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ARTICLE

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Contrasting sources for lead in Cu-polymetallic and Zn–Pb mineralisation in Ireland: constraints from lead isotopes

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Abstract Devonian red bed-hosted deposits in SW Ireland occur either as low-grade stratiform disseminations and minor veinlets with bornite and djurleite, or as major quartz veins with copper-polymetallic deposits. Pb isotopic ratios vary according to the style of mineralisation. For disseminated sulphides, there is a considerable scatter of lead isotope compositions. These appear to define a mixing line between a basement source and a more radiogenic component, which may have been granite-derived detrital minerals in the red beds. For minor veinlets there is a more restricted distribution of lead isotopic data, which could be interpreted in terms of fluid flow homogenising the wide spread of Pb isotope ratios from the disseminated sulphides. This is consistent with published sulphur isotope data. Major quartz veins show a clustered array of Pb isotopic ratios and it is suggested that the bulk of the metals were derived after Variscan compression, from a basement source with a minor contribution from red beds. Lower Carboniferous limestone-hosted deposits form three groups: Cu–Ag ± Hg–As–Sb–U epigenetic vein-hosted deposits; Cu–As ± Zn, Pb, Ag, Co, Ni stratabound deposits; and Cu–As ± Pb, Ag, Mo, Co, Ni epigenetic vein deposits. Lead isotope compositions for the stratabound deposits have a very restricted range for each locality and plot close to the same mixing line as the Carboniferous Zn–Pb deposits of Central Ireland. It is suggested that the lead in both areas has been derived from a similar basement source. The model age of ca. 350 ± 10 Ma for stratabound mineralisation is close to that of their host rocks. Lead isotope data for the epigenetic Cu–As vein deposits suggest a similar source, but a younger age of 280 ± 10 Ma for mineralisation. This 280 ± 10-Ma age has important implications for the timing of the Variscan orogeny in SW Ireland. Because chalcopyrite–tennantite occurs along pressure solution cleavage planes that have been deformed by thrusting, the emplacement of the mineralised tectonic Ross Island sheet, west of Killarney, must post-date 280 Ma. The difference in the ore assemblage between the limestone-hosted Cu-polymetallic deposits of Ireland, and the penecontemporaneous Zn–Pb deposits of Central Ireland may be because of differences in the underlying lithology. In the SW, up to 6 km of red beds underlie the limestone-hosted stratabound Cu-polymetallic deposits whereas, in Central Ireland, the Zn–Pb ore-bearing carbonate rocks are underlain by lower Palaeozoic greywackes with a minimal thickness of late Devonian red beds. However, the isotopic evidence only indicates a major red bed source of metals at Ardtully. Elsewhere, unless the metals in the red beds originated from a basement rather than a granite source, a significant red bed contribution to the metals seems unlikely. An alternative possibility is that copper ores were derived from an extension of the Ordovician island arc of SE Ireland.

Keywords Copper-Polymetallic · Ireland · Lead isotopes · Zinc–Lead

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Introduction

In the last 30 years, studies of Irish mineral deposits have concentrated on the economically important Zn–Pb deposits of central Ireland (reviewed in Andrew 1993). In addition there are well-documented occurrences of low-grade Cu-dominated mineralisation in Devonian sandstones of SW County Cork (Reilly 1986;

Ni Wen et al. 1996). Between these two areas are a number of small, poorly-described deposits of polymetallic Cu–Ag sulphides, which are not necessarily of economic significance, but which are of considerable importance in the understanding of the mineralising processes elsewhere in southern Ireland. There is an abundance of lead isotope data published on the base metal deposits of central Ireland (Greig et al. 1971; Boast et. al. 1981; Boast 1983; Caulfield et al. 1986; O'Keeffe 1986; LeHuray et al. 1987; O'Keeffe 1987) with detailed studies of the Navan (Mills et al. 1987) and Harberton Bridge deposits, (Gallagher et al. 1992). Dixon et al. (1990) used these data, combined with whole-rock lead isotope data for unmineralised Lower Palaeozoic basement rocks along strike from those basement rocks underlying or hosting base metal mineralisation, to show that the Carboniferous-hosted Zn–Pb deposits can be interpreted as being derived from the basement. Fluid inclusion and isotope data from these sulphide-bearing Lower Palaeozoic veins indicate that regional flow of seawater-derived fluids occurred in the fractured basement underlying the Carboniferous basins (Everett et al. 1999a, 1999b).

Lead isotope data for the low grade Cu-dominated mineralisation hosted in Devonian red beds and the Carboniferous rocks of the Munster Basin are limited, although a preliminary discussion of these data in Ixer and Pattrick (1995) suggested that they showed a number of different mineralising events. The data were subsequently used in attempts to provenance early Bronze Age metal artefacts from the British Isles (Rohl and Needham 1998; Ixer 1999) but with little success as acknowledged by Ixer (2000). This paper presents new lead isotope data for copper deposits hosted in red beds and for the small Cu–As–Ag deposits of the Munster Basin. These lead isotope data have a direct bearing on metal sources for a range of deposit types in southern and western Ireland and have important implications for arguments concerning the origin of the major Zn–Pb deposits of the Irish Midlands.

General geological setting

Regional geology

The geological framework of Ireland consists of a mosaic of domains, each of which records a part of the geological time-scale stretching back almost 2 billion years. The Caledonian orogeny, which affected the whole of Ireland between the late Silurian and middle Devonian, resulted from the collision of three plates, Laurentia, Avalonia/Cadomia and Baltica, after the closing of the proto-Atlantic (Iapetus) Ocean (Soper and Hutton 1984; Soper 1988). Between 435 and 410 Ma, Cadomia collided with Laurentia along the Iapetus suture. The north-easterly-trending suture zone, which extends across central Ireland, divides Ireland into two crustal blocks, a north-west terrane (NWT) and a south-east terrane (SET), which had quite different histories prior to the Silurian. Basement rocks in Ireland are subdivided into pre-Caledonian and Caledonian age rocks similar to those observed along strike in Britain.

Pre-Caledonian basement

In the NWT, the pre-Caledonian basement is composed of Lewisian, Grenvillian and Neoproterozoic Dalradian rocks (Holland et al. 1979). Lewisian rocks are limited to the island of Inishtrahall, whereas Grenville age (Lewisian) basement xenoliths occur in late Palaeozoic diatremes in central Ireland (Strogen 1974). Rocks of the Dalradian Supergroup of the NWT crop out extensively in NW Ireland. These accumulated in a linear basin, which extended at least 700 km from Connemara to the Shetland Islands (Harris et al. 1978).

The SET is composed of Late Proterozoic gneisses that crop out in the Rosslare Complex (Max and Long 1985; Dixon et al. 1990). Reconstructions of Acadian plate tectonics indicate that these form part of the Avalonian terrane of North America and Wales (Pickering et al. 1988; Soper 1988). Kennan et al. (1979) suggested that the pre-Caledonian basement extends under much of central Ireland.

Caledonian basement

The pre-Caledonian basement is overlain by Ordovician and Lower Silurian rocks. Phillips et al. (1976) recognised two faunally distinct terranes. To the north-west of the Iapetus suture, the succession is largely turbiditic with local basic volcanic rocks. To the south-east of the suture, Upper Ordovician and Lower Silurian turbidites were derived from a volcanic arc with a sialic basement and were subjected to very low grade metamorphism and deformation during the Caledonian orogeny.

Cover sequence

Crustal sag in mid to late Devonian led to the Caledonian basement being unconformably overlain by Middle Devonian to Lower Carboniferous fluvial sedimentary rocks, known as the Old Red Sandstone facies. These were deposited in fault-bounded continental basins (the Munster Basin) that formed during a period of extension related to continental rifting (Phillips and Sevastopulo 1986). Sandstones were deposited by river systems in a relatively flat desert environment. Tongues of coarser sands and gravels were deposited in basin margins with finer material carried towards the centre of the basin. These sediments consolidated to form a group of rocks known as the red beds. In the Irish Midlands, the red beds are up to 300 m in thickness, although typically they are less than 100 m (Emo and Grennan 1982). In contrast, in the south-west, the red beds are over 6 km thick in the Kenmare Valley of the Munster Basin, a half-graben bounded by a fault-zone passing through Dingle Bay (Gardiner and MacCarthy 1981; Williams et al. 1989). Extension continued from the late Devonian through to mid Carboniferous.

The overlying Lower Carboniferous succession reflects a marine transgressive sequence of late Courceyan 'layer-cake' carbonate rocks (Hitzman 1999). (Courceyan is a chronostratigraphic term used in Ireland and the UK, which approximately corresponds to the Tournasian epoch.) Limestones were deposited on deltaic sands and muds. It is these 'layer-cake' carbonate rocks that host most of the Zn–Pb deposits in Ireland and the Cu–As deposits of Ross Ireland, Muckross and Ardtully in the Kenmare Valley. These widespread carbonate rocks were succeeded during Chadian to Arundian times by a more complex facies mosaic consisting of juxtaposed basinal and shallow marine carbonate strata. By Holkerian times, basinal areas were infilled and there was little progradation of shelf facies over basinal facies (Hitzman 1999). The carbonate sequence generally thins northwards.

Variscan orogeny

Variscan compression began in late Carboniferous because of collision between Gondwana and Laurentia–Baltica, resulting in the closure of the Rheic and Proto-Tethyan oceans (Windley 1995). Compression resulted in large-scale folding in the south of Ireland and subsequent south-to-north-directed thrusting as the crust continued to shorten (Meere 1995a). The heat flow associated with basin extension and Variscan compression was much higher than normal, which resulted in metamorphism of the whole red bed succession. Temperatures reached a peak of 300–400 °C during the early extensional phase (Meere 1995b; Ni Wen et al. 1999) with later deformation occurring at lower temperatures (Meere 1995b). There has been considerable discussion about when mineralisation took place and whether metal movement occurred during extensional crustal thinning, or during the compressional phase (e.g. Andrew 1993; Johnston 1999; Wright et al. 2000).

