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A review of lead and sulphur isotope investigations of Irish sediment-hosted base metal deposits with new data from the Keel, Ballinalack, Moyvoughly and Tatestown deposits.

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Abstract

Combined lead and sulphur isotope studies have been carried out on four different types of Irish base metal deposits hosted by Lower Carboniferous limestones with similar simple mineralogy. The deposit at Keel, Co. Longford, is controlled by a fault system that intersects the basement, and may represent a feeder zone. Ballinalack, Co. Westmeath, is a stratabound but not stratiform deposit, and occurs within stromatactitic Waulsortian mudbank knolls. Moyvoughly, Co. Westmeath, is a stratabound deposit, locally controlled by minor faults. Tatestown, Co. Meath, is a stratabound and arguably a stratiform deposit with mineralization closely associated with a normal fault.

New lead isotope data from Tatestown, Keel, Ballinalack, and Moyvoughly, together with published data from Tynagh, Navan and Silvermines fall into two distinct clusters: to the south and east, $^{206}\text{Pb}/^{204}\text{Pb} \approx 18.23$, $^{207}\text{Pb}/^{204}\text{Pb} \approx 15.58$, $^{208}\text{Pb}/^{204}\text{Pb} \approx 38.09$; to the north and west, $^{206}\text{Pb}/^{204}\text{Pb} \approx 17.98$, $^{207}\text{Pb}/^{204}\text{Pb} \approx 15.53$, $^{208}\text{Pb}/^{204}\text{Pb} \approx 37.85$. However, additional data show that there is a continuum of lead isotope values that fall on a linear trend on a $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ plot. These values appear to depend only on geographical location and not on style of mineralization, or age of host rock. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios can be contoured. The contours parallel NE trends of Caledonide inheritance.

Sulphur isotope ratios are highly variable. Ore stage sulphides at Keel have $\delta^{34}\text{S}$ values of -13.8 to $+1.0\%$ with galena and sphalerite precipitated in apparent isotopic equilibrium over a temperature range of 100 to 250°C. The $\delta^{34}\text{S}$ values at Moyvoughly are similar, -13.5 to 1.0% , but are not in isotopic equilibrium. At Tatestown most of the ore sulphides have positive $\delta^{34}\text{S}$ values but the range is wide, from -23.6 to $+14.4\%$. At Ballinalack the range is also wide, from -36.4 to 0% with most late stage galenas being isotopically light ($\approx -20\%$). Barite from the four deposits has a narrow range of sulphur isotopic values, $+18.9$ to $+22.5\%$, probably derived from Lower Carboniferous seawater. The $\delta^{34}\text{S}$ values appear to reflect depositional environment and suggest that sulphur was derived both locally and from a deep-seated source, whereas the lead isotope data indicate mainly a lower crustal origin for lead.

Previous isotope investigations of deposits in Ireland are reviewed. It is clear from the geological and geochemical evidence that all sediment-hosted base metal deposits in central Ireland are not emplaced by the same mechanism, even though they are of the same age. Syngenetic, syndiagenetic and epigenetic processes have all contributed by varying degrees to ore emplacement at each deposit.

Introduction

Sediment-hosted Pb-Zn deposits including both sedimentary-type stratiform and stratabound deposits are widespread classes of deposits. Despite the widespread distribution and economic importance of these deposits, their origins are only partially understood. For example, opinions on the origin of stratiform deposits are divided between two schools of thought; one postulating that the deposits are syngenetic, and the other postulating that the deposits are diagenetic or epigenetic. Despite several recent studies, debate still continues on the nature of transporting fluids in Mississippi Valley-type and other stratabound deposits (Sverjensky, 1981; Giordano and Barnes, 1981).

Petrological, geochemical and isotopic studies by Williams, (1976; 1978a; 1978b; 1979), Williams and Rye (1974), and Rye and Williams (1981) have clearly demonstrated the close genetic link between the sedimentary stratiform type Pb-Zn deposits, and the stratabound Mississippi Valley-type (MVT) deposits at McArthur River. These studies also indicate that much of the mineralization in the strati-

form deposits took place below the sediment-water interface (Rye and Williams, 1981).

Studies of McArthur River and related deposits have led Gustafson and Williams (1981) to suggest that sediment-hosted Pb-Zn deposits should be considered a broad class of related deposits rather than a large number of distinct types based on narrowly defined criteria. This view is consistent with the views of Gilmour (1976) who showed that sediment-hosted deposits of different types commonly grade into one another.

The consensus is that stratabound ores of the world were precipitated from basinal brines that circulated through basin-wide aquifers. However, the heat source for the hydrothermal fluids, the sources of sulphur and base metals, and the mechanisms of precipitation of the sulphides are still, in most cases, not established or only partially understood.

Sulphur may be introduced into the brines as sulphate by dissolution of pre-existing evaporite minerals followed by inorganic (Barton, 1967) or organic (Shearman, 1971) reduction of sulphate. Alternatively, sulphur may be intro-

duced as reduced sulphur; (1) by mixing of the brines with water enriched in H₂S by bacterial sulphate reduction (Beales and Jackson, 1965; Jackson and Beales, 1967), (2) by dissolution of pre-existing sulphides (Lovering, 1961), or (3) by thermal degradation of organic sulphur-bearing hydrocarbons in petroliferous material (Skinner, 1967).

A number of possible precipitation mechanisms also exist. In sulphate-bearing brines, precipitation of sulphides could occur by reduction of sulphate by a source of reduced carbon. The addition of reduced sulphur to a metal-bearing brine could result directly in precipitation of metal sulphide. If low concentrations of reduced sulphur and base metals are maintained in a brine, then precipitation of metal sulphides can occur by cooling, dilution or neutralization.

Recent studies of MVT and sediment-hosted Pb-Zn deposits in general have put severe constraints on the precipitation mechanism, the plumbing system, and the possible sources of fluids and ore constituents (see McLimans, 1977; Giordano, 1978; Sverjensky et al., 1979; McLimans et al., 1980; Giordano and Barnes, 1981; Sverjensky 1981). For example, work by Sverjensky et al. (1979) on lead and sulphur isotopes of galenas demonstrated that lead and sulphur must have been transported together in the Buick mine area of SE Missouri, that the Lamotte Sandstone must have been an aquifer, and that there were at least two sources of lead and sulphur. One source likely was the marine sediments of the basin, the other being either the Pre-Cambrian basement or detritus derived from the basement.

Although in Ireland there is a clear association of Pb + Zn ± Cu ± Ag ± Hg ± Cd sulphides and barite with Courceyan (Lowest Dinantian) carbonates, the nature of the association, and the genesis of these deposits remains in dispute. Russell et al. (1981, 1982) view the deposits as having a syndimentary/sedimentary exhalative origin. This view is not shared by Hutchison (1983), who states "the Lower Carboniferous deposits of Ireland are clearly epigenetic", an opinion also held by Ridge (1984). A hybrid model for the origin of the Silvermines orebodies has been proposed by Taylor and Andrew (1978); in this model, the lower ores were deposited epigenetically in a feeder zone, and the upper ores resulted from submarine exhalations.

Models for the genesis of Irish deposits are based mainly on studies of Silvermines (Graham, 1970; Greig et al., 1971; Coomer and Robinson, 1976; Taylor and Andrew, 1978; Taylor, 1979 and 1984); and Tynagh (Russell, 1974 and 1975; Boast, 1978 and 1983; Riedel, 1980; Boast et al., 1981a, b; Probert, 1983; Samson and Russell, 1983). In order to be able to evaluate syngenetic, epigenetic or hybrid multi-stage models for the genesis of the Irish deposits, and to compare them to other presumably similar deposits, we have studied deposits hosted by Dinantian calcareous sediments with varying styles of mineralization and structures over a wide geographical area.

Previous isotope and fluid inclusion studies of Irish base metal deposits

Isotope studies

The Mogul deposit at Silvermines, Co. Tipperary, has been the subject of three stable isotope investigations. Graham (1970) and Greig et al. (1971) concluded that there was only one source of sulphur; Graham proposed seawater sulphate, whereas Greig et al. proposed deep-seated sulphur. The incompatibility of these models led Coomer

and Robinson (1976) to reinvestigate the deposits. They concluded that both of the earlier studies were only partially correct, in that there may have been two sources of sulphur, one deep-seated, and the other from sea-water sulphate. The $\delta^{34}\text{S}$ values in these studies were not put in the framework of a paragenetic sequence, but rather were grouped according to orebody and mineral specimen (see Figs. 1a and 1b). At Silvermines there are two mineralized horizons, a lower dolomite and an upper dolomite. Taylor and Andrew (1978) reviewed the previous investigations and produced a complex two stage epigenetic model for the lower ore bodies and suggested that the Upper G and B stratiform ore bodies were syngenetic, with the lower ore bodies representing feeders for the upper ore bodies. Boyce et al. (1983b) proposed a syngenetic model for the upper ore body and for the nearby Ballynoe deposit, in which the faults acted as feeder zones from which dense saline brine emanated on to the sea floor, while at the same time slumping took place. These are interesting models that probably have much merit, but they are difficult to assess because textural and paragenetic data have only recently been published (Andrew, this vol.). Taylor (1984) noted that palaeotopography controls the localization of sulphide mineralization of the stratiform orebodies at Silvermines. This observation would be expected of an orebody of sedimentary-exhalative origin, but, while supportive, is not by itself conclusive evidence of sedimentary-exhalative origin for the stratiform deposits at Silvermines.

Greig et al. (1971) also published $\delta^{34}\text{S}$ values for 13 samples from Gortdrum and Tynagh. These values fell within the range obtained from sulphides from Silvermines. However, as Boast et al. (1981a) remarked, "unfortunately the spatial and paragenetic relations of these samples are unknown, and restricted the interpretation based on a comparison with the Silvermines deposits 40km to the south".

Boyce et al. (1983b) made a detailed sulphur isotopic study of small pyritic structures from the Ballynoe barite deposit. These structures have been interpreted as small fossil hydrothermal chimneys (Larter et al., 1981 and Russell et al. 1982). These structures are subdivided into two types, primarily on the basis of mineralogy and textures, and their sulphur isotope systematics are distinct. $\delta^{34}\text{S}$ in pyrite from type II has a range of -24 to -16‰, but with a narrower range within a single tube. Peripheral barite from type I tubes has a range of $\delta^{34}\text{S}$ from +14.2 to +20.4‰ and these values have an apparent bimodal distribution. All values fall within the ranges already discussed. However $\delta^{34}\text{S}$ pyrite values are unusually light, as low as -42.5‰. This value is over 60‰ lighter than contemporaneous seawater (Thode and Monster, 1965), but could have been produced by bacterial fractionation. Boyce et al. (1983b) note that no remains of sulphate-reducing bacteria have been identified, but they suggest that the high organic carbon content of type I pyrite (8.5%) is indirect evidence of a bacterial presence.

