timing of the mineralisation. At the Courtbrown deposit, the most prominent deformation microstructure preserved is well-developed pressure-shadows surrounding large sphalerite grains that overprinted dissolution seams (Fig. 8A). The pressure-shadows are cemented by fibrous dull luminescent calcite cement that has grown parallel to the stretching direction. Although early Namurian basin inversion in the Limerick Syncline is the first major deformation event recorded in the Shannon Trough, it appears to have been restricted to the south-eastern regions (Strogen 1988). Similarly, it is

unlikely that the pressure-shadows are the result of extensional faulting because the fibrous calcite cement has grown perpendicular to bedding, which would require a compressional setting. Therefore, in the absence of a major basin wide deformation event prior to the latest Palaeozoic, it is likely that the pressure-shadows are Variscan in origin and that the mineralisation pre-dates Variscan deformation.

Absolute age constraints for mineralisation

The paragenetic relationships discussed above may be used to generate maximum and minimum age constraints for mineralisation by comparison with the burial and deformation history of the Courtbrown area. The bulk of the Courtbrown mineralisation is hosted by the basal beds of the Waulsortian Limestone (Grennan 1986). Therefore, the following discussion relates specifically to the timing of events at this stratigraphic interval.

The ore-stage mineralisation is hosted by macro-stylolites and dissolution seams. If a minimum burial depth of about 800 m is required for the initiation of these structures, this depth represents the minimum amount of stratigraphic cover achieved prior to mineralisation. This depth corresponds to an approximately early Chadian age for the Courtbrown area (Fig. 10). However, as mineralisation is observed overgrowing replacement dolomite rhombs that also replace stylolites, it is likely that the mineralising event occurred at depths in excess of the minimum required for stylolite formation (i.e. in excess of 800 m depth). Consequently, the early Chadian age (~350 Ma) can only be used as a maximum age for the mineralisation, as the mineralisation may be significantly younger (Fig. 10).

The main phase of Variscan deformation and the formation of pressure-shadows around sphalerite places a minimum age on the timing of mineralisation. The precise timing for the onset of Variscan deformation is difficult to ascertain, because most of the stratigraphic record for this event has been removed by erosion. However, based on Variscan structures from the western half of central Ireland, Coller (1984) suggested that the age of the main ductile deformation is between post-Westphalian B (~307 Ma; Harland et al. 1990) and pre-Upper Permian. This age is further supported by Hitzman (1999) and Fitzgerald et al. (1994) who have also suggested a Late Carboniferous age for the main episode of Variscan deformation.

Comparisons with other Zn–Pb deposits in Ireland

Mineralisation ages for Zn–Pb deposits in Ireland are generally poorly constrained because attempts to directly date the deposits have been largely unsuccessful. Much of the early work from the 1960s to the 1980s on deposits such as Tynagh (Derry et al. 1965; Banks 1985)

and Silvermines (Boyce et al. 1983; Andrew 1986), concluded that mineralisation occurred syngenetically or during early diagenesis in the late Courceyan or early Chadian (Hitzman and Beaty 1996). However, re-evaluation of this earlier work, along with the discovery of epigenetic mineralisation (Harberton Bridge, Lisheen, and Galmoy), has questioned the validity of the 'Irish-type' syngenetic model, and subsequently the late Courceyan to early Chadian age.

Navan is the largest Zn–Pb deposit in Ireland and is often considered to have the most well-constrained mineralisation age. At the Navan deposit, the late Chadian–Arundian (~345 Ma) Boulder Conglomerate contains mineralised clasts thought to be derived from the underlying Pale Beds ore. Therefore, a pre-Arundian age is indicated for the bulk of the mineralisation, with the base-metal sulphide minerals considered to be early diagenetic and partly syngenetic in origin (Ashton et al. 1986, 1992; Anderson et al. 1998). However, Peace and Wallace (2000) have used diagenetic observations to argue that the mineralisation at Navan is completely epigenetic and must be Holkerian (343 Ma) or younger.

Results from the Lisheen Zn–Pb–(Cu) deposit in the Rathdowney Trend also indicate an epigenetic origin for mineralisation (Shearley et al. 1996; Sevastopulo and Redmond 1999). Sevastopulo and Redmond (1999) have suggested that the mineralisation within the Rathdowney Trend is probably younger than early Arundian in age. Although they have not attempted to place a minimum age on the mineralisation, they believe an Asbian or younger age cannot be excluded.

Significantly, the epigenetic mineralisation at the Courtbrown and Lisheen deposits is concentrated near the stratigraphic base of the Waulsortian Limestone. This stratigraphic position is similar to that of the classic 'Irish-type' mineralisation at Silvermines and Tynagh. This similarity raises questions about the nature of the classic syngenetic 'Irish-type' deposit model.

Conclusions

The Courtbrown deposit is an epigenetic Zn–Pb deposit in which the base-metal sulphide minerals are mainly hosted by stylolites and dissolution seams. There were two episodes of sulphide mineral formation: an early episode of pyrite precipitation, and a later episode of sulphide precipitation during which the ore was emplaced.

The timing of mineralisation has been constrained by comparing the deposit-scale diagenetic and mineralisation history with the regional burial and deformation history. This approach supports the following conclusions regarding the timing of mineralisation:

The main episode of mineralisation occurred at depths in excess of approximately 800 m, indicating a maximum early Chadian age (~350 Ma) for the mineralisation in the Courtbrown area.

Pressure-shadows surrounding coarsely crystalline sphalerite constrain the timing of mineralisation to before late Westphalian-Stephanian (~307 Ma) Variscan deformation.

Homogenisation temperatures for primary fluid inclusions within calcite cements (precipitated pencon-temporaneously with mineralisation) have a strong mode at about 170–180 °C. These temperatures are almost certainly not representative of mineralisation temperatures and were probably generated by heating and deformation during maximum burial prior to or during Variscan deformation.

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