Mineralisation styles and occurrences

There are a number of occurrences of copper mineralisation in south-west Ireland (Fig. 1) although these are minor when compared with the Zn–Pb deposits of the Irish Midlands. Some of these copper-bearing localities in the Munster Basin have been mined since the Bronze Age (O'Brien et al. 1990; O'Brien 1994), although the main period of extraction was the 19th century (Reilly 1986; Cowman and Reilly 1988). There are two groups of copper deposits; generally small-scale deposits hosted by Devonian ORS (Old Red Sandstone) red beds (Fig. 1), and copper-rich polymetallic deposits hosted by Carboniferous limestones of Courceyan age (Fig. 1), although the ore petrology of the epigenetic Courceyan-hosted veins is very similar to the mineralogy of the late major veins in the ORS red-beds.

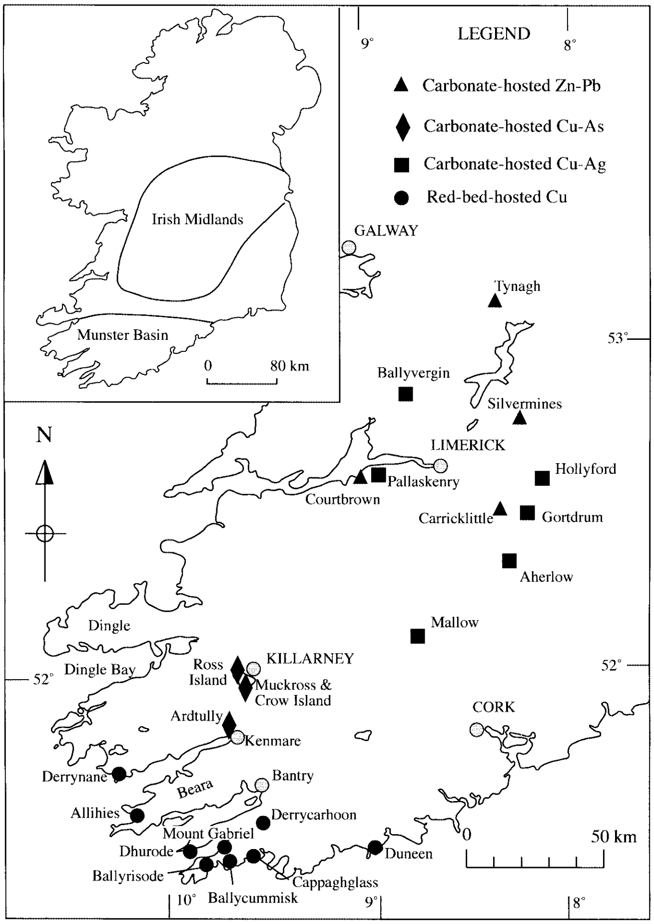

Fig. 1 Location map of ore deposits in southwest Ireland showing the Zn–Pb deposits hosted in carbonate rocks, the copper-polymetallic deposits hosted by Lower Carboniferous limestones of Courceyan age and copper deposits hosted by Devonian red beds. *Inset* shows the location of the Munster Basin and Irish Midlands

Copper deposits hosted by Devonian red beds

Deposits hosted by Devonian red beds occur at Allihies in the Beara Peninsula (Sheridan 1964) and at a number of other localities in the far south-west where three associations have been recognised (Ni Wen et al. 1996, 1999; Table 1).

1. Disseminated copper ores. Low-grade stratiform disseminated copper sulphides occur in more than 100 scattered localities (Snodin 1972). The copper minerals only occur in thin green to grey shaley horizons intercalated with the red beds mainly towards the top of the Castlehaven Formation. Mineralised beds are generally <3 m thick, with copper grades typically <1 wt% even where historically mined (O'Brien et al. 1990; O'Brien 1994). Originally, the sulphide mineralogy was bornite, djurleite and chalcopyrite, with traces of wittichenite (Cu_3BiS_3); (Ixer 1994). This sulphide deposition has been attributed to diagenetic reduction of sulphate in the presence of organic matter by bacterial action (Snodin 1972). As pressure solution cleavage developed, metals were removed from domains that developed cleavage, and were redeposited in adjacent narrow, sulphide-rich zones or in minor segregation veins (Ni Wen et al. 1999). The original mineral assemblage was modified to secondary bornites, often with chalcopyrite and covelline lamellae, and to a range of other copper sulphides (Ni Wen et al. 1996, 1999).
2. Simple copper ores in minor quartz veins. The copper ores occur in thin veinlets with accessory calcite ± chlorite. The sulphide mineralogy is the same as that of the disseminated stratiform deposits and they occur in the same stratigraphic horizons. The veinlets are abundant and form a 'boxwork' with individual veins orientated roughly parallel to bedding, or at a high angle to bedding along spaced cleavages. They are poorly mineralised and have been interpreted as metamorphic segregation features (Ni Wen 1991; Meere 1995b; Ni Wen et al. 1996, 1999). Fluid inclusions within minor veins were trapped at peak metamorphic conditions of 300–400 °C and 1–3 kbar (Ni Wen et al. 1996).
3. Polymetallic ores in major quartz veins. The ore assemblage comprises copper and copper–iron sulphides, Mo, Pb and Bi phases, sulpharsenides and antimony-bearing sulphosalts (Ni Wen et al. 1996).

Table 1 Descriptive details of the host rock lithology, and ore mineralogy of all types of deposits hosted by Devonian red beds. The location of these ore deposits are shown in Fig. 1

Deposit	Host rock lithology	Characteristics of mineralisation
Disseminated ore grades typically < 1 wt% Cu (Snodin 1972; Jackson 1980)		
Derrynane	Ballytrasna Formation – the medial equivalent of the distal Castlehaven Formation (MacCarthy 1990)	Disseminated djurleite ± chalcopyrite ± bornite infill pore spaces; later copper sulphides along spaced cleavage
Derrycarhoon	Castlehaven Formation	Disseminated chalcocite with minor bornite
Mount Gabriel	Green-grey siliclastics and minor carbonate-bearing horizons (cornstones) of the Castlehaven Formation	Stratiform disseminated bornite and djurleite ± wittichenite infill pore spaces in sandstones and siltstones; later sulphides within thin (< 5 cm), quartz–phyllosilicate, veinlets along spaced cleavage
Ballyrisode	Castlehaven Formation	Stratiform copper sulphides
Minor veins. Thin quartz + calcite ± chlorite veins		
Cappaghglass	Top Castlehaven Formation, Toe Head Formation	Thin quartz veins, bornite–chalcopyrite–galena, minor chalcocite, tennantite, pyrite
Major veins. Thick laterally extensive quartz veins		
Dhurode	Fluvial Toe Head and Old Head Sandstone Formations	Vein, > 300 m long, 2 m wide, along a dextral E–SE fault, cross cutting folds, (Snodin 1972) Two mineral associations: (1) Chalcopyrite–arsenopyrite–tetrahedrite–bournonite–meneghinite–galena, with rare molybdenite, pyrite and sphalerite (2) Late chalcocite–djurleite-bornite–molybdenite–native bismuth, rare wittichenite (Ni Wen 1991)
Ballycummisk	Top Castlehaven Formation	Three paragenetic stages: (1) Early quartz + barite + haematite, with sericite, carbonates, chlorite and TiO_2 minerals (2) Quartz with molybdenite, tetrahedrite, bornite, chalcopyrite and pyrite with calcite, ankerite, sericite, chlorite and TiO_2 minerals (3) Quartz–carbonate with minor tetrahedrite and chalcopyrite
Allihies	Sandstones of the Caha Mountain Formation	Chalcopyrite + tetrahedrite in quartz veins (Cole 1922). Estimated 1 Mt of copper ore mined at 3% Cu grade (Reilly 1986)

These major veins, which are up to 2 m wide, are laterally extensive structures, often associated with E–W faults. At the south-east margin of the Munster Basin they occur in the Toe Head and Old Head Sandstone Formations higher in the stratigraphic succession than the disseminated stratiform mineralisation. At Allihies, close to the basin depocentre, major vein mineralisation occurs in the Caha Mountain Formation (Pracht personal communication). Sulphide-poor barite veins also occur especially around Mount Gabriel (Ni Wen 1991; Ixer 1994; Ni Wen et al. 1996). The major veins post-date the main phase of ENE–WSW Variscan folding (Sheridan 1964) and were formed after peak metamorphism when fluids scavenged Mo, Pb, Sb, As and Bi from large volumes of rock. These fluids deposited the major vein concentrations often in faults, and at higher stratigraphic levels than the stratiform disseminated deposits (Ni Wen et al. 1999). These metamorphic fluids were trapped at post-peak metamorphic conditions at 280–350 °C and < 600 bars (Ni Wen et al. 1996).

The stratiform type (1) deposits have been interpreted as diagenetic in origin (Snodin 1972; Reilly 1986), or magmatic and related to unexposed granites (Evans 1976; Daltry 1985). These interpretations contrast with more recent detailed studies that have provided considerable evidence that the ore-forming fluids of the West Carbery district, especially those associated with the type (2) vein deposits, were metamorphic in origin (Ni Wen et al. 1996, 1999). Textural relationships of these ores have been described elsewhere (Ni Wen et al. 1996, 1999).