Boast (1978 and 1983) and Boast et al. (1981a and b) conducted textural and isotopic investigations of sediment-hosted base metal deposits in Ireland, with an emphasis on Tynagh. Boast et al. (1981a) published $\delta^{34}\text{S}$ values of sulphides and sulphates from samples carefully located in three dimensional space, and placed them in the following paragenetic framework. The first sulphides were precipitated during early diagenesis, possibly as iron monosulphides (Berner, 1984). They are now preserved as iron disulphides, mainly pyrite with minor marcasite. Sphalerite was the dominant phase in Stage 2 mineralization that post-

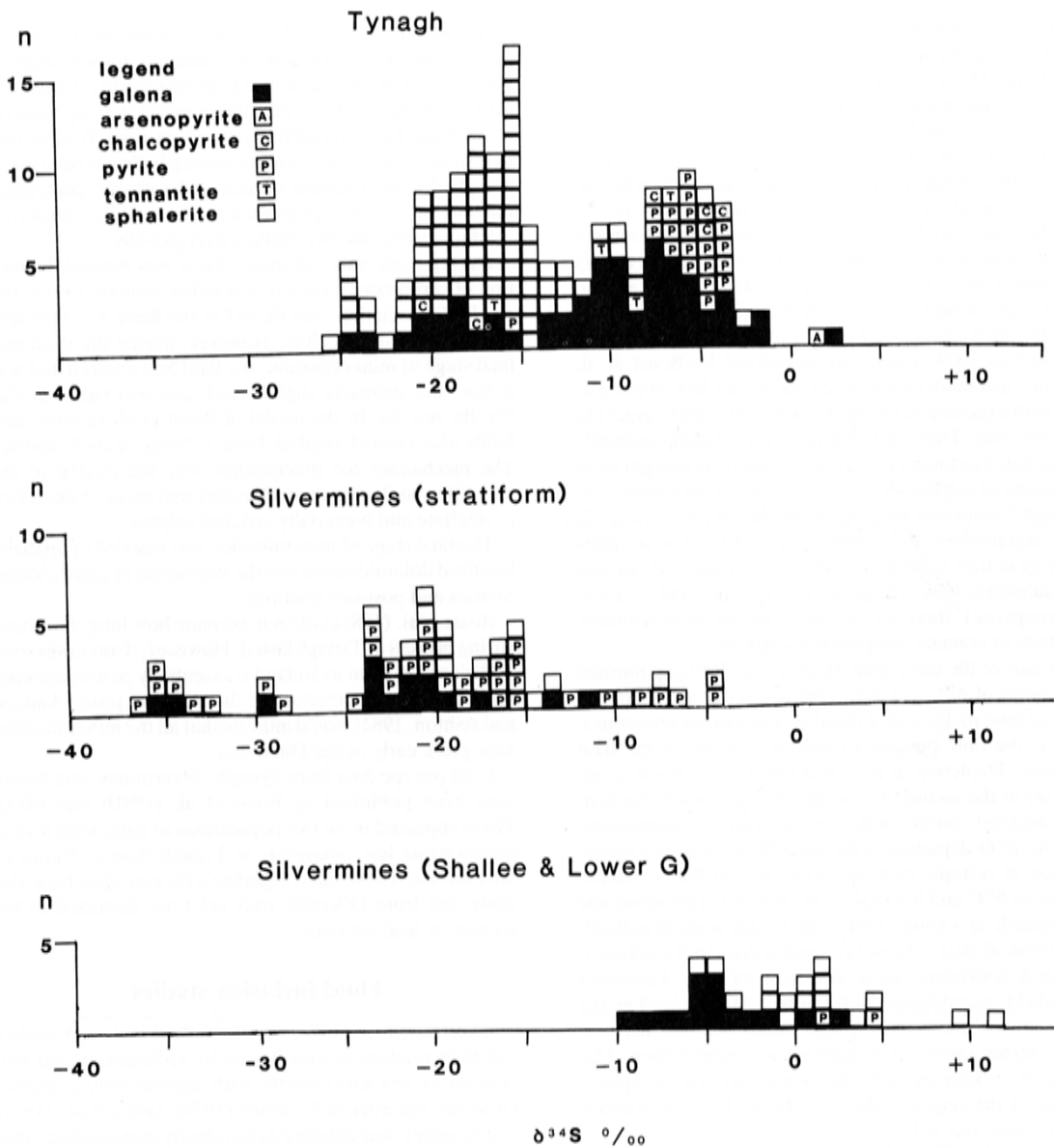


Figure 1. Sulphur isotopic composition of ore stage sulphides at Silvermines; (a) discordant mineralization, (b) stratiform mineralization. (Original data from Graham (1970), Greig et al. (1971), and Coomer and Robinson (1976)), (c) Sulphur isotopic composition of ore stage sulphides at Tynagh. (Original data from Boast et al. (1981a). Data from drill holes distal from the mine have been excluded.

dated early diagenesis, but was not considered by Boast et al. (1981a) to be epithermal. Stage 2 sphalerite is fine grained and often banded; colour changes within bands are due more to differences in sphalerite/carbonate ratios than in compositional changes in sphalerite. In Stage 3 infilling, the dominant style of mineralization was medium- to coarse-grained epigenetic galena, often associated with coarse sparry barite, tennantite and accessory sulphides.

Riedel (1980) used different terms to describe the paragenetic sequence at Tynagh, but conceptually agreed with Boast (1978) and Boast et al. (1981a). All who have examined this deposit (Boast, 1978; Hutchings, 1979; Riedel, 1980; Boast et al., 1981a) reason that the textural aspects of Stage 3 epigenetic ore (cross-cutting, veining, replacement and rimming of earlier sulphides) clearly show that this is the latest stage of sulphide deposition.

Boast et al. (1981a) recognized a post-ore stage of carbonate mineralization that is mainly coarse white calcite with ferroan dolomite and occasional small specks of chalcopyrite.

A histogram of $\delta^{34}\text{S}$ data for Tynagh is shown in Figure 1c. (As originally presented by Boast et al. (1981a) these data were grouped in individual paragenetic stages; however had the $\delta^{34}\text{S}$ data been grouped by phase, the histograms would not be significantly different.) The ranges of $\delta^{34}\text{S}$ data by ore stage are: Stage 1 (with the exception of one point), -8.0 to -3.1‰ ; Stage 2, -26.0 to -4.1‰ (mean of -17.2‰); Stage 3, -23.0 to $+11.1\text{‰}$ (mean of -8.7‰). Barite coexists with both Stage 2 and 3 sulphides. The ranges of Stage 2 and Stage 3 barites are similar Stage 2, $+17.4$ to $+20.2\text{‰}$ (mean of $+18.4\text{‰}$); Stage 3, $+18.5$ to 21.1‰ (mean of $+19.7\text{‰}$). Stage 3 barite is more abundant.

Both groups fall well within (albeit at the heavy end of) the range of Dinantian seawater $\delta^{34}\text{S}$ sulphate as reported by Thode and Monster (1965), and also Claypool et al. (1980). Thus contemporaneous seawater was the probable source of sulphate for barite at Tynagh.

The mean $\delta^{34}\text{S}$ value of all barite at Tynagh is only 25‰ heavier than Stage 1 sulphide. If the barite $\delta^{34}\text{S}$ reflected ambient Dinantian seawater sulphate, this depletion in $\delta^{34}\text{S}$ could be explained by kinetic fractionations during bacterial reduction of seawater sulphate. Stage 2 sulphides (mainly sphalerite) were even lighter (23 to 45‰, mean around 35‰) than ambient seawater. Although the possibility of equilibrium fractionation between sulphide and sulphate in the 300° to 100°C range was considered by Boast et al. (1981a), this model is discarded due to the lack of correlation with expected zonation and $\delta^{34}\text{S}$ values with respect to a feeder zone. Thus sulphur derived from bacteriogenically fractionated reduction of seawater sulphate is thought to be the source of sulphur for the second stage of mineralization.

Stage 3 sulphides are isotopically heavier than Stage 2. Two explanations are possible, either there was an influx of deep-seated sulphur of unspecified origin, or, as two late sulphides have $\delta^{34}\text{S}$ of +7.0‰ (galena) and +11.1‰ (arsenopyrite), there was abiogenic reduction of seawater sulphate or connate (unspecified) sulphate.

As part of the same study Boast et al. (1981a) published the results of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses of ore stage carbonates, of host rocks, and of distal unmineralized limestones. This is the only published study of its kind on the Irish deposits. Depletion in $\delta^{13}\text{C}$ is attributed by Boast et al. (1981a) to the mixing of host-derived carbon with bacterially oxidized carbon and, during Stage 4, deep-seated carbon; $\delta^{18}\text{O}$ depletion of the mineralized host is a consequence of isotopic exchange with the ore fluids. Similar ranges of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are noted at Tatestown and Ballinalack in a companion study to this work (Caulfield, unpublished data). However, preliminary $\delta^{18}\text{O}$ relations between coexisting calcite dolomite pairs at Tatestown (Caulfield, unpublished data) can best be explained by the interaction of fresh water with seawater that was intermittently highly saline due to high rates of evaporation. This model is in keeping with the overall palaeogeographical setting of the region in the early Dinantian (see Andrew and Poustie, this vol.).

Boast et al. (1981a) concluded that Lower Carboniferous sea-water acted as the source of sulphate for the precipitation of barite. Open-system bacterial reduction of seawater sulphate generated reduced sulphur that precipitated sulphides in Stages 1 and 2. During Stage 3, isotopically heavier sulphur ($\delta^{34}\text{S} > 0\text{‰}$) was introduced from the fault zone, and mixed with bacteriogenic H_2S migrating into the Waulsortian mudbank limestones to precipitate Stage 3 sulphides and sulphosalts. In the model of Boast et al. (1981a), all mineralizing fluids ascended from a depth that is not well specified (although it might have become deeper with time) along the Tynagh Fault. The ascending hydrothermal fluids which were initially rich in iron and silica ascended and vented on to the sea floor in a basin to the north of the Tynagh mudbank, depositing the distal iron formation; this process began in the late Courcayan stage. Slumping of Waulsortian carbonates and rapid burial of organic matter was due to growth faulting. Local centres of anaerobic bacterial activity reduced sea-water sulphate, and early iron sulphides were precipitated. Ambient temperatures within the sediment were low (probably much less than 50°C).

During later stages of mudbank accumulation, forcible

injection of hydrothermal fluids into semilithified sediment resulted in the production of a dilatant fracture/breccia system. Temperatures of 100°C precluded local bacterial activity; however, reduced sulphur generated by bacteria in off-bank facies possibly migrated into the Waulsortian limestones. Zinc- and barium-carrying hydrothermal fluids mixed with the reduced sulphur and with the contemporaneous sea water, precipitating the mainly sphaleritic sulphide/barite microcrystalline overgrowths.

During early mineralization, there was limited dissolution of carbonates; porosity was either primary or was the result of brecciation, and the pH of the fluids was probably neutral to mildly alkaline. However, during the third and final stage of mineralization, the fluid had evolved and was hotter, was probably slightly acid, and was richer in Cu, Pb, Ba and As. In the model of Boast et al. (1981a), late fluids also carried sulphur from a "deep-seated" source. The mechanism for precipitation was the mixing of the metalliferous fluid with much cooler marine pore fluids rich in sulphate and bacterially-reduced sulphur.

The final stage of mineralization was marked by spatially localized dolomitization and the deposition of calcite within cavities and post-ore fractures.

Boast et al. (1981a) did not estimate how long the mineralizing process at Tynagh lasted. However, if mineralization in the central plain in Ireland is essentially penecontemporaneous, then the structure of the Navan deposit (Andrew and Ashton, 1982) would indicate that all the mineralization took place early in the Dinantian.

Lead isotope data from Tynagh, Silvermines, and Navan have been published by Boast et al. (1981b and 1983). There appeared to be two populations of data, with lead in galena being less radiogenic at Tynagh than at Navan or Silvermines. These data, together with new data from this study and from O'Keeffe (this vol.) are discussed in the section on lead isotopes.

Fluid inclusion studies

When Roedder (1976) reviewed fluid inclusion studies and their relation to ores hosted by sedimentary and volcanic rocks, few data from the Irish deposits were available. However, the work of Patterson (1970), Greig et al., (1971) and Roedder (unpublished data), clearly demonstrated that the hydrothermal fluids that emplaced the sulphide minerals in the Irish deposits were considerably warmer than fluids in MVT deposits.

In a detailed study of feeder zones in the Silvermines area, Samson and Russell (1983) found that homogenization temperatures of ore and gangue minerals range from 50° to 260°C (mode at 200°C), with a wide range of salinities (from 0 to 25 equivalent weight % NaCl with most falling in range 12-22 equivalent weight % NaCl). There is an inverse correlation between temperature and salinity. Probert (1983) examined fluid inclusions from six Irish deposits. Overall temperatures ranged from 120° to 220°C, with temperature differences ranging from 40° to 80°C in any single deposit. Salinities were from 3 to 12 equivalent weight % NaCl. No daughter minerals or hydrocarbons were found. Probert did not find any evidence of boiling. However, Samson and Russell (1983) reported vapour-rich and low saline condensate fluid inclusions, and regarded this as evidence that on occasions the solutions boiled. A brine at 220°C containing 15 equivalent weight % NaCl would need the equivalent of 200m of hydrostatic pressure to prevent boiling (Haas, 1971). Probert (1983) does not comment on any relation between salinity and temperature.

Roedder (1976) reports homogenization temperatures at Keel of 176° to 185°C, and freezing point depression of -7.3° to -8.0°C which yielded salinities of 10.9 to 11.7 equivalent weight % NaCl when calculated by the method of Potter et al. (1978). In this study (see below) we found primary inclusions in sphalerites from the Quartz Pebble Conglomerate at Keel that homogenized at 117° to 123°C and had salinities of 17-22 equivalent weight % NaCl. Secondary inclusions had similar salinities. Thus, it appears that the inverse correlation between temperature and salinity is a phenomenon not confined solely to the Silvermines deposit.

Further isotopic investigations

The deposits selected for this study are Keel, Ballinalack, Moyvoughly and Tatestown. Access was permitted by Riofinex to Keel, by Noranda to Ballinalack (now operated by Billiton), and by Irish Base Metals (now Ennex International PLC) to Tatestown and Moyvoughly. As these deposits are discussed in detail elsewhere in this volume by Slowey (Keel), Jones and Brand (Ballinalack), Poustie and Kucha (Moyvoughly), and Andrew and Poustie (Tatestown), only brief reviews of the deposits are given below.

Keel, Co. Longford

The zinc-cadmium deposit at Keel occurs approximately 12 km south of the town of Longford, and near the village of Ardagh.

The deposit occurs on the down-faulted southern flank of a NE-trending Lower Palaeozoic inlier. Green, slaty, low-grade Silurian metasediments are unconformably overlain by a sequence of microconglomerates, quartzose sandstones and quartz pebble conglomerates. These are followed by the carbonate-dominated Mixed Beds, bioclastic limestone and Waulsortian mudbank limestone of Courceyan age. Mineralization consists mainly of pyrite, sphalerite, galena and argentiferous tetrahedrite with calcite and quartz gangue (Patterson, 1970). Mineralization occurs in five or more fault-controlled breccia zones and in fracture infillings. Infilling ore and gangue minerals are often euhedral. Unlike the other deposits in this study, mineralization at Keel is highly discordant and occurs in the uppermost Silurian metasediments as well as in the overlying Courceyan strata (up to the top of the Mixed Beds). A stratiform barite lens with lesser amounts of pyrite, sphalerite and minor galena has recently been discovered near the base of the Waulsortian at Garrycam, approximately 1 km east of Keel (Slowey, this vol.).

Ballinalack, Co. Westmeath

The deposit at Ballinalack is located about 14 km NW of Mullingar. The Ballinalack deposit is hosted in Courceyan Waulsortian mudbank limestones mainly on the downthrown side of a major NNE-trending fault. However, unlike many of the deposits of this type in the Irish central plain, the fault does not juxtapose the Old Red Sandstone facies with the immediate host rocks. Mineralization in the upper ore lens occurs mainly in a system of stromatolite cavities of the type described by Bathurst (1982) located in a series of four mudbank knolls that are subparallel to the fault.

Our work to date and the published work of Jones and Bradfer (1982) indicate that early mineralization is dominantly sphalerite which lines the interior of the stroma-

tactis cavities. High grade mineralization occurs in a style much like that at Tatestown, the early ores have been brecciated and recemented with pyrite, sphalerite and galena. However, brecciation appears to be restricted for the most part to the ores and not the host rock. The implications are that the cavities were open during mineralization and remained an active site for brecciation and mineralization throughout the ore-forming process. Clearly mineralization processes started during the early diagenesis of the host rocks and near the sediment-water interface.

Moyvoughly, Co. Westmeath

This deposit occurs in Moyvoughly Townland, County Westmeath, near the town of Moate. The deposit is hosted by gently folded Courceyan shallow-water sandy and oolitic limestones, and basal shales. Mineralization occurs on the upthrown side of a normal fault in what are known locally as the Moyvoughly Beds. The local controls of mineralization are somewhat different from the other deposits in that ore is localized in a series of small faults and joints located about 200 m away from the main fault zone. Mineralization consists mostly of sphalerite and pyrite with subordinate amounts of galena and gangue. The mineralization is found in narrow, steeply-dipping fault fissures and joint-like fractures in sandy and oolitic limestones (Schultz 1971, Irish Base Metal company records, and our own data).

Tatestown, Co. Meath

The Tatestown prospect lies about 3 km NNW of the large Navan deposit near the town of Navan, Co. Meath. The deposit straddles the Blackwater River approximately 5 km upstream from the confluence of the Blackwater and the Boyne. The part of the orebody on the west bank of the Blackwater is known as the Scallanstown prospect. The samples for this study were collected from drill core from the eastern (Tatestown) side of the deposit.

The deposit is localized mainly along the northern downthrown side of a normal fault that trends approximately easterly. The dip of the fault is 60° and total throw is about 80 m. Similar but less extensive mineralization is found at the same stratigraphic level on the upthrown block. The main ore lens is generally stratiform, and it deepens westwards.

The host rocks at Tatestown form part of the SW-plunging Navan anticline which is cored by a highly tectonized sequence of Ordovician and Silurian strata and chloritized alkali syenites (Romano, 1980).

The regional stratigraphy has been described in some detail by Andrew and Ashton (1982). The host rocks at Tatestown are part of the Pale Beds of Courceyan 3 age (Sevastopulo, 1979), a sequence of birds-eye micrites, bioclastic and oolitic calcarenites, and arenaceous and silty calcareous mudstones. Of special interest is the presence of a nodular chalcedony layer found in the underlying Laminated Beds, identified by Gustafson (1981, cited as a personal communication in Andrew and Ashton, 1982) as a replaced evaporite. Given the low palaeolatitude of Ireland in the Dinantian (Ziegler, 1982), the environment of deposition and the water depth of many of the Dinantian sediments, local formation of evaporites is unsurprising and their presence is often shown on palaeogeographic maps (MacDermot and Sevastopulo, 1972, Naylor et al., 1980). The only direct observation was that of Sheridan et al. (1967). The presence of gypsum at Strokestown and Roscommon (and possibly Lough Sheelin) has been reported recently by Philcox (1984).

Deposits hosted by calcareous Dinantian sediments in central Ireland are generally mineralogically simple viz. pyrite ± marcasite with sphalerite and galena and often argentiferous arsenic and antimony-bearing sulphosalts. Texturally, however, the ores are complex. At Tatestown, early vein pyrite is often associated with sphalerite/carbonate intergrowths banded perpendicular to bedding. Such mineralization is often brecciated and repeated. Often the laminae are vertical, sometimes colloform and only rarely parallel the bedding. The fine laminae found at Navan on the scale of a hand specimen (Andrew and Ashton, 1982) are not as well developed at Tatestown. Late coarse galena fills voids and replaces pre-existing sulphides. Brecciation and cementation by vein carbonate further disrupt the textural continuity of ore sulphides. While sulphide mineralization seems to have taken place early beneath the sediment-water interface, the textures of both banded sphalerite and later coarse galena are disrupted by compaction during diagenesis (see Andrew and Poustie, this vol.).

Summary of geological settings

The deposits studied are hosted by rocks of similar age and have similar mineralogy. However, the styles of mineralization differ. Tatestown is a stratabound, and arguably a stratiform, deposit with mineralization closely associated with a major normal fault. Thus, Tatestown appears to be similar to Silvermines (Taylor and Andrew, 1978) and Tynagh (Boast et al., 1981a). Ballinalack is a stratabound, but not a stratiform, deposit. Although there are major normal faults nearby, the main mineralized zone does not abut the fault but is confined to stromatactitic cavities in Waulsortian mudbank knolls. The Keel deposit occurs within large faults and joints that intersect the basement rocks and is probably neither stratiform nor stratabound, and may represent a feeder zone like the lower orezones at Silvermines, with the Garrycam deposit being analogous to the Ballynoe deposit. Moyvoughly is a stratabound, but not a stratiform, deposit located near a major fault and locally controlled by minor faults and joints about 200m from the major fault.