Polymetallic Cu–Ag–As deposits hosted by Carboniferous limestones

Located between the copper deposits of the south-west, and the economically important carbonate-hosted Zn–Pb deposits of the Irish Midlands (Fig. 1), are a series of Courceyan carbonate-hosted polymetallic Cu–Ag–As deposits. These fall into three groups according to whether they are stratabound or epigenetic (Table 2), and whether Ag or As is dominant (Fig. 1):

1. Cu–Ag ± Hg–As–Sb epigenetic deposits. Veins are characterised by chalcopyrite with native silver, bornite, chalcocite and other ore minerals. The most important of these deposits is Gortdrum (Fig. 1), which was exploited for Cu and Hg from 1968 to 1975 (Thompson 1966; Steed 1986). An irregular network of cross cutting carbonate veins are associated with breccias. The ore assemblage is characterised by chalcopyrite, tennantite and local Hg

Table 2 Descriptive details of the limestone-hosted copper-polymetallic deposits in the Munster/Shannon Basin. Host rock lithology is Courceyan Ballysteen Formation limestone, the lateral equivalent of the Argillaceous Bioclastic Limestone in the Irish Midlands. Locations of the deposits are shown in Fig. 1

Location of deposit	Characteristics of mineralisation
Ross Island	
Stratabound ore at Blue Hole	Chalcopyrite–pyrite, with lesser amounts of galena and sphalerite and trace amounts of arsenopyrite, tennantite and marcasite. The ores are pyrite- or chalcopyrite-rich. They underlie sphalerite-rich banded ores that have galena-, chalcopyrite- or tennantite-rich bands. Pyrite, arsenopyrite and tennantite are present in minor to trace amounts
Crow Island	
Stratabound ore	Cu–As ± Zn, Pb, Co, Ni, Ag stratabound deposit characterised by chalcopyrite–tennantite–bornite and sphalerite–galena mineralisation, ± Fe, Co and Ni sulpharsenides. Mined for copper 1812–1813
Muckross	
Stratabound ore	Stratabound Cu–Pb–Zn with minor Co and Ag, Mo sulphides and sulpharsenides (Ixer and Pattrick 1995; Ixer and Budd 1998)
	Banded pyrite-chalcopyrite and sphalerite–chalcopyrite–galena ores with arsenopyrite and minor tennantite, cobaltite, molybdenite and stromeyerite
	Coarse-grained chalcopyrite–tennantite–arsenopyrite ores. The amount of arsenopyrite and its wide-ranging chemistry are noteworthy
	Later cross-cutting chalcopyrite–tennantite
Ross Island	
Epigenetic veins at Western Mine	Thin cross cutting chalcopyrite–tennantite veinlets with minor copper- and nickel-bearing cobaltite and trace amounts of pyrite, marcasite, arsenopyrite, molybdenite, bornite, galena, sphalerite and stromeyerite
	Bunches of coarse-grained massive chalcopyrite–bornite/'idaite' and tennantite accompanied by minor to trace amounts of cobaltite, arsenopyrite, molybdenite, galena, sphalerite and pyrite
Ardtully	
Epigenetic veins	Veins of bornite–'idaite'–tennantite, chalcopyrite and trace amounts of cobaltite. Copper–dolomite association. Four lodes with galena (Cole 1922)

enrichment near the surface, and bornite and chalcocite at depth. Other vein deposits are small and are associated with folds, flexures and shearing. They occur at Aherlow (Romer 1986), Ballyvergin (Andrew 1986) and Mallow (Wilbur and Royall 1975; Wilbur and Carter 1986). A descriptive summary of the Cu–Ag ± Hg–As–Sb deposits is given by Andrew (1993).

2. Cu–As ± Zn, Pb, Co, Ni, Ag stratabound deposits. These occur within Courceyan Ballysteen Formation limestones and are characterised by chalcopyrite–tennantite–bornite and sphalerite–galena mineralisation, ± Fe, Co and Ni sulpharsenides. The deposits are small and are present at Ross Island, Crow Island (Lough Leane) and Muckross (Fig. 2). On Ross Island, stratabound mineralisation at the Blue Hole mine (Fig. 2) comprises horizons of massive chalcopyrite–pyrite with minor galena and sphalerite with traces of arsenopyrite and tennantite, passing up into banded, dark ore comprising sphalerite and galena accompanied by minor pyrite, chalcopyrite and traces of arsenopyrite and tennantite (Ixer and Pattrick 1995, 2002; Ixer and Budd 1998). Thin sulphide–calcite veinlets cross cut the bedded ores. On the Muckross Peninsula, about 2.5 km south of Ross Island, stratabound sulphides are confined to a particular layer 10–50 mm thick, close to a shale unit within Courceyan limestones. A wide range of primary copper–iron–lead–zinc sulphides and sulpharsenides, together with silver and molybdenum minerals are present (Table 2). An extensive range of secondary minerals has been documented by Moreton et al. (1998).
3. Cu–As ± Pb, Ag, Mo, Co, Ni epigenetic vein deposits. Thin cross-cutting veins are well-developed at Western Mine on Ross Island (Fig. 2) and Ardtully. At Western Mine, thin calcite veinlets up to 2 cm thick, contain disseminations of intergrown chalcopyrite–tennantite accompanied by minor nickeliferous cobaltite, molybdenite and pyrite and trace amounts of secondary stromeyerite and native silver (Ixer and Pattrick 1995; Ixer and Budd 1998). Spoil material near the entrance to the mine shows abundant calcite veining with up to 50% vein material, although 20–30% veining is more typical. Although epigenetic mineralisation at the Western Mine occurs only 150 m from the stratabound mineralisation at Blue Hole, there are no stratabound sulphides at surface in Western Mine. Historically, copper was mined from several veins around Ardtully in the Kenmare Valley (Pracht 1997). There is almost no trace now of the original copper mineralisation at Ardtully, but material from the spoil comprises complex bornite, 'idaite', tennantite with minor chalcopyrite and cobaltite intergrown with coarse-grained baroque dolomite. Cole (1922) reported eight Cu lodes with tetrahedrite and bornite and four Pb lodes in a group of mines that produced 59 t of ore with 4% Cu in 1911. More than 400 t of Ag-bearing galena was also mined (Pracht 1997). The Pb lodes were entirely within limestone, whereas the Cu veins occurred either in the limestone, the Carboniferous slate or in the Old Red Sandstone.

The carbonate-hosted Cu–Ag deposits of Gortdrum, Aherlow, Ballyvergin and Mallow are considered by

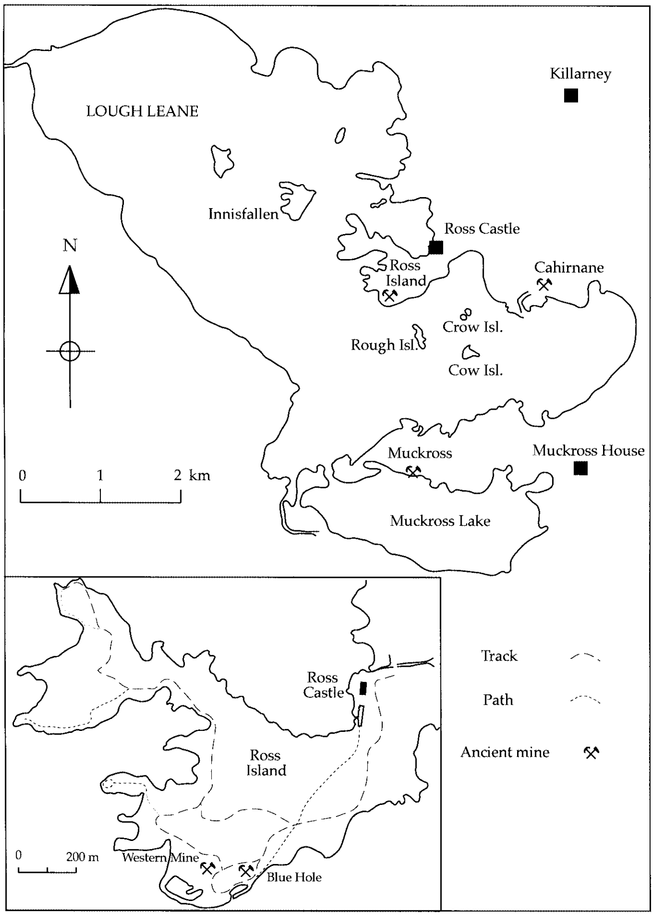

Fig. 2 Location map of the copper-polymetallic deposits near Killarney. *Inset* shows the location of Blue Hole and Western Mine on Ross Island

Andrew (1993) to be hosted by the Mellon House and Ringmoylan Formations of earliest Courceyan age (*Polygnathus spicatus* and *P. inornatus* conodont biozones). The younger age of the host rocks at Ross Island means that not all of the deposits are located stratigraphically within the transitional basal argillaceous limestone sequence as envisaged by Andrew (1993).