Lead isotope investigations

Methods

In the section on sulphur isotopes, we shall show that the range of sulphur isotopic composition of galenas from each deposit is wide, and that there are distinct differences in the range of $\delta^{34}\text{S}$ galena between individual deposits. Galenas analysed for lead isotopic composition were fractions of the same samples on which $\delta^{34}\text{S}$ analyses had been made, and were selected to represent the range of $\delta^{34}\text{S}$ values of the four deposits. Additional samples from Tynagh, Silvermines and Navan were taken from a suite of hand specimens collected by B.J. Skinner in 1974, and only their approximate location is known. However, the spatial relation of the samples from Keel, Ballinalack, Moyvoughly and Tatestown is known to within 10cm (the limit of accuracy of the drilling and drill hole logging records). Samples from Avoca (SE Ireland) and Tyndrum (Scotland) were acquired by A. P. LeHuray.

Lead was purified from dissolved galenas by electrodeposition and was analysed by the silica gel-phosphoric acid method on the Micromass 30 at Lamont-Doherty Geological Observatory.

Each dissolved sample was run at least twice, and the reported numbers are averages of the separate runs. All ratios have been normalized to NBS 981 common-lead standard, which was analysed every day that lead was run. Reported ratios are believed to be within 0.1% of absolute.

New data

Tatestown

Seven galenas from Tatestown with $\delta^{34}\text{S}$ values ranging from -5.1 to $+12.2\%$ were analysed for lead isotope composition. The lead isotope ratios of the seven are essentially identical, within analytical error, averaging $^{206}\text{Pb}/^{204}\text{Pb} = 18.224 \pm .006$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.572 \pm .008$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.078 \pm .020$. These averages are plotted as "Tt" on Figure 2.

Navan

Two galenas from Navan, having $\delta^{34}\text{S}$ of $+8.9$ and -11.9% , yielded lead isotope ratios that are essentially identical and agree well with those reported by Boast et al. (1981b) and Boast (1983). Average values are $^{206}\text{Pb}/^{204}\text{Pb} = 18.230 \pm .023$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.585 \pm .021$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.118 \pm .057$, and are plotted as "N" on Figure 2. The variation evident in Navan samples is due to data from Boast et al. (1981b) which suffered from a component of ^{204}Pb error (Boast, 1983).

Silvermines

One galena from Silvermines yielded lead isotope compositions of $^{206}\text{Pb}/^{204}\text{Pb} = 18.261$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.592$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.153$. These ratios also agree within error with those reported for Silvermines by Boast et al. (1981b). The averages of all ratios are plotted as "S" in Figure 2.

Keel

Eight galenas from Keel with a range of $\delta^{34}\text{S}$ from -10.1 to $+1.0\%$ also have nearly constant lead isotope ratios, averaging $^{206}\text{Pb}/^{204}\text{Pb} = 17.997 \pm .018$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.536 \pm .010$, and $^{208}\text{Pb}/^{204}\text{Pb} = 37.900 \pm .037$ ("K" on Fig. 2).

Ballinalack

Three galenas with $\delta^{34}\text{S}$ ranging from -22.6 to -15.8% were analysed from the Ballinalack deposit. As in other deposits, lead isotope ratios showed little variation, and average $^{206}\text{Pb}/^{204}\text{Pb} = 17.967$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.529$, and $^{208}\text{Pb}/^{204}\text{Pb} = 37.806$ ("B" on Fig. 2).

Moyvoughly

Four Moyvoughly galenas ranging in $\delta^{34}\text{S}$ values from 11.9 to $+0.4\%$ have uniform lead isotope ratios averaging $^{206}\text{Pb}/^{204}\text{Pb} = 17.989$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.537$, and $^{208}\text{Pb}/^{204}\text{Pb} = 37.849$ ("M" on Fig. 2).

Tynagh

Analysis of one galena from Tynagh resulted in lead isotope composition essentially indistinguishable from the average of the data from Boast et al. (1981b). Our sample yielded ratios of $^{206}\text{Pb}/^{204}\text{Pb} = 18.041$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.541$, and $^{208}\text{Pb}/^{204}\text{Pb} = 37.921$. (Averaged with the data from Boast et al. (1983) as "Ty" on Fig. 2). For all data $^{206}\text{Pb}/^{204}\text{Pb} = 18.038 \pm .011$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.524 \pm .013$, $^{208}\text{Pb}/^{204}\text{Pb} = 37.874 \pm .039$.

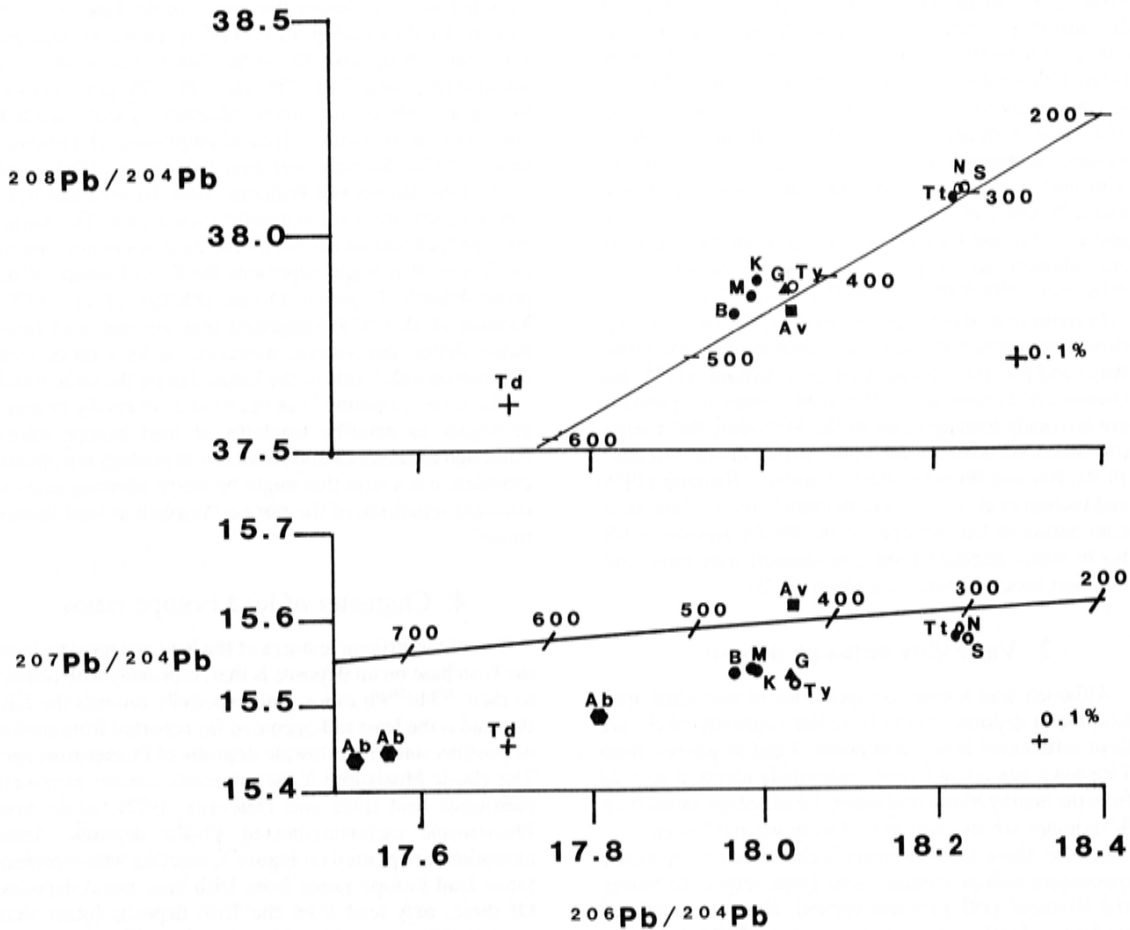


Figure 2. Lead isotope ratios of mineral deposits in Ireland and Scotland. Ab, Aberfeldy; Td, Tyndrum; B, Ballinalack; M, Moyvoughly; K, Keel; G, Gortdrum; Ty, Tynagh; Av, Avoca; Tt, Tatestown; N, Navan; S, Silvermines. Open symbols include new data averaged with data from Boast et al. (1981b) as amended by Boast (1983).

Other deposits

We have also included in Figure 2 previously unpublished data from the Ordovician volcanogenic exhalative Avoca deposit ("Av" on Fig. 2) as well as from the Tyndrum and Aberfeldy deposits in the Dalradian of Scotland ("Td" and "Ab" on Fig. 2).

In the course of analysing lead isotope compositions, we routinely check for the qualitative amount of thallium (^{203}Tl , ^{205}Tl) and bismuth (^{209}Bi). These elements chemically similar to lead, generally are present in galena to some degree and are not efficiently separated by the electrodeposition technique used. No galena from any Irish carbonate-hosted Pb-Zn deposit contained more than trace amounts of thallium or bismuth.

Discussion

The lead isotope data from these seven Irish carbonate-hosted base metal deposits have several striking features: (1) Lead isotope compositions are essentially uniform within a given deposit; (2) There are at least two, and probably three, distinct lead isotope "groups" among the carbonate-hosted Pb-Zn deposits, although O'Keefe (this vol.) has shown that there is a continuum of lead isotope ratios both within the Dinantian-hosted deposits and a

similar trend in small deposits in the Longford-Down Massif; (3) Lead isotope ratios parallel basement trends of Caledonide inheritance, and closely follow geophysically identified basement structures; (4) Lead isotope ratios in the deposits in central Ireland are among the least radiogenic so far found in sediment-hosted Pb-Zn deposits anywhere in the world; (5) Lead isotopes do not show any covariance with $\delta^{34}\text{S}$ values in galenas.

1. Variation within individual deposits

Unlike many other carbonate-hosted Pb-Zn deposits, galena leads in the Irish occurrences display little intradeposit heterogeneity. In most cases, standard deviations of the means at the 95% confidence interval (2σ) are better than 0.1% of the ratios. Deposits such as those in the Mississippi Valley (Doe and Delevaux, 1972) often have a wide range of lead isotope ratios. Less well-known examples of variable within-deposit lead composition include such diverse deposits as those of the Appalachian Valley Zn+Pb district (Foley et al., 1981), and the sandstone-hosted Pb+Zn deposits of Scandinavia (Rickard et al., 1981; Bjørlykke and Thorpe, 1982).

Recent combined studies of lead and sulphur isotopes in deposits with wide ranges in isotopic composition of both elements have suggested the importance of mixing of two

fluids in the ore-forming process (Sverjensky et al., 1979; Rickard et al., 1981; LeHuray, 1984 and Crocetti et al., 1984). Conversely, the relative uniformity of lead isotope ratios within individual Irish carbonate-hosted Pb-Zn deposits indicates a well-homogenized source or sources of lead. The cause of, in some cases, extreme variability in sulphur isotope composition is not elucidated by any covariance with lead. Galenas analysed from the Tatestown deposit had $\delta^{34}\text{S}$ values of -5.1 , -2.0 , $+4.3$, $+6.8$, $+9.7$, $+11.1$, and $+12.2\%$ and yet lead isotope ratios are fairly consistent, showed no spatial trend, and no correlation of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, or $^{208}\text{Pb}/^{204}\text{Pb}$ with $\delta^{34}\text{S}$.

In terms of lead isotopes, the Irish deposits may be most closely compared with the Pb-Zn deposits of the McArthur River and Mt. Isa regions, Australia. Richards (1975) and Gulson (1975) have shown that lead isotope compositions are internally homogeneous in the McArthur River deposits, which are hosted in dolomitic-pyritic shales (Williams, 1978a; Rye and Williams, 1981). Similarly, Richards (1975) and Gulson et al. (1983) have demonstrated the homogeneous nature of lead isotopes in the Pb-Zn deposits at Mt. Isa in which mineralization is associated with carbonate-rich host rocks (Mathias and Clark, 1975).

2. Variability between deposits

Although lead isotope compositions of individual Irish base metal deposits exhibit little heterogeneity, there are large differences between deposits. Lead in galenas from Tatestown has isotope ratios essentially identical to lead from the nearby Navan orebodies. Lead isotope ratios from Silvermines are also similar to Tatestown and Navan.

Lead in these three deposits is characterized by nearly concordant isotope compositions (with respect to Stacey and Kramers' (1975) growth curves), although calculated model ages for these deposits (averaging $\sim 280\text{Ma}$) are over 70Ma too young. A similar situation is found at Mt. Isa, where the nearly concordant lead isotope ratios yield model ages younger than the presumed age of the deposits (Richards, 1975; Page, 1981; Gulson et al., 1983).

Lead isotope compositions in the Ballinalack, Moyvoughly, Keel and (to a lesser extent) Tynagh deposits are also similar to each other, but are quite distinct from the Navan-Silvermines group (Fig. 2). That Ballinalack, Moyvoughly, and Keel share virtually identical lead isotope ratios suggests that they may have shared a single homogenized source of lead. The slight but significantly higher $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in the Tynagh deposit, on the other hand, indicate an additional component of lead.

The radical difference in lead isotope ratios between Navan, Tatestown and Silvermines on the one hand, and Ballinalack, Moyvoughly, Keel and Tynagh on the other, indicates that different source regions contributed lead in differing proportions to the two groups. A similar situation may exist in the McArthur River region. Gulson's (1975) work indicates that, whereas individual McArthur River deposits are homogeneous, there are substantial differences between deposits.

3. Lead groupings and geographical trends

When all lead data (Boast et al., 1981a; Boast, 1983; this paper) are combined it is clear that lead isotope ratios of ore deposits become increasingly radiogenic to the SE. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios can be contoured regardless of the age of the host rock or the style of mineralization, and these contours trend NE-SW, subparallel to features of Caledon-

ide inheritance, including the course of the Iapetus Suture as postulated by Phillips et al. (1976). However, lead isotope ratios of deposits SE of the Suture fall on the same linear trend (on a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot) as those of deposits NW of the Suture. Magnetic, gravity and field studies of the midlands of Ireland emphasize NE structural trends of Caledonide inheritance (Max et al., 1983; Jacob et al., 1984; Brown and Williams, 1984; Browne and Reid, 1984). Lead isotope ratios parallel these trends. The Navan-Nenagh fault system has been described as a major structural feature that might represent the line of suture of the proto-Atlantic (Iapetus) Ocean (Phillips et al., 1976). Kennan et al. (1979) suggested that uranium/lead ratios might define this suture, however, as lead ratios from deposits on either side of the suture fall on the same trend.

The term "isoplumb" has been used informally by many geologists to describe isopleths of lead isotope ratios. Although dictionaries and glossaries of geology are already crowded, it is a term that might be worth adopting to avoid constant repetition of the phrase "isopleth of lead isotope ratios".

4. Character of lead isotope ratios

One of the striking features of the lead isotope data from the Irish base metal deposits is that, especially with respect to their $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, and especially towards the NE, the lead is the least radiogenic so far reported from similar or possibly similar worldwide deposits of Phanerozoic age. The classic Mississippi Valley deposits contain extremely radiogenic lead (Doe and Delevaux, 1972), as do most Phanerozoic carbonate-hosted Pb-Zn deposits. Some exceptions are plotted on Figure 3, together with representative lead isotope ratios from Irish base metal deposits. Of these, only lead from the Irish deposits (other than those in Kildare) and from Pine Point have $^{207}\text{Pb}/^{204}\text{Pb}$ ratios that fall below Stacey and Kramers' (1975) growth curve. The Gays River, Nova Scotia, deposit in Mississippian carbonates, is also notable for its relatively unradiogenic lead (Akande and Zentilli, 1984).

Lead isotope ratios of several Proterozoic sediment-hosted deposits are also plotted on Figure 3. All of these are somewhat radiogenic relative to the ages of their host rocks. Mt. Isa and McArthur River have been briefly discussed elsewhere. The Sullivan Pb-Zn deposit, British Columbia, is hosted in Middle Proterozoic clastic sediments, and contains somewhat radiogenic lead. Balmat is a lead-poor, marble-hosted Zn deposit that has recently been described as a Mississippi Valley-type deposit (Whelan et al., 1984), but unlike the Irish deposits, lead in Balmat galenas is isotopically heterogeneous. Like those in Ireland, however, the least radiogenic Balmat galenas are notable for their relatively low $^{207}\text{Pb}/^{204}\text{Pb}$ ratios.

The unradiogenic lead in Irish carbonate-hosted deposits provides information on the sources of metals in these ores. The geographical distribution of the lead isotope groupings indicates direct involvement of local basement. Kennan et al. (1979) have suggested that the paratectonic Caledonides in Ireland might be underlain by pre-Caledonian basement. The basis for this suggestion is the report by Strogen (1974) of the discovery of gneissic xenoliths of undetermined age in Viséan volcanic agglomerates in Co. Offaly and Co. Westmeath. Lewisian age rocks are known from Northern Ireland (MacIntyre et al., 1975) as well as late Pre-Cambrian equivalents of the Scottish Dalradian. Late Proterozoic rocks crop out in SE Ireland, where no older basement is exposed.

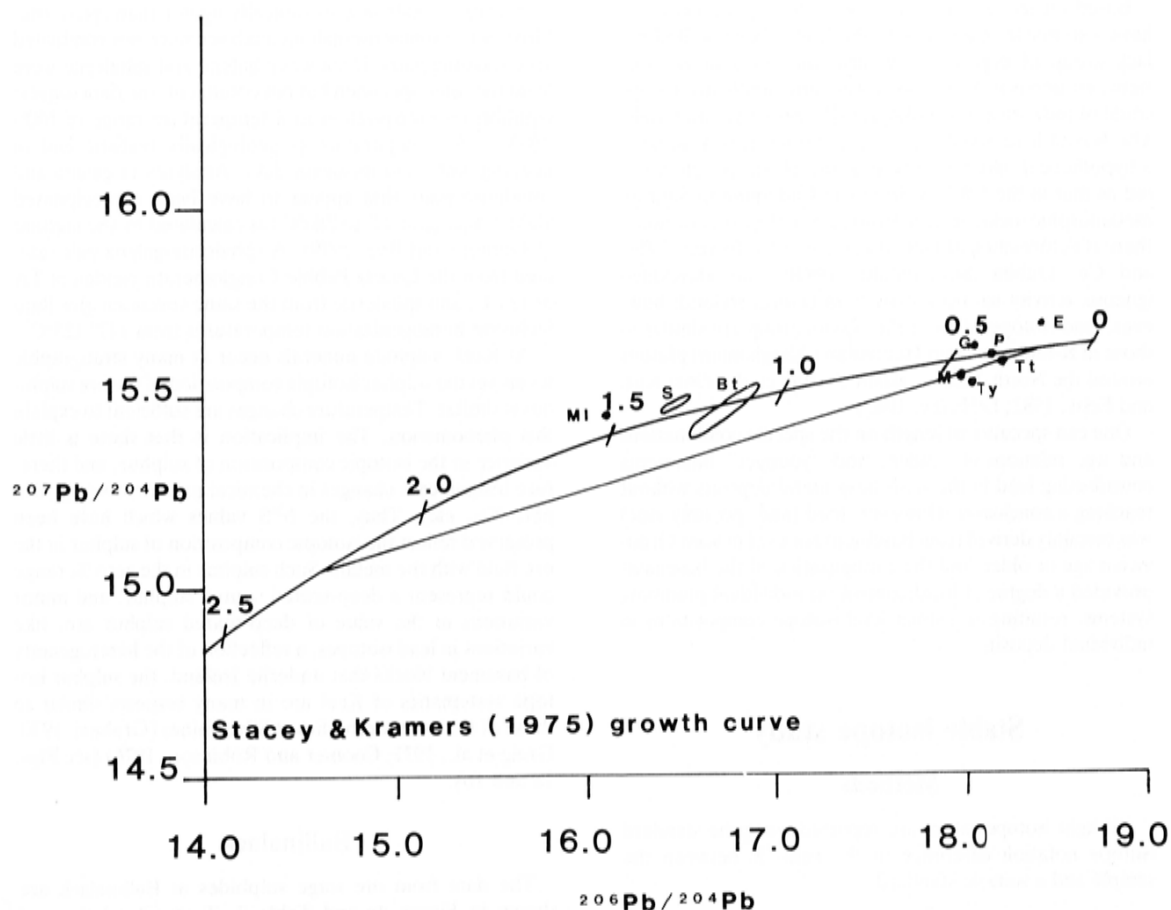


Figure 3. Comparison of lead isotope ratios from Irish deposits with other sediment-hosted lead-zinc deposits. Symbols as for Figure 2 with MI, Mount Isa; S, Sullivan; Bt, Balmat, G, Gays River; P, Pine Point; E, Economic. Data sources for Figure 3: Gays River, Nova Scotia (Akande and Zentilli, 1984). Pine Point and Economic, British Columbia (Andrew et al., 1984), Mount Isa, Queensland (Richards, 1975; Gulson et al., 1983).

5. Lead and sulphur isotope ratios

Lead isotope ratios in Irish carbonate-hosted Pb-Zn deposits do not covary in any way with sulphur isotope values. As will be discussed later, sulphur appears to be derived mostly locally, whereas lead reflects basement sources.