Lead isotope studies

Introduction

Russell (1968) first proposed that the source of lead and other metals in the Carboniferous carbonate-hosted base metal deposits of the Irish Midlands was the underlying Caledonian basement rocks. Subsequent lead isotope studies provided further evidence in support of this hypothesis (Boast et al. 1981; Boast 1983; Caulfield et al. 1986; O'Keeffe 1986, 1987; LeHuray et al. 1987; Dixon et al. 1990). From the published data on galena from these deposits two particular features emerge (Fig. 3a, b):

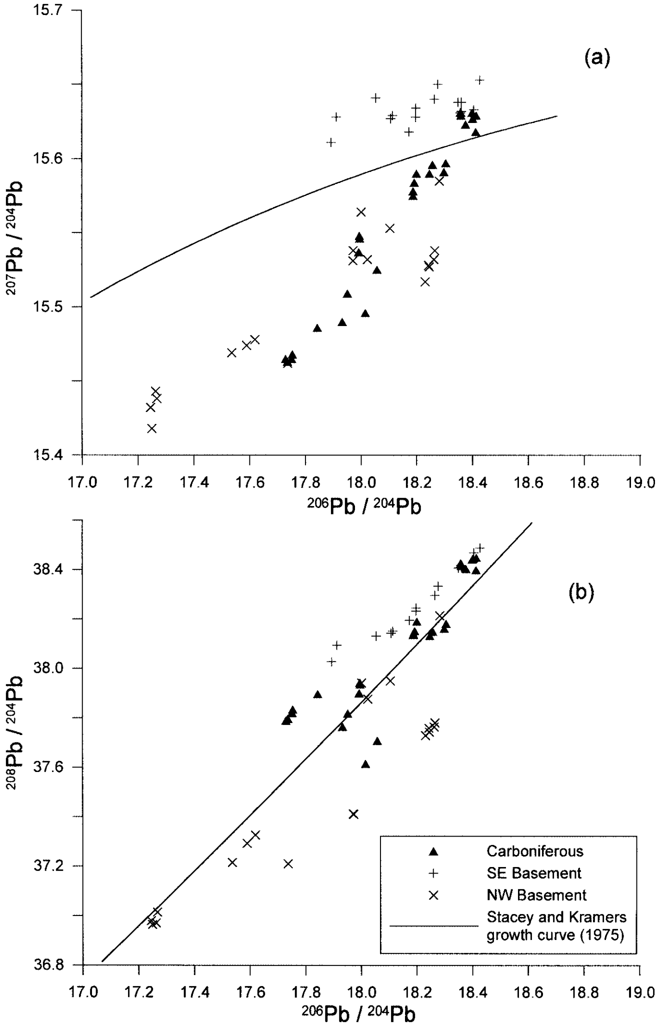

Fig. 3a,b Published lead isotope data for Irish Carboniferous zinc–lead deposits and SE and NW basement-hosted sulphide-bearing veins. **a** $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$; **b** $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$. Data from Boast et al. (1981), Boast (1983), Caulfield et al. (1986), O'Keeffe (1986, 1987), LeHuray et al. (1987) and Dixon et al. (1990), Growth curve from Stacey and Kramers (1975) included for reference

1. There is a linear trend of isotopic data on the $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ plot.
2. There is a systematic geographical variation of the $^{206}Pb/^{204}Pb$ data across Ireland (Dixon et al. 1990) with compositions becoming more radiogenic from NW to SE irrespective of mineralisation style, age or host rock (Fig. 4). Most authors consider this reflects a variation in the lead source, with a less radiogenic source in the NW and a more radiogenic source in the SE (Caulfield et al. 1986; O'Keeffe 1986; Dixon et al. 1990). The data array for the Carboniferous carbonate-hosted Zn–Pb deposits is interpreted as a mixing line between leads derived from these two source areas. 'Isoplumbs' of $^{206}Pb/^{204}Pb$ parallel structures and lithological contacts within the Cale-

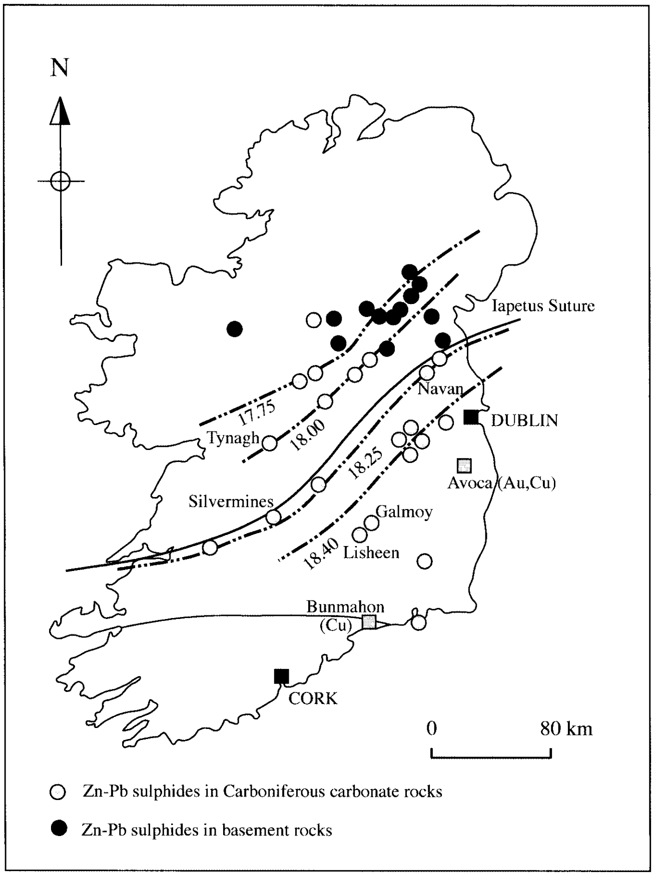

Fig. 4 Contoured values of $^{206}Pb/^{204}Pb$ for Irish zinc–lead deposits. After Dixon et al. (1990)

donian basement and are generally oblique to the strike of Carboniferous lithologies (Fig. 4).

A basement source of lead is further suggested by the occurrence of fracture-fill mineralisation that extends beneath Carboniferous-hosted deposits into basement rocks. In addition, mineralisation also occurs in the basement away from known carbonate-hosted deposits (Halliday and Mitchell 1983; Morris 1984; Andrew 1986; O'Keeffe 1986). Everett et al. (1999a) provided good evidence for the flow of mineralising fluids in Lower Palaeozoic rocks and, based on fluid inclusion temperatures, suggested that fluids may have penetrated to depths of at least 3–5 km. In addition, carbon, oxygen, strontium and sulphur isotope data from basement-hosted veins beneath the ore deposits imply that there is a metasedimentary basement-equilibrated hydrothermal fluid component in the mineralising systems (Everett et al. 1999a).

Until now, only limited lead isotopic data were available for the low-grade Cu-dominated mineralisation hosted Devonian red beds in the Munster basin. In addition, few data exist for carbonate-hosted Cu–Ag deposits other than for Gortdrum (Steed 1986; Duane 1988).

A comprehensive suite of ore types for this study has been collected in-situ, from drill core when available, and also from spoil heaps of old mines both because they contain unexposed lithologies and because the sulphide minerals are generally less weathered than in surface outcrops. Data from this study have been combined with earlier data obtained from mineralised samples selected by Ixer and briefly discussed by Ixer and Pattrick (1995) and partially published by Rohl (1995, 1996).

Analytical procedures

Samples, all of which had previously been studied and described in reflected light, were crushed in a tungsten carbide mortar and pestle at the NIGL laboratory at BGS Keyworth. When possible individual grains of galena were hand picked under ethanol, with the aid of a binocular microscope. Galenas were then digested in 8 N nitric acid, evaporated, re-dissolved in 6 N hydrochloric acid and evaporated. Minerals other than galena, were dissolved in 1 N hydrobromic acid and put through an AG1 ×8 anion exchange column to purify the lead. The 6 N HCl eluant was evaporated. All samples were then picked up in 2% nitric acid and diluted to the appropriate strength for the Plasma 54. The solution was spiked with thallium at 10 ppb to correct for mass discrimination. Analysis was undertaken on a PIMMS Plasma 54 (plasma ionisation multimass spectrometer). The reproducibility of NBS 981 standard ($n = 27$) during the period of analyses: $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ were all $\pm 0.05\%$ (2σ) whereas the reproducibility of the $^{208}Pb/^{206}Pb$ was 0.02% (2σ). Replicate analyses of three of the samples analysed by Rohl (1996) were included in this study (Mount Gabriel MG3A; Ross Island, Ross 5/10.35* and Ross 93A) to compare data produced in this study with those obtained by Rohl (1996). The data (Tables 3 and 4) show very similar $^{206/204}Pb$ ratios for all three pairs of samples as might be expected although there is more variation in the $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios. There is no consistent pattern: two of Rohl's samples show higher ratios for both isotopes (5.10.35 and 93A) and one is lower (93A); therefore both sets of data can be combined to form a more comprehensive data set as there is no systematic difference in the data sets.

Results

All the lead isotope data from this study are given in Tables 3 and 4 and are listed along with the data of Rohl (1995). Also included are data for Duneen, a galena-bearing deposit in Upper Devonian–early Carboniferous basin margin clastics of south-west Co. Cork (O'Keeffe 1986). These data are graphically presented in Figs. 5 and 6.

Sulphide mineralisation hosted by Old Red Sandstone red beds

There is a considerable variation in the isotopic ratios depending on the style of mineralisation. For the disseminated stratiform mineralisation (Table 1), there is a considerable inhomogeneity of data on both $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ (Fig. 5a) and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ plots (Fig. 5b), with a particularly wide spread of data for the radiogenic samples from Mount Gabriel. Minor, copper-bearing veinlets display a more restricted distribution on both Fig. 5a and b and show the same spread as data from the major quartz veins.

Table 3 Lead isotope data for Old Red Sandstone-hosted copper deposits. For details of ore assemblages of material analysed by Rohl, see Rohl (1995, 1996). The Duneen galenas analysed by O'Keefe (1986, 1987) are from a 30-cm-wide quartz vein in Upper Devonian–Early Carboniferous Kinsale Formation (see Fig. 1 for geographic location). *qu* Quartz; *arsenopy* arsenopyrite; *born* bornite; *ccite* chalcocite; *cpy* chalcopyrite; *gal* galena; *haem* haematite; *tenn* tennantite

Sample no.	Analyst	Main mineral assemblage	$^{208}/^{204}$Pb	$^{208}/^{206}$Pb	$^{207}/^{204}$Pb	$^{207}/^{206}$Pb	$^{206}/^{204}$Pb
Derrynane – disseminated							
95-DN1	Rohl (1995)		39.569	1.9651	15.742	0.7818	20.136
95-DN2	Rohl (1995)		39.361	1.9596	15.738	0.7835	20.086
Derrycarhoon – disseminated							
95-DC	Rohl (1995)		38.310	2.0719	15.565	0.8418	18.490
DCH	Rohl (1995)		38.217	2.0453	15.626	0.8363	18.685
Ballyrisode – disseminated							
95-B1	Rohl (1995)	Copper ores	39.460	2.0223	15.678	0.8035	19.512
BRS	Rohl (1995)	Copper ores	39.175	1.9777	15.699	0.7926	19.808
Mount Gabriel – disseminated							
MG3 A[a]	This study	ccite, born	38.502	2.0132	15.654	0.8185	19.125
MG3 A[a]	Rohl (1995)	ccite, born	38.355	2.0053	15.646	0.8180	19.127
MG 3 B	This study	ccite, born	38.263	2.0936	15.594	0.8532	18.276
Skeagh 1	This study	qu, born	38.627	2.0384	15.647	0.8257	18.950
CS 92.1	Rohl (1995)		38.560	1.9042	15.710	0.7758	20.250
Mine 9	Rohl (1995)		40.095	1.9673	15.693	0.7700	20.381
MG 311-A	Rohl (1995)	ccite, born	40.245	1.9495	15.741	0.7625	20.644
MG 311-E	Rohl (1995)	ccite, born	41.423	1.9000	15.784	0.7240	21.802
Cappaghglass – minor veins							
Cappagh 1	This study	born	38.963	2.0604	15.614	0.8257	18.911
Cappagh 3	This study	born	38.145	2.0986	15.593	0.8578	18.177
CAPP	Rohl (1996)	gal	38.183	2.1006	15.608	0.8586	18.177
C12	Rohl (1995)		38.371	2.0993	15.644	0.8559	18.278
Dhurode – major veins							
DHU	Rohl (1996)	gal	38.320	2.0925	15.622	0.8530	18.313
Dhrode 2	This study	cpy–ccite	38.439	2.0788	15.614	0.8444	18.491
Dhrode 6	This study	arsenopy	38.798	2.0605	15.608	0.8289	18.830
Dhrode 21.8	This study	gal	38.287	2.0922	15.610	0.8530	18.300
Ballycummisk – major veins							
1.87.11	Rohl (1995)	cpy	38.126	2.0813	15.579	0.8505	18.318
BCM	Rohl (1995)	cpy	38.190	2.0804	15.596	0.8496	18.357
Bally A	This study	born	38.245	2.0569	15.621	0.8402	18.593
Bally 19-6	This study	haem-rich qu-vein	38.253	2.0425	15.623	0.8342	18.729
Bally 19-13	This study	cpy, tenn, haem	38.620	2.0396	15.629	0.8254	18.935
Cork 2	This study	Complex Au-ore	38.198	2.0932	15.573	0.8534	18.249
Allihies – major veins							
95-All	Rohl (1995)	cpy, born	38.701	2.0751	15.633	0.8382	18.650
BMR All 93.1	Rohl 1995	cpy, born	38.654	2.0762	15.610	0.8384	18.618
BMR All 93.2	Rohl (1995)	cpy, born	38.665	2.0531	15.621	0.8295	18.833
Duneen							
Dnm.1	O'Keeffe (1986)	gal	38.221	2.1036	15.606	0.8589	18.169
Dnm.2	O'Keeffe (1986)	gal	38.217	2.1034	15.605	0.8589	18.169
Dnm.3	O'Keeffe (1986)	gal	38.224	2.1033	15.609	0.8589	18.173
Dnm.4	O'Keeffe (1986)	gal	38.242	2.1038	16.610	0.9137	18.178

[a] Data for sample MG3A have been provided from Rohl, and has been re-analysed in this study

Sulphide mineralisation, hosted by the Courceyan Ballysteen Formation limestones

Lead isotope data for Ross Island and Muckross (Table 4, Fig. 6) are more consistent than the red bed-hosted deposits. Except for the Ardtully sample, which is anomalously radiogenic, the ratios are similar to those for the Carboniferous hosted Zn–Pb deposits of the Irish Midlands, such as Silvermines and Courtbrown (Fig. 1).

There is a consistent variation within the set of isotopic data (Fig. 7). Stratabound mineralisation from Muckross has slightly lower ^{206}Pb/^{204}Pb and higher ^{207}Pb/^{204}Pb than stratabound mineralisation from Blue Hole or Crow Island, whereas the veins at Western Mine

Table 4 Lead isotope data for carbonate-hosted copper-polymetallic ore deposits. For details of ore assemblages of material analysed by Rohl, see Rohl (1995, 1996). *born* Bornite; *ccite* chalcocite; *cpy* chalcopyrite; *gal* galena; *haem* haematite; *pyr* pyrite; *sphal* sphalerite; *tenn* tennantite

Sample no.	Analyst	Main mineral assemblage	$^{208}/^{204}$Pb	$^{208}/^{206}$Pb	$^{207}/^{204}$Pb	$^{207}/^{206}$Pb	$^{206}/^{204}$Pb
Ross Island epigenetic – Western Mine							
Ross 1	Rohl (1995)	cpy, tenn	38.123	2.088	15.593	0.854	18.261
Ross3/12. 35	This study	cpy, tenn	38.093	2.085	15.576	0.853	18.271
Ross 4	This study	cpy, tenn	38.087	2.087	15.578	0.853	18.252
Ross 5	This study	cpy, tenn	38.088	2.093	15.587	0.856	18.202
Ross 5/2.90	Rohl (1995)	cpy	38.126	2.087	15.594	0.854	18.266
Ross 5/10.35[a]	This study	cpy, tenn	38.116	2.086	15.583	0.853	18.269
Ross 5/10.35[a]	Rohl (1995)	cpy, tenn	38.194	2.088	15.607	0.853	18.290
Ross 6	This study	cpy–born	38.025	2.085	15.585	0.854	18.239
Ross Island stratabound – Blue Hole							
Ross 7	Rohl (1995)	sphal, gal	38.099	2.096	15.562	0.856	18.175
Ross 8	This study	sphal, gal	38.065	2.097	15.583	0.858	18.155
Ross 9	Rohl (1995)	sphal, gal, py	38.122	2.097	15.600	0.858	18.178
Ross 10	Rohl (1995)	sphal, gal	38.149	2.097	15.610	0.858	18.190
Ross 93	Rohl (1995)	cpy, py, gal	38.099	2.097	15.594	0.859	18.164
Ross 93A[a]	This study	cpy, py, gal	38.084	2.097	15.589	0.858	18.164
Ross 93A[a]	Rohl (1995)	cpy, py, gal	38.136	2.098	15.601	0.858	18.174
Ross 122.3	Rohl (1995)	cpy, pyr	38.094	2.096	15.593	0.858	18.175
Ross 122.9	This study	pyr, cpy, gal	38.036	2.096	15.576	0.858	18.148
Ross 397	This study	cpy, py	38.127	2.096	15.606	0.858	18.188
Blueholes X	This study	sphal, gal	38.028	2.096	15.568	0.858	18.145
Crow Island							
Crow1	Rohl unpublished data	gal	38.074	2.097	15.591	0.859	18.156
Crow2	Rohl unpublished data	gal	38.057	2.097	15.586	0.859	18.147
Muckross stratabound							
Muckross 6	Rohl (1995)	sphal–gal	38.071	2.098	15.590	0.859	18.144
Muckross 7	Rohl (1995)	cpy–py	38.063	2.098	15.588	0.859	18.143
Muck 9	This study	tenn–cpy	38.005	2.098	15.567	0.859	18.119
Muck X	This study	cpy–py	38.161	2.101	15.613	0.860	18.166
Ardtully epigenetic							
AK-1	This study	cpy, tenn	38.243	1.743	15.797	0.720	21.943

[a] Data for samples Ross 5/10.35 and Ross 93A have been provided from Rohl, and have been re-analysed in this study

are markedly more radiogenic. If the ^{206}Pb/^{204}Pb data are interpolated graphically using the values of Boast et al. (1981), Muckross stratabound samples give an errorchron age of 355 ± 10 Ma, Crow Island 350 ± 10 Ma and Blue Hole stratabound mineralisation at 340 ± 10 Ma. Although it could be argued that error bars on the analytical data would negate this interpretation, it is nevertheless consistent with the field observation that Muckross mineralisation occurs at a slightly lower stratigraphic level than Blue Hole and is broadly consistent with an estimated conodont age of 355 Ma for Ross Island. Epigenetic vein deposits at Western Mine, Ross Island, which can be seen in a hand specimen to cross-cut stratabound sulphides at Blue Hole, give an errorchron age of 270–290 Ma. These are all geologically feasible ages, consistent with field observations.

Interpretation – constraints on metal sources

Lead isotope data published for Carboniferous-hosted Zn–Pb deposits of central Ireland define a linear ^{206}Pb/^{204}Pb–^{208}Pb/^{204}Pb trend (Dixon et al. 1990). This trend reflects a sedimentological mixing in Lower Palaeozoic greywackes of lead derived from two different sources: one a low radiogenic source in the basement of NW of Ireland, the other a more highly radiogenic basement source in the SE. The carbonate-hosted Cu-polymetallic deposits described here show an affinity with the Carboniferous Zn–Pb deposits, whereas the red bed hosted deposits of the Munster Basin and copper–dolomite association of Ardtully have different and distinctive isotopic ratios. These comparisons and contrasts are important for interpreting the source of the lead and other metals in the deposits.

Sulphide mineralisation hosted by Old Red Sandstone red beds

The red-bed hosted Cu deposits form a coherent data set although there is a considerable inhomogeneity of data on both ^{206}Pb/^{204}Pb vs. ^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb vs.