Discussion of lead data

The distribution and character of lead isotope ratios may be interpreted in several ways. The end-member scenarios may be described as: (1) the geographical division of lead isotope compositions reflects an abrupt change in the isotopic character of the basement from SE to NW, and (2) the data fall on a mixing trend and, with analyses from additional deposits, the gaps between lead isotope groups will be filled. Work by O'Keeffe (this vol.) and work in progress by Caulfield et al. (1985a, b) partially supports the second end-member hypothesis, yet geographical trends in the data remain, suggesting to us that both end-member models are, to some extent, applicable.

Two isotopically distinct segments of basement juxtaposed beneath central Ireland could explain the geographic trend of lead isotope compositions on the mixing trend. Lead in deposits NW of the Navan-Nenagh line is character-

ized by relatively low $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{308}\text{Pb}/^{204}\text{Pb}$ ratios as well as by unradiogenic $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. Such lead could have been derived from a mixture of old, granulitic basement (Lewisian?) in which radiogenic growth of lead was retarded by low U/Pb ratios (Doe and Zartman, 1979) and some younger rocks, such as the Caledonian metamorphic complex. Lead isotope data from deposits in the Scottish Dalradian reported by Swainbank et al (1981) and in this paper (Fig. 3) illustrate the extremely unradiogenic nature of $^{207}\text{Pb}/^{204}\text{Pb}$ ratios in lead believed to be derived in part from old, U/Pb-poor basement. The lead in the Ballinalack-Tynagh grouping of deposits need not have been derived directly from old cratonic rocks. At least some of the protoliths in the Caledonian metamorphic complex were likely to have been clastic rocks derived from older material. A plumbing system that operated only in the schists of the metamorphic complex could have then picked up a component of this older lead, resulting in a uniquely unradiogenic final product.

A best fit line drawn through the Navan-Silvermines and Ballinalack-Tynagh lead isotope data has a slope of about 0.149, which corresponds to a source "age" of about 2,350Ma. We believe that the basin in which the Dinantian limestones were deposited could not have contributed significantly to the lead in the ores; our arguments are discussed in a later section.

Based on the present data, the Navan group need not have a source in common with the less radiogenic Ballinalack group of deposits. The difference in lead isotopes between deposits in the northwest and southeast groups could be indicative of completely different source materials. The Navan lead isotopes could be the result of lead from a hypothetical, older basement in the SE (although not as old as that in the NW), or from the Cadomian to Silurian metamorphic rocks, or from a mixture of the two. Although there is deformation of Hercynian age in the Boyne Valley and Co. Dublin (Sevastopulo, 1981b), no Hercynian igneous activity has been proven in central Ireland; however, lead isotope ratios of the Navan group are similar to those in K-feldspars from Hercynian (Alleghanian) plutons around the North Atlantic Basin (Vitrac et al., 1981; Kish and Feiss, 1982; LeHuray, 1982).

One can speculate at length on the specific combinations and age relations of "older" and "younger" basements contributing lead to the Irish base-metal deposits without reaching a conclusion. However, lead (and, possibly zinc) was certainly derived from basement rocks of at least Ordovician age or older, and the configuration of the basement provided a degree of local control on individual plumbing systems, resulting in distinct lead isotope compositions in individual deposits.

Stable isotope study

Methods

All light isotope values are reported using the standard isotope notation difference in the ratio *R* between the sample and a suitable standard

$$\delta\text{‰} = \left(\frac{R_{\text{sample}}}{R_{\text{unknown}}} - 1 \right) \times 1,000; \quad R = \frac{{}^{34}\text{S}}{{}^{32}\text{S}}$$

The reference standard used for sulphur is Cañon Diablo troilite (Thode et al., 1961). The actual working standards used for sulphur were Park City pyrite and a synthetic ZnS.

Sulphur as SO₂ was analysed relative to the working standard on a Nuclide Corp. Nier type 60 degree ratio mass spectrometer. Instrumental corrections were applied to raw analyses (Craig, 1957; Deines, 1970). Reproducibility for the ZnS standard is $\pm 0.05\text{‰}$.

Sample specimens were examined under a binocular microscope at high magnification. Single crystals were removed with a dental tool. Fine-grained samples and specimens for paired analyses were collected using a dental drill with a fine drill bit (0.5mm). Very fine-grained diagenetic pyrite was recovered from apparently unmineralized limestone by acid digestion after the method of Zhabina and Volkov (1978). X-ray diffraction was used to check purity of phases.

Sulphides were oxidized to SO₂ by heating in a vacuum to 1150°C with excess cupric oxide in the presence of copper metal at 550°C. Sulphates were converted to SO₂ by direct combustion, and the SO₂ was passed over a copper trap at $\sim 550^\circ\text{C}$.

Results

Keel

Sulphur isotope values of ore stage sulphides at Keel are shown in Figure 4a and Table 1. The range of $\delta^{34}\text{S}$ values is from -13.7 to $+0.5\text{‰}$ with most falling in the range -8 to -1‰ .

In general, galena is isotopically lighter than sphalerite. Most of the sphalerite-galena analyses were not conducted on coexisting pairs. Even when galena and sphalerite were from the same specimen but not cotangent, the data suggest equilibrium precipitation in a temperature range of 100°–250°C. This temperature is geologically realistic and in keeping with fluid inclusion data. Analyses of galena and sphalerite pairs that appear to have been coprecipitated yield $T\Delta_{\text{sphal-gal}}$ of 42° to 286°C (as calculated by the method of Ohmoto and Rye, 1979). A sphalerite-galena pair sampled from the Quartz Pebble Conglomerate yielded at $T\Delta$ of 121°C, and sphalerite from the same specimen give fluid inclusion homogenization temperatures from 117°–123°C.

At Keel, sulphide minerals occur at many stratigraphic levels yet the sulphur isotopic composition of the ore sulphides is similar. Temperature changes are sufficient to explain this phenomenon. The implication is that there is little variance in the isotopic composition of sulphur, and therefore insignificant changes in chemical parameters (e.g. Eh, pH, fO₂, etc). Thus, the $\delta^{34}\text{S}$ values which have been preserved reflect the isotopic composition of sulphur in the ore fluid with the metals. Such sulphur in the zero ‰ range could represent a deep-seated source sulphur, and minor variations in the value of deep-seated sulphur are, like variations in lead isotopes, a reflection of the heterogeneity of basement blocks that underlie Ireland. The sulphur isotope systematics of Keel are in many respects similar to those of the lower orebodies at Silvermines (Graham, 1970; Greig et al., 1971; Coomer and Robinson, 1976) (see Figs. 1a and 1b).

Ballinalack

The data from ore stage sulphides at Ballinalack are shown in Figure 4c and Table 2. Textural relations of sphalerite and galena at Ballinalack suggest that they were not coprecipitated, and the sulphur isotope systematics indicate a lack of equilibrium precipitation. $\delta^{34}\text{S}$ pyrite suggests that pyritic sulphur was derived mainly from bacteriogenic reduction of ambient seawater ($\approx +20\text{‰}$). Sphalerite has a wide range of $\delta^{34}\text{S}$ values (-27 to 0‰). Galena has a narrower range (-30.8 to -14.8‰ with most values clustering around -20‰). Ore stage pyrite has a range from -36.4 to -15.9‰ but seems to have bimodal distribution. The lighter group of pyrites average around -32‰ and isotopically heavier pyrites have values similar to galenas. Dinantian sea-water sulphate had a $\delta^{34}\text{S}$ value around $+20\text{‰}$. Sulphate-reducing bacteria could produce the fractionation needed to produce the light sulphur found at Ballinalack. However, most bacteria only work effectively below 80°C (Skinner, 1979). If the fluids at Ballinalack had the same range of temperatures as other deposits in Ireland (Samson and Russell, 1983; Probert, 1983), then, in order to precipitate the metals directly from isotopically light bacteriogenic H₂S, there must have been migration of H₂S-bearing fluids laterally from either the same, or another, sedimentary facies. This is similar to the hypothesis invoked by Boast et al. (1981a) to explain the genesis of Stage 3 sulphides at Tynagh. Alternatively one could have had some sort of batch processing, of the sort suggested by Jones and Brand (this vol.) who interpret the textures as showing that mineralization was an episodic process. After H₂S is produced from sulphate by bacteria, a pulse of hot, metalliferous fluid enters the system precipitating sulphides but stopping H₂S production. The system then cools down, bacteria become re-established and the process is repeated.

A more likely explanation is that the light sulphur was derived from pre-existing minerals. Jones and Brand (this vol.) note replacement of FeS₂ by sphalerite and galena. Thus the precursor could be diagenetic pyrite, or if mineralization was sufficiently early in the diagenetic history of the host, iron monosulphides (Berner, 1984).

At Ballinalack some of the sphalerites fall in the range -5 to 0‰. Thus a deep-seated component in the sulphur cannot be ruled out. The distribution of δ³⁴S values can be thus explained as follows. Either all the sulphur is derived bacteriogenically, or else there were two sources of sulphur, (a) a deep-seated sulphur with a value similar to Keel (-5 to 0‰) and (b) light sulphur (< -30‰) produced by bacteriogenic reduction of +20‰ seawater sulphate. The light sulphur probably had been fixed as iron sulphide (Berner, 1984). The resulting distribution was a result of the mixing of these two sources.

Moyvoughly

The δ³⁴S sulphide data from Moate is shown in Figure 4b and Table 3. Although these data have an almost identical range of values as the Keel deposit, the distribution is quite different. Galena and sphalerite were not precipitated in isotopic equilibrium. Had they been coprecipitated at the 120°-220°C temperatures reported by Probert (1983), then sphalerite should consistently have δ³⁴S values of 3.0 to 4.7‰ heavier than coexisting galena (Ohmoto and Rye, 1979). The textures do not suggest coprecipitation. Barite at Moyvoughly has δ³⁴S values of +18.9 and +22.4‰ i.e. within the range of Dinantian sea-water sulphate.

As at Keel and Ballinalack, again there does seem to be a component of deep seated sulphur, but, if present, the second sulphur component is not as light as at Ballinalack. This could reflect heterogeneities within the rocks that underlie the Dinantian strata. However, a very late-stage diagenetic pyrite has δ³⁴S = +3.3‰ suggesting that the system was closed or partially closed. There is certainly a local sulphur component related to the depositional environment.