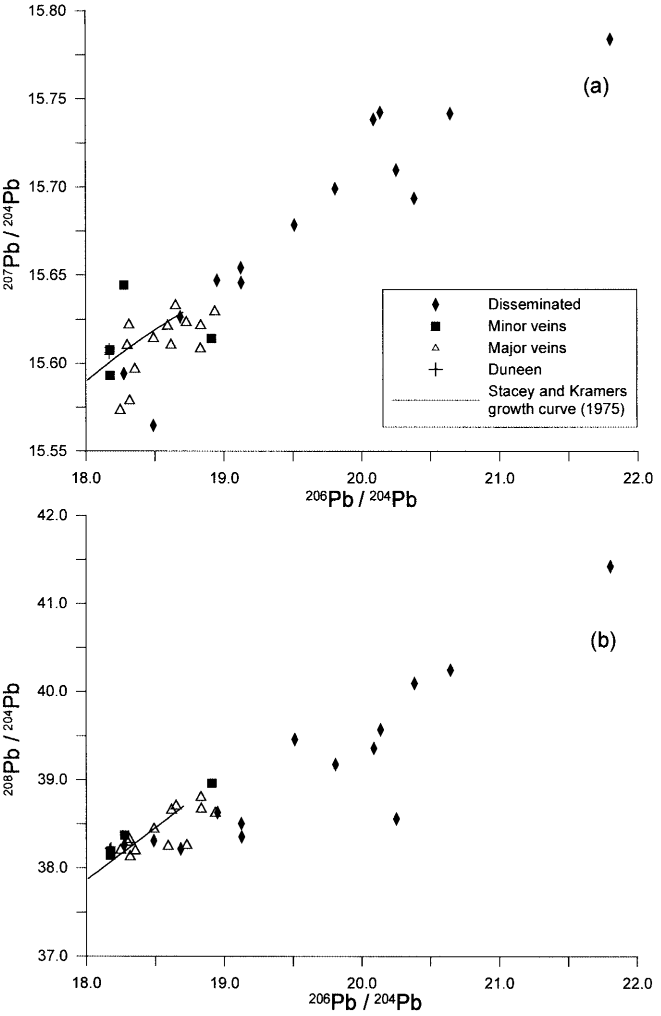

Fig. 5a,b Lead isotope data for all classes of Old Red Sandstone-hosted copper ore deposits of SW Ireland. **a** $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$. **b** $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$

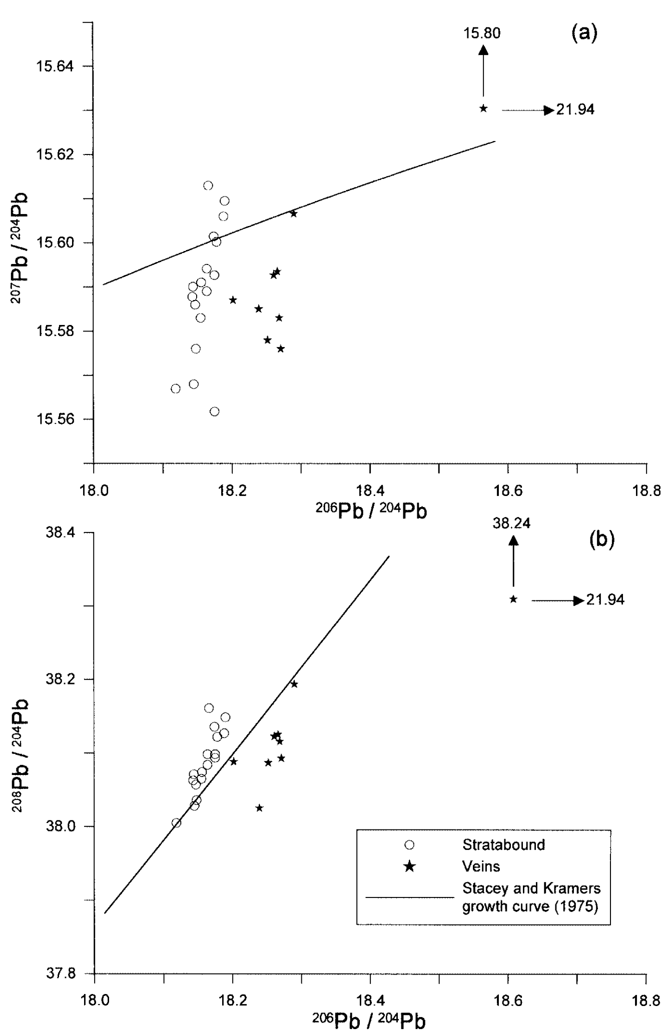

Fig. 6a,b Lead isotope data for carbonate-hosted copper-polymetallic ore deposits. **a** $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$; **b** $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$

$^{208}Pb/^{204}Pb$ plots (Fig. 5), particularly for the radiogenic samples from Mount Gabriel.

Lead isotope ratios for the disseminated sulphides, especially those from Mount Gabriel, appear to define a mixing line between a source from the NW and SE basement and a more radiogenic component. It is envisaged that the source of this radiogenic lead is heavily influenced by the presence of granite-derived detrital minerals disseminated in the red beds. Duane (1988) suggested an analogous origin for uranium in the Gortdrum deposit and a similar assemblage of detrital minerals to Gortdrum is found in the red beds. Zoned zircons, TiO_2 minerals, tourmaline, carbonaceous matter/graphite plus trace amounts of chromite, magnetite and ilmenite occur, with authigenic overgrowths on tourmaline and TiO_2 (Ixer 1994). Duane (1988) envisaged that the unroofing of the HHP Leinster granite (O'Connor 1982) provided the source materials for Gortdrum. For the red beds of SW Ireland, the source rocks of the detrital mineral is more likely to have been a granite to the west.

In contrast to the disseminated sulphides from Mount Gabriel and other areas, lead isotope data for sulphides from the minor veinlets in the red beds are more tightly constrained with lower $^{206}Pb/^{204}Pb$ ratios than the disseminated mineralisation. Isotopic data for the minor veins could be interpreted in terms of a fluid flow homogenising the wide spread of Pb isotope values from the disseminated sulphides. This is consistent with sulphur isotope data (Ni Wen et al. 1996), which indicates that sulphides in the minor veins were remobilised stratiform disseminated sulphides. For Duneen, where galena occurs in a 30-cm-wide quartz vein in Upper Devonian–early Carboniferous Kinsale Formation, the lead isotope data given by O'Keefe (1987) are identical to that of other minor veins in the red beds.

For the major veins at Allihies, Dhurode and Ballycummisk, the lead isotope data form a well-defined group on the $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$ plot. This group lies between the mixing line for the basement-derived Carboniferous-hosted Zn–Pb sulphides, and the mixing

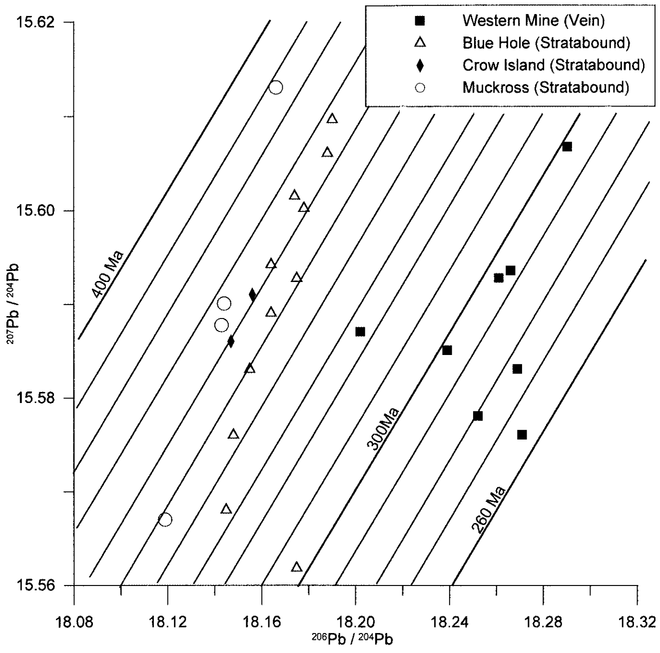

Fig. 7 Lead isotope data ($^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$) for carbonate-hosted copper-polymetallic ore deposits with model ages for Ross Island and Muckross samples by deposit type and locality

line for the disseminated red bed-hosted copper mineralisation (Fig. 8). It seems plausible to suggest that the bulk of the lead and other metals in the major veins were derived from the basement beneath the red beds, with only a minor contribution of metals from a red bed source.

The carbonate-hosted Cu-polymetallic deposits of SW Ireland described here, together with the Cu deposit of Gortdrum (Duane 1988), show an affinity with the Carboniferous Zn–Pb deposits of central Ireland. On Pb isotope diagrams (Fig. 8) the lead from the stratabound Cu–As–Pb–Zn ± Ag–Co–Ni–Mo assemblage plots close to the same mixing line as the carbonate-hosted Zn–Pb deposits, towards the end member defined by the SE basement source. This implies that the lead in the stratabound carbonate-hosted Cu-polymetallic deposits was derived dominantly from a basement source in much the same way as for the Courceyan Zn–Pb deposits of central Ireland, as described by Everett et al. (1999b). For the epigenetic veins, lead isotope values have similar $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios to the stratabound ores, but have higher $^{206}Pb/^{204}Pb$ ratios. This may reflect a different time of extraction rather than a different source.

The Cu–Pb mineralisation at Ardtully differs from other deposits because of the copper–dolomite association, and its distinctive highly radiogenic isotopic signature. According to Russell (1983), this copper–dolomite association forms when late-stage 'spent' fluids pass through a significant thickness of oxidised continental red beds picking up copper and other metals. The depocentre of the Munster Basin is in the region of the Kenmare River close to Ardtully, where the thickness of the red beds is in excess of 6 km (Williams et al. 1989; MacCarthy 1990). Therefore, it would seem feasible that the Ardtully carbonate-hosted Cu and Pb were derived solely from within the red beds. As with the metals at Mount Gabriel, it is envisaged that the highly radiogenic nature of the samples originates from granite-derived detrital minerals disseminated in the red beds.