Tatestown

Tatestown has a lead isotope signature different to the three deposits in the midlands, but similar to Navan and Silvermines. Ore stage sulphides have δ³⁴S values ranging from -23.6 to +14.4‰ (Fig. 4d). Pyrite is light (-23.6 to -13‰). Galena and sphalerite both have wide ranges of values (galena -18.16 to +12.5‰), sphalerite -17.2 to +14.4‰, but mainly in the range -3 to +12‰ with median value around +7‰. As the textures suggest, they are rarely in isotopic equilibrium. Where galena and sphalerite appear to be coprecipitated, isotopic fractionation temperatures calculated by the method of Ohmoto and Rye (1979) were 137° and 178°C. As Probert (1983) has reported fluid inclusion temperatures of 140°-190°C, it seems that these isotopic fractionation temperatures are realistic. Tatestown is the only deposit in Ireland (for which data has been published) that has such an isotopically heavy sulphur component. In all other investigations, only four δ³⁴S sulphides heavier than +5‰ have been reported, two from the top of the Lower G orebody at Silvermines, and two from a diamond drill hole 3.62km east of Tynagh (Graham, 1970; Coomer and Robinson, 1976; Boast et al., 1981a).

The Micrite Unit that hosts the mineralization at Tatestown was deposited on a tidal flat (Andrew and Poustie, this vol.), and given the low palaeolatitude (Ziegler, 1982), evaporation would have been high, and conditions would

have been conducive to the formation of evaporite deposits. Indeed, replaced evaporites have been identified in this part of Ireland (Andrew and Ashton, 1982). The dissolution and abiogenic reduction of sulphate would yield isotopically heavy sulphur. However, in the lower temperature range indicated by fluid inclusion studies (Probert, 1983) and by sulphur isotope fractionation geothermometry, abiogenic reduction of sulphate is slow and ineffective (Ohmoto and Lasaga, 1982).

There is also isotopically light sulphur in the Tatestown deposit. This is most probably from diagenetic pyrite emplaced as a consequence of bacteriogenic reduction of seawater sulphates. Because the lead isotopes indicate a deep-seated source, like the other deposits, a deep-seated component of sulphur cannot be ruled out. However, the spread of δ³⁴S values at Tatestown make it impossible to recognize such sulphur.

Summary of sulphur data

(1) δ³⁴S values from feeder zone deposits such as the Silvermines lower G orebody and Keel have sulphides with δ³⁴S values close to 0‰ which allows the possibility of a deep-seated origin for sulphur. Galena and sphalerite in these deposits are usually close to, or in, isotopic equilibrium with Δ_{sph-gn}, yielding isotopic fractionation temperatures that match fluid inclusion data.

(2) In the other deposits studied, sulphur was derived from the host rocks and from the fluids within them, usually as a consequence of bacteriogenic reduction of seawater sulphate. Where evaporites were present in the stratigraphic column, there was an isotopically heavy component of sulphur.

(3) Seawater sulphate was the source of SO₄²⁻ for barite in all of the deposits.

Timing

Any model for the genesis of Irish sediment-hosted Zn-Pb-Ba deposits must consider the timing of mineralization. Unlike MVT deposits that were emplaced after burial and lithification of the host rocks, Irish deposits, other than the MVT-affinity deposits presently known in Co. Kildare, are classed with those deposits emplaced early in the sedimentation and diagenesis of the host rocks (Gustafson and Williams, 1981). Emplacement of the stratiform Ballynoe barite deposit at Silvermines appears to have started on the sea floor (Taylor and Andrew, 1978; Taylor, 1984; Andrew, this vol.). Mineralization at Tynagh, Ballinalack, Moyvoughly and Tatestown seems to have started prior to the lithification of the host rocks and are thus classified as syndiagenetic (Boast et al., 1981a; Jones and Bradfer, 1982; Jones and Brand; Poustie and Kucha; Andrew and Poustie, all this vol.). Mineralization in the Kildare region (Harberton Bridge and Allenwood West) was emplaced after lithification of the host rocks and is in part hosted by post-Courceyan strata (Holdstock, 1982; Emo, this vol.). Thus on a regional scale, mineralization would appear to have taken place on a timescale in excess of 5 Ma.

On a local scale it is possible to estimate the timing of mineralization. All lenses (1 to 5) in the 2 Zone at Navan are truncated against an angular unconformity. The ore lenses are hosted by Courceyan Pale Beds and are unconformably overlain by Arundian Boulder Conglomerate and Upper Dark Limestone (Andrew and Ashton, 1983a).

Whether this unconformity represents a period of Chadian uplift and pre-Arundian erosion (Andrew and Ashton, 1982) or submarine slumping (Boyce et al., 1983a) is a matter of conjecture. Clearly most mineralization was emplaced prior to the Arundian, and either during the Chadian or before. Textural evidence is interpreted as indicating that mineralization in the deepest (5) lens at Navan occurred pencontemporaneously with shallow-water carbonate deposition (Andrew and Ashton, 1982). The lower part of the Pale Beds is underlain by 50-100m of strata deposited during marine transgression over low metamorphic grade Lower Palaeozoic metasediments. The rocks hosting many of the deposits described in this volume were also deposited shortly after transgression, and ore textures indicate that sulphide mineralization started early in the diagenetic history of the host rock (Jones and Brand; Poustie and Kucha; Andrew and Poustie, all this vol.).

Basin development and mineralization

Although the whole of central Ireland can be considered a basin, geophysical studies (Brown and Williams, 1985; Williams and Brown, this vol.) have shown that there are several sub-basins, and that mineralization tends to occur at the margins of these smaller basins. These smaller basins would be categorized as second order basins by Large (1980 and 1983). Since these basins are thought by Lydon (this vol.), and by Williams and Brown (this vol.) to be a possible source of both the metals and the fluids which were responsible for the emplacement of the deposits in central Ireland, it is necessary to consider the dimensions of the basins. The Trim No. 1 exploration well is 20km SSW of Navan; 1,821m of Dinantian strata were intersected in this drill hole and, with the addition of strata preserved down-flank from the well, Sheridan (1972b) has estimated the total thickness of Dinantian sedimentary rock in this part of Ireland to be 2 219m. The width of sub-basins in central Ireland varies. Based on geophysical studies (Williams and Brown, this vol.) basins vary between 12 and 25km in width, and are elongated parallel to trends of Caledonide inheritance (i.e. NE). Lydon (this vol.) demonstrates that it is theoretically possible to leach the required amount of metal from compaction of the volume of sediments that have produced these Dinantian strata.

Sevastopulo (1982) identifies the 401m thick Bray Hill Formation of reef micrites in the Trim No. 1 well as being Waulsortian. He notes that it was originally identified as being Holkerian and Asbian in age, but adds that "it is now known to be Waulsortian", a conclusion which was based on conodont assemblages. The original dating by Sheridan (1972b) was based on foraminiferal assemblages. Most of the sediments preserved in the Trim No. 1 well were deposited after the main mineralizing events at Navan. Whereas it is possible that the lowermost part of Rathmolyon Shale Formation is upper Courceyan, the paucity of fauna made zonal determination impossible (Sheridan, 1972b). The only strata of proven Courceyan age are the Rathmolyon Basal Clastic Formation (probably equivalent to the Navan Pale Beds) of which 342.9m were intersected at Trim, although the base of this Formation was not reached. By analogy with other boreholes in Ireland, Sheridan (1972b) suspects the presence of Old Red Sandstone-type continental facies close to the bottom the Trim No. 1 well.

The estimated true thickness of the Rathmolyon Basal Clastic Formation is 300-330m, and it has been divided into four members by Sheridan (1972b).

Table 5.

Member	Intersection	Drilled Thickness
Sandy limestones and shales	1478.3-1542.3m	64.0m
Oolitic limestones and shales	1542.3-1649.0m	106.7m
Oolites	1542.3-1583.4m	41.1m
Limestones and shales	1583.4-1615.4m	32.0m
Oolites	1615.4-1649.0m	33.6
Limestones, shales and mudstones	1649.0-1746.5m	97.5m
Sandstones and siltstones (bottom of Formation not reached)	1746.5-1821.2m	74.7m

Table 5. Lithology of the lower section of the Trim No. 1 well (from Sheridan, 1972b).

Given the above lithologies it is unlikely, unless there was extensive dissolution during diagenesis, that the original thickness of un lithified Courceyan sediment was much in excess of 500m.

Fluid inclusion and sulphur isotopic fractionation geothermometry indicate that temperatures in all of the mineralizing fluids reached 180°C. In the Late Devonian-Early Dinantian, central Ireland was subjected to tensional forces (Leeder, 1982; Bott, 1982) which possibly were related to the closure of the Hercynian Mid-European Sea (Bott et al., 1984; Williams and Brown, this vol.). Heat flow might have been slightly higher than usual, but it is unlikely that fluids with temperatures of 180°C could be generated in the required timespan in only 500m of sediment. At both Silvermines and Keel, mineralization similar in style to the non-stratiform Dinantian-hosted ore occurs in metasedimentary strata well below the main ore zones. Such mineralization is not likely to have derived metals from Dinantian basinal fluids.

We find it unlikely that the Dinantian basins were the major source of hot metalliferous fluids, but could have contributed to the ore forming process as a source of some sulphur.

The model of Williams and Brown (this vol.) does demonstrate the spatial affinity between discovered deposits of Zn±Pb±Ba and fault-bounded edges of second order basins. These faults are of Caledonide inheritance that intersect the Lower Palaeozoic and older strata that underlie the Dinantian sediments. From drilling in the Kola Peninsula (Soviet Union), it is known that metalliferous fluids circulate at great depths along cracks and microfractures (Kozlovsky, 1984). Fluids of this type probably circulated in the Lower Palaeozoic and older rocks beneath central Ireland, and were available to be tapped by deep-seated faults that were reactivated during the development of second order basins.

Discussion

Although sediment-hosted deposits of Zn±Pb±Ba in Ireland occur in differing structural settings and have variable styles of mineralization, they have, regardless of size or economic importance, many common characteristics.