Discussion

Ross Island shows similarities both with the Zn–Pb deposits of the Irish Midlands and the Cu deposits of the far SW of Ireland. The Cu–As deposits on Ross Island are hosted in the same Courceyan carbonate formation

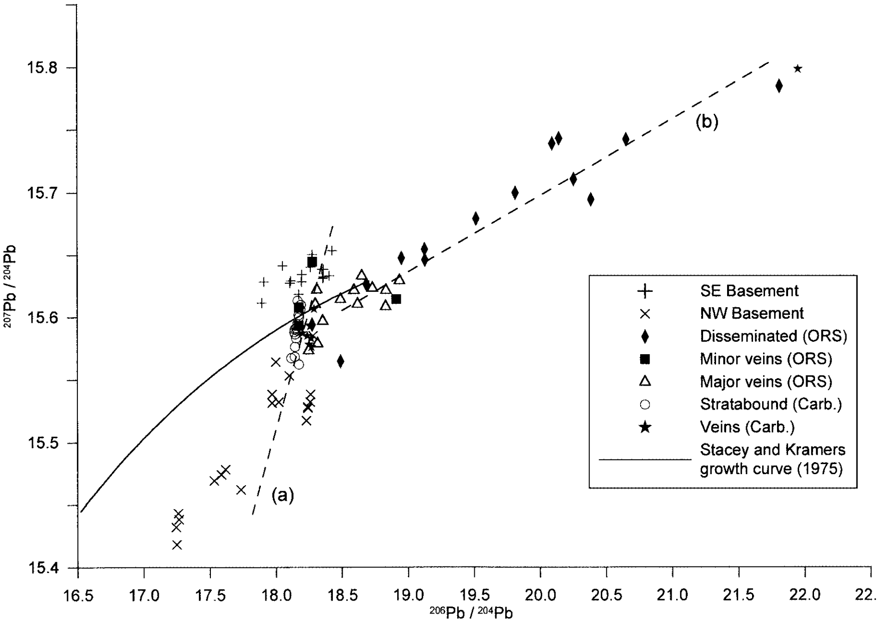

Fig. 8a,b Isotope data for Carboniferous zinc–lead, red-bed hosted copper and carbonate-hosted copper-polymetallic ores showing multiple sources for Irish base metal mineralisation. **a** Mixing line for Lower Palaeozoic lead between an unradiogenic source in NW Ireland and more radiogenic source in SE Ireland. Source of basement data as in Fig. 2. **b** Mixing line for disseminated metals in red beds between a radiogenic source ascribed to granite-derived detrital minerals within the red beds and a Lower Palaeozoic basement component as the Zn–Pb deposit at Silvermines and elsewhere, and carry the same metal assemblage in the stratabound mineralisation at Blue Hole as in the Irish Midlands. This implies that there is a temporal link between these two different types of deposits in spite of the fact that Ross Island is copper dominated and the Irish Midlands are Zn–Pb dominated. In addition, although the host rock differs, the ore petrology of the later epigenetic Cu mineralisation at Western Mine on Ross Island is very similar to the mineralogy of the late red-bed hosted, major vein sulphide assemblage of the Munster Basin. In both settings, sulphides lie along spaced cleavages. In core samples from Ross Island, in particular, it is clear that some chalcopyrite–tennantite grows along pressure solution cleavage in the host limestones, and in the Munster Basin, Cu and Cu–Fe sulphides occur along spaced cleavages. This demonstrates that some ores are associated with cleavage formation and, therefore, are temporally linked to early Variscan tectonism.

In Ireland, peak metamorphic temperatures of 300–400 °C were achieved during extension and high heat flow associated with the formation of the Munster Basin (Meere 1995b; Ni Wen et al. 1996). Subsequent compressional tectonics of the Variscan orogeny resulted in the formation of a spaced pressure solution cleavage during initial layer parallel shortening (Cooper et al. 1984, 1986; Meere 1995a). In the red beds, primary copper minerals were removed from domains where cleavage formed and re-deposited in adjacent narrow zones or in minor segregation veins. Later folding is thought to have controlled megascopic fluid flow in the Munster Basin (Meere and Banks 1997) whereas subsequent high angle reverse faults are thought to be either reactivated extensional structures in the case of the Munster Basin (Price and Todd 1988; Meere 1992) or controlled by Caledonian basement architecture in the Irish Midlands (O'Reilly et al. 1999). The major red bed-hosted veins originated after peak metamorphism from lower temperature circulating fluids that scavenged metals from large volumes of rock and deposited sulphides in major veins, often in fault zones (Ni Wen et al. 1996, 1999). A decrease in temperature from peak metamorphic conditions is associated with trapped fluids from veins ascribed to the Variscan compressional phase, in Ireland (Ni Wen et al. 1996) and in northern France (Kenis et al. 2000), and a final stage of veins in France, associated with post-orogenic extension, which trapped fluids at even lower temperatures (Kenis et al. 2000).

It is envisaged that the radiogenic lead in the red bed-hosted disseminated sulphides was derived from disseminated detrital minerals sourced from granite to the west of the basin. Sediment input to the Munster Basin was influenced by stable areas occupied by granitic plutons both to the east and west of the basin, and by late Devonian times the major transport direction appears to have been from the west (MacCarthy 1990). Geophysical evidence for an unexposed granite to the west of the Munster Basin is given by Conroy (in Murphy 1990). Assuming that this granite has a similar age to the Leinster granite and other Caledonian plutons (ca. 400 Ma), exhumation of the intrusion must have occurred by late Devonian because the Castlehaven Formation that hosts the disseminated mineralisation has a stratigraphic age of ~380–370 Ma. In addition, there is clear evidence that, based on the sudden appearance of microcline feldspar (Penney 1979) in the Ballyhoura Mountains, a granite source was unroofed by Kiltorcan times (Upper Devonian–Lower Carboniferous). There is also granite-derived muscovite in lowermost Courceyan limestones north of Mallow (Clipstone and Roycroft 1992). Exhumation and erosion of Caledonian granites must have occurred within 20 million years of emplacement. Such rapid exhumation of granite plutons following orogenesis is documented from elsewhere in the Caledonides notably in Scotland (Oliver et al. 2000).

The red bed-hosted minor and major veinlets which show more tightly constrained $^{206}Pb/^{204}Pb$ ratios than the disseminated mineralisation are interpreted in terms of a fluid flow homogenising the wide spread of Pb isotope values from the disseminated sulphides. For the major veins at Allihies, Dhurode and Ballycummisk, which developed after major folding (Sheridan 1964), the lead isotope data plot close to that of basement-derived Carboniferous sulphides. Stable isotope data presented by Ni Wen et al. (1996) indicate that the metamorphic fluids responsible for deposition of sulphides in the major veins were trapped in the temperature range 280–350 °C. Assuming an elevated gradient of ca. 40 °C per km, then these fluids either circulated to or originated from depths of at least 6 km in order to attain such high temperatures. Because the thickness of the red beds beneath Dhurode and Ballycummisk is between 2 and 3 km (Fig. 2, Williams et al. 1989) an involvement of the basement is implied. Therefore, it is suggested that the majority of the lead and other metals in the sulphides of the major veins were most likely derived from clay minerals within the Lower Palaeozoic rocks during dehydration reactions associated with greenschist facies metamorphism with only a minor component from breakdown of detrital minerals in the red beds.

There has been much debate as to whether metamorphic fluids escape in a single-pass flow or circulate in large-scale hydrothermal systems (Phillips et al. 1994), and although there have been theoretical arguments against mass fluid flow, Ferry (1988a, 1988b), Yardley et al. (1991) and others, suggest that fluid flow occurred during or after peak metamorphism in large hydrothermal systems. Although the evidence from fluid inclusion, stable isotope and ore studies (Ni Wen et al. 1996, 1999) indicate that major fluid movement was post peak metamorphism, the inhomogeneity of the lead isotope data in this study does not suggest large-scale hydrothermal systems.

At Muckross, Crow Island and Ross Island, the early stratabound Cu–As–Pb–Zn ± Ag–Co–Ni–Mo assemblage is regarded as syngenetic to diagenetic. Because their isotope ratios plot close to the same mixing line as the carbonate-hosted Zn–Pb deposits, towards the end member defined by the SE basement source on Pb isotope diagrams (Fig. 8), it is suggested the main source of the lead was basement-derived. Any contribution of lead from the red beds must either have been minor or else the lead and other metals originated from leachable clays and detrital minerals that had themselves been derived from the basement rather than a granite source. Certainly, Ross Island, Muckross and Crow Island are close to the Variscan Front, where the siliciclastic red beds are thinner (ca. 1,000 m) than at deposits such as Allihies (ca. 5,500 m of upper ORS; Williams et al. 1989) and Mount Gabriel (ca. 2,750 m; Williams et al. 1989).

Chalcopyrite–tennantite with minor copper- and nickel-bearing cobaltite and rare trace amounts of pyrite, marcasite, arsenopyrite, molybdenite, bornite, galena, sphalerite and stromeyerite were deposited in veinlets and along spaced cleavages. For the epigenetic veins, lead isotope values have similar $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios to the stratabound ores, but have higher $^{206}Pb/^{204}Pb$ ratios, which may reflect a different time of extraction from the same basement source as the stratabound lead. Ultimately, thrusting occurred on Ross Island and veins were rotated into a subparallel alignment with the cleavage. Virtually all mineralisation pre-dated thrusting and is restricted to the Ballysteen Formation limestones, which confirms the original observations of Weaver (1838).

For the copper–dolomite vein mineralisation at Ardtully, the distinctive radiogenic isotopic signature has been interpreted as originating from granite-derived detrital minerals disseminated in red beds. The copper–dolomite association has been attributed to late-stage fluids deriving metals from a significant thickness of oxidised continental red beds (Russell 1983). A copper–dolomite association is very weak to absent at Ross Island, where the underlying red beds were much thinner than at Ardtully, but has been recorded from Tynagh (Banks and Russell 1992). A similar copper–dolomite association at Great Orme, North Wales, has also been shown to have a highly radiogenic signature (Ixer and Davies 1996).

The difference in overall setting between the Courceyan limestone Cu-dominated assemblages of Muckross, Crow Island, Ross Island and Ardtully and the Courceyan limestone- and dolostone-hosted Zn–Pb deposits in the Irish Midlands, is the thickness of red beds beneath the carbonate rocks between these two areas with <300 m of red beds in the Irish Midlands. Therefore, it is tempting to suggest that the difference in ore assemblage between the two areas might be a result of copper derivation from red beds in the south-west. Although the radiogenic lead isotope data for samples from Ardtully can be interpreted as being caused by derivation of metals entirely from within the red beds, there is little isotopic evidence for a major red bed contribution to the Cu-dominated assemblages of Muckross, Crow Island and Ross Island, unless the lead and other metals in the red beds originated from minerals that had themselves been derived from the basement rather than a granite source. An alternative possibility is that the Palaeozoic basement in the south-west was more copper-rich than that beneath the Irish Midlands, and was perhaps derived from an Ordovician island arc. Preserved remnants of a volcanic island arc formed above a south-easterly-dipping subduction zone occur in south-east Ireland. Cu–Zn–Pb mineralisation occurs at the top of a major cycle of acid volcanism of Llandeilo-Ashgill age at Avoca Mine, from where 16 Mt of Cu were extracted in the period 1958–1962 (Williams et al. 1986). Along strike at Bunmahon, copper mineralisation is associated with basic volcanics of Upper Ordovician age (Phillips and Sevastopulo 1986). If this island arc were projected beneath the Devonian–Carboniferous cover of the Munster Basin, then it would sub-crop in the vicinity of Kenmare.

Recent work has highlighted the fact that stratabound replacive mineralisation dominates the Irish deposits (e.g. Johnston 1999; Reed and Wallace 2001). However, the occurrence of bedded barite at Ballynoe, Silvermines (Mullane and Kinnaird 1998) together with pyritised worm tubes (Boyce et al. 1999) implies that seafloor hydrothermal exhalation did occur and that mineralisation was initiated by late Courceyan times (ca. 355 Ma, Boyce et al. 1999). The stratabound mineralisation at Muckross, Crow Island and Ross Island is in the same limestone formation as the bedded barite in the Ballynoe pit at Silvermines. The model age assigned here of $\sim 360 \pm 15$ Ma for stratabound ores at Muckross, is close to the host rock Ballysteen Formation limestone, which has been assigned an age of ca. 355 Ma on the basis of conodont data (*Psuedopolygnathus multistriatus* conodont biozone; Jones and Somerville 1994). This coincidence of dates is consistent with a syngenetic to early diagenetic origin for the formation of the carbonate-hosted stratabound sulphides.

Field evidence indicates that in many localities, e.g. Lisheen and Galmoy, mineralisation is intimately associated with faulting and the occurrence of extensive tabular bodies of dolomite matrix breccia (Johnston 1999). At Navan, the main feeders to the ore deposit were minor E–NE, NE and N–NE-trending normal faults (Blakeman et al. 1999). The Navan deposit has been dated as Chadian/early Arundian (ca. 345 Ma) largely on the basis of mineralised clasts found in syndepositional conglomerates overlying an erosion surface that truncates the orebody (Ashton et al. 1992; Anderson et al. 1998). The age assigned to the mineralisation at Navan is consistent with previous ages obtained for the Navan, Tynagh and Lisheen Zn–Pb and Gortdrum Cu–Ag ± Hg deposits of Midland province (Table 5). Later mineralisation associated with post-Waulsortian breccia-hosted deposits, e.g. Kildare (Johnston 1999), are evidence for the continuation of sulphide deposition into Arundian times (ca. 345 Ma). (Waulsortian Limestone is a stratigraphical unit that hosts significant Irish Zn–Pb deposits.) Therefore, all available evidence indi-

Table 5 Published age dates for Irish base metal mineralisation

	Age in Ma	Technique	Source
Navan	345	Sedimentological and structural studies	Anderson et al. (1998)
Tynagh	348 ± 22	Pb/Pb	Boast et al. (1981)
Lisheen	350–337	Stepwise $^{40}Ar/^{39}Ar$ heating of micas	Hitzman et al. (1994)
Gortdrum	340 ± 20	U/Pb	Duane et al. (1986)
	359 ± 26	Pb/Pb	Duane et al. (1986)
	> 300 and 275	K/Ar	Halliday and Mitchell (1983)
Courtbrown	350–307	Sedimentological evidence	Reed and Wallace (2001)
Muckross	~360 ± 15	Pb/Pb	This study
Crow Island	350 ± 10	Pb/Pb	This study
Ross Island – Blue Hole	340 ± 10 stratabound	Pb/Pb	This study
Silvermines	~271 ± 24	Pb/Pb	Boast et al. (1981)
Ross Is. – Western Mine	260–290 epigenetic	Pb/Pb	This study
SW Cu-ores	~290	K/Ar	Halliday and Mitchell (1983)

cates the sulphide deposition spanned a period of > 20 Ma.

A much younger model age of 270–290 Ma has been determined for the carbonate-hosted epigenetic chalcopyrite–tennantite associated with minor veinlets at Western Mine (Fig. 7). This would imply a Permian age for the mineralisation if the lead had evolved in a single stage system. Halliday and Mitchell (1983) determined similar K–Ar ages on clay concentrates from samples associated with mineral deposits, including the Cu deposits of SW Ireland. The most unambiguously defined ages are from Duneen Bay (281–293 Ma: four samples), Ballydehob (280 and 285 Ma) and Derryginagh (290–308 Ma). Ages from other deposits like Cappaghglass (276–290 Ma) and Mountain Mine, Allihies (261–290 Ma) are in also in general agreement. Halliday and Mitchell (1983) suggest that the within-site spread of data does not represent ore formation over tens of millions of years, rather it being caused by minor effects of hydrothermal degassing and post-mineralisation disturbances. They suggest a mineralising event close to 290 Ma, which is the time of granite emplacement in SW England.

This 270–290 Ma model age for cleavage-controlled mineralisation has important implications for the timing of the Variscan orogeny in SW Ireland. Because pressure solution cleavage developed during folding and before faulting and thrusting, the 270–290 Ma age date for ores associated with the cleavage implies that the thrusting episode that emplaced the tectonic sheet of Ross Island must be younger than this. Certainly, in the seven borehole cores drilled in the vicinity of the Bronze Age Mines (Nex et al. 2002), which cut through the thrust plane, there is no evidence of any mineralisation associated with either the thrust plane, or in the limestones structurally below, suggesting that there was no remobilisation after thrusting at Ross Island.

Clearly, the spaced-cleavage controlled ore assemblage of Cu sulphides in both the red beds and carbonate-hosted deposits have similar ages. However, evidence for this later event is also evident in the Zn–Pb deposits of the Irish Midlands. Halliday and Mitchell (1983) state that there is evidence for a later event ca. 275 at Gortdrum, whereas Boast et al (1981) calculated model ages of 271 ± 24 Ma for galena from Silvermines.

The source of the fluids that penetrated into the basement of south-west Ireland has not been resolved. For the Zn–Pb deposits of the Irish Midlands, two main alternatives have been proposed: a hydrothermal circulation initiated during extension (e.g. Russell 1983; Everett et al. 1999b) or a topographically expelled fluid from the Variscan orogen (e.g. Hitzman 1995; Hitzman et al. 1998). Everett et al. (1999b) presented fluid inclusion data from Lower Palaeozoic-hosted sulphide-bearing veins and showed significant variation reflecting systematic lateral changes, which would be inconsistent with an aquifer-confined topographic flow model. However, Wright et al. (2000) show that no single fluid flow model is valid. A hybrid model involving both regional and localised fluid flow systems is more appropriate (Garven et al. 1999; Wright et al. 2000).

Conclusions

The most important consequence of this work is the recognition of two phases of mineralisation in southern Ireland, one during Carboniferous basin extension, the other during Variscan compression. An age of 360–340 Ma has been calculated for the Carboniferous-hosted stratabound mineralisation at Muckross, Crow Island and Ross Island with mineralisation associated with Variscan compression suggested between 290 and 270 Ma.

There appears to be a temporal relationship between Carboniferous stratabound Cu–As–Ag–Zn–Pb polymetallic deposits in southern Ireland, and the Zn–Pb deposits of the Irish Midlands. The difference in the ore assemblage between the two areas might be caused by copper derivation from red beds in the south-west where the limestones that host the stratabound Cu-polymetallic deposits are underlain by several kilometres of red beds, in contrast to the ore deposits of the Irish Midlands, which are underlain by Lower Palaeozoic greywackes where intervening red beds are either absent or of minimal thickness. The isotopic evidence does not clearly indicate that the red beds have made a contribution to the copper in the deposits at Ross Island, Crow Island and Muckross unless the lead in the red beds originated from a basement rather than a granite source. It is only for the data from Ardtully that a derivation of metals from within red beds is implied. An alternative possibility is that the Palaeozoic basement in the south-west was more copper-rich than that beneath the Irish Midlands perhaps derived from an Ordovician island arc.

The later phase of mineralisation at ca. 270–290 Ma was associated with Variscan compression. In the red beds, remobilised disseminated ores were deposited along spaced cleavages and minor veinlets and major sulphide-bearing veins formed after folding. At the same time, in the carbonate-hosted deposits, a similar basement-derived chalcopyrite–tennantite assemblage was deposited along spaced cleavages and in veins.

It is concluded that disseminated mineralisation in the red beds, and the veins at Ardtully, are sourced entirely within the red beds, that minor veins in the red beds are remobilised sulphides from the disseminated ores, and that the metals within red bed-hosted major quartz veins and carbonate hosted ores are predominantly derived from a SE-type basement.

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