The deposits occur mostly in Lower Dinantian sedimentary rock, usually of Courceyan age. These sediments were

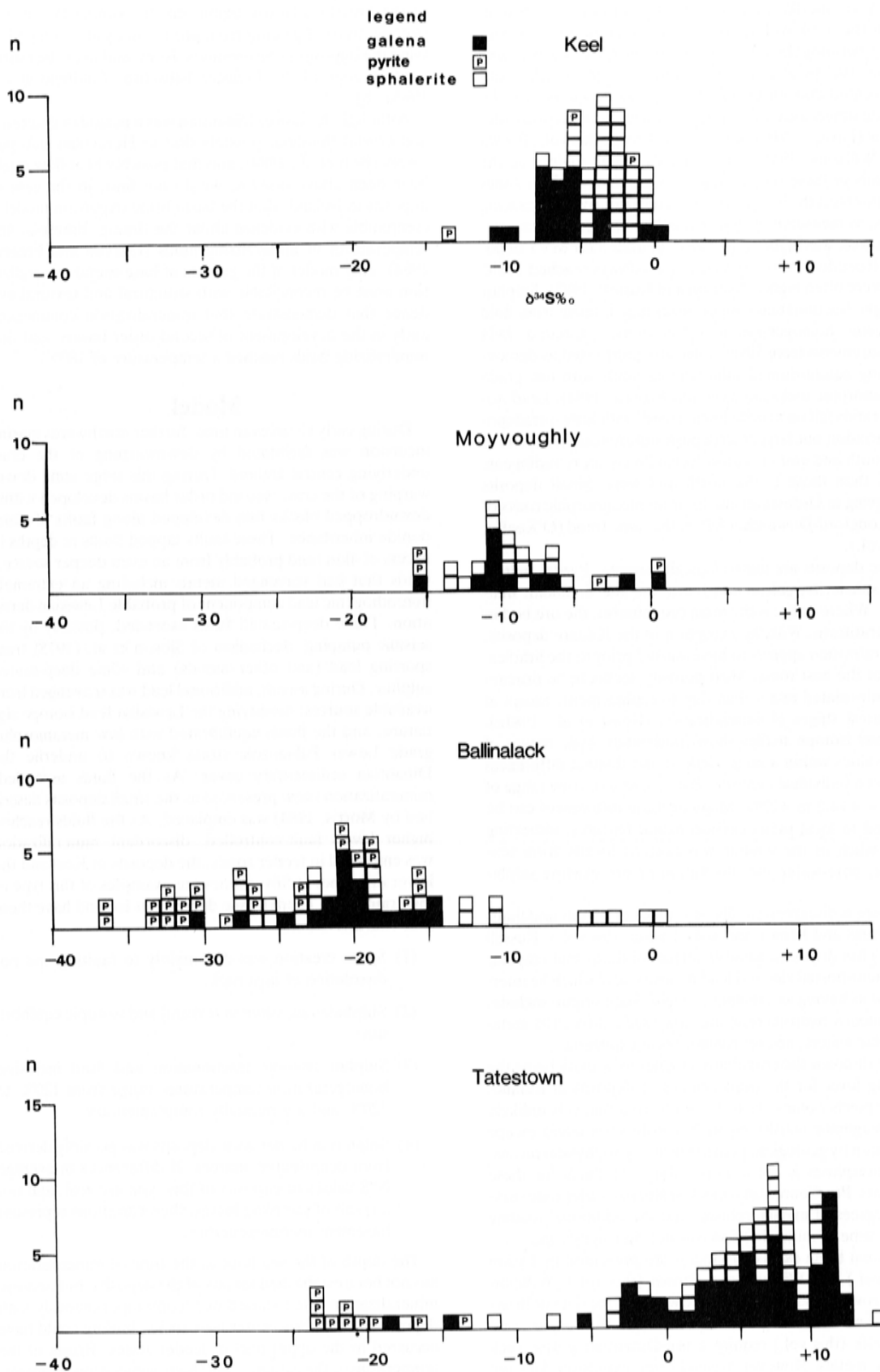


Figure 4. Sulphur isotopic composition of ore-stage sulphides at (a) Keel, (b) Moyvoughly, (c) Ballinalack, (d) Tatestown.

deposited shortly after northwards marine transgression. As in the north of England, two interconnected processes were operating (Bott et al., 1984). Broad-scale downwarping of the crust permitted marine incursion, and synchronous differential downdropping of blocks along faults of Caledonide inheritance led to the development of second order basins (Large, 1980; Williams and Brown, this vol.; Brown and Williams, 1985). The deposits occur mainly at the margins of these second order basins, close to fault zones that intersect the basement. The temperatures of emplacing fluids, as measured by fluid inclusion homogenization temperatures, was higher than those tabulated for MVT deposits (Roedder, 1976). Temperatures always reached 180°C and were often higher (Samson and Russell, 1983). Sulphur isotopic fractionation temperatures match those from fluid inclusion homogenization temperatures. Limited D/H measurements from Silvermines are interpreted as demonstrating equilibrium of mineralizing fluids with low grade metamorphic rocks (Samson and Russell, 1984). Lead isotope ratios fall on a single linear trend, with little intradeposit variation but large interdeposit differences. Deposits to the south and east of central Ireland have more radiogenic leads than those to the north and west. Small deposits occurring in Ordovician and Silurian metamorphic rocks of the Longford-Down inlier fall on the same trend (O'Keefe, this vol.).

The deposits are mineralogically simple. Pyrite, marcasite, sphalerite, galena and barite are the dominant minerals. Where barite is the main ore mineral, the ore bodies are stratiform. With the exception of the Kildare deposits, mineralization appears to have started prior to the lithification of the host rocks. Most porosity seems to be primary or fault-related rather than due to replacement, except at the latest stages of mineralization (Boast et al., 1981a). Sulphur isotope studies show moderately wide ranges of $\delta^{34}\text{S}$ values within a single deposit and distinct differences between individual deposits. Barite had a narrow range of $\delta^{34}\text{S} = +14.2$ to $+22\%$. Many of these differences can be related to local palaeoenvironmental features, indicating that much of the sulphur was derived locally from seawater, pore-water and dissolution of pre-existing sulphides.

There is disagreement about sources of metals and fluids (Williams and Brown, this vol.; Lydon, this vol.). Russell (1983) has discussed possible origins of fluids that emplace sediment-hosted zinc and lead deposits, and which he interpreted as having an exhalative origin. Such origins include, (a) igneous hydrothermal and magmatic drive, (b) metamorphic waters, and (c) basinal brine expulsion.

We discount the probability of igneous activity being the driving force for the emplacement of deposits in Ireland; the deposits occur over such a wide area that it is unlikely that magmatic activity on such a wide scale could escape detection by geological, geochemical or geophysical means. Metamorphism is not a likely source of fluids for these deposits. Pre-Courceyan rocks had already undergone varying degrees of metamorphism, and the additional loading at the time of mineralization was not that significant.

Basinal brine expulsion models are presented by Lydon (this vol.) and Williams and Brown (this vol.). Williams and Brown do not accept that the lead isotope data of Boast (1978 and 1983) Boast et al. (1981b), this paper, and O'Keefe (this vol.) require a pre-Dinantian source rock for the metals. However, basinal brine expulsion does not explain the continuity of trend of lead isotope ratios in deposits of presumed Carboniferous age (O'Keefe, this vol.) hosted by Ordovician and Silurian metamorphic rocks

in the Longford-Down region, nor the similarities of lead isotope ratios of galenas from pre-Courceyan strata underlying the deposits at Silvermines, Keel, and near the north-western edge of the Leinster batholith (Caulfield et al., 1985a, b).

Although the Lower Dinantian was a period of extension and crustal thinning, possibly due to Hercynian slab-pull forces (Bott et al., 1984), and that possibly heat flow might have been above normal, we do not find, in the case of deposits in Ireland, that the basin brine expulsion model is compatible with evidence about the timing, timespan and temperatures of mineralizing fluids (Garven and Freeze, 1984). Any model of the genesis of base-metal mineralization must be reconcilable with structural and textural evidence that demonstrate that mineralization commenced early in the development of second order basins, and that mineralizing fluids reached a temperature of 180°C.

Model

During early Courceyan time, further northwards marine incursion was facilitated by downwarping of the crust underlying central Ireland. During this large scale downwarping of the crust, second order basins developed within downdropped blocks that developed along faults of Caledonide inheritance. These faults tapped fluids at depths in excess of 4km (and probably from an even deeper source), fluids that had scavenged metals including an extremely nonradiogenic lead component of probable Lewisian derivation. These deep-seated fluids ascended, possibly by the seismic pumping mechanism of Sibson et al. (1975) transporting lead (and other metals) and some deep-seated sulphur. During ascent, additional lead was scavenged from available sources, modifying the Lewisian lead isotope signature, and the fluids equilibrated with low metamorphic grade Lower Palaeozoic strata known to underlie the Dinantian sedimentary cover. As the fluids ascended, mineralization (now preserved as the small deposits described by Morris, 1984) was emplaced. As the fluids reached higher levels fault-controlled, discordant mineralization was emplaced in feeder zones; the deposits at Keel and the lower ore zones at Silvermines are examples of this type of mineralization. Feeder zone deposits in Ireland have these four characteristics:

- (1) Space creation was due mainly to faulting and not dissolution of host rock.
- (2) Sulphides are often in textural and isotopic equilibrium.
- (3) Sulphur isotopic fractionation and fluid inclusion homogenization temperatures range from 120°C to 220°C and are mutually complementary.
- (4) Sulphur in feeder-zone deposits was possibly derived from deep-seated sources. If differences in average $\delta^{34}\text{S}$ values of deposits of this type are real, and not a result of sampling biases, then variations represent basement inhomogeneities.

The depth of the sea floor at the time of mineralization has not been established for any of the deposits, but because mineralization often started penecontemporaneously with deposition of shallow-water host rocks, boiling could have occurred in the upper part of feeder zones. Brines of the temperatures, the salinities, and homogenization temperatures found in inclusions in ore stage minerals would need the equivalent of 200m of hydrostatic pressure to prevent boiling (Haas, 1971). Sulphide deposition continued within

sediments undergoing diagenesis and lithification within primary cavities (such as the stromatactis cavities at Ballinalack). If exhalation of the hydrothermal solution occurred (above the sediment/water interface) and metals were still in solution, and the temperature, salinity and density of the fluid was such that it was not dispersed (cf. Sato, 1972), then it is possible to form syndimentary exhalative ore bodies (see Large, 1980 and 1983; Russell et al., 1981; Russell, 1983; for discussion of these types of orebodies). Palaeotopographical controls might localize mineralization (Taylor, 1984). Examples of deposits of this type are the Ballynoe barite and the B and Upper G Zones at Silvermines.

Should dispersion occur, any sulphides not oxidized could form nucleation sites for syndimentary mineralization. The syndimentary deposits were emplaced within the host sediment, during lithification and compaction, with the spent fluids debouching to produce manganese and iron aureoles. Textures are varied. Impersistent laminae possibly represent overgrowths of fine sulphides deposited on the sea floor. Sulphides are usually not in textural or isotopic equilibrium. Sulphur isotopes show that sulphides in these deposits contain sulphur which was derived mainly from local sources, with the possibility of a deep-seated sulphur component (examples are Tynagh, Ballinalack, and Tatestown). During the latter stages of mineralization, veining and cross cutting epigenetic mineralization were emplaced at the same horizons.

Are Dinantian sediment-hosted deposits of $Zn \pm Pb \pm Ba$ in central Ireland syndimentary (syngenetic), syndimentary (diagenetic) or epigenetic? In a different tectonic setting, Eldridge et al. (1983) considered the application of these terms, as applied to Kuroko deposits, to be misleading when discussing interrelated processes that affect the same body of rock in a relatively short time interval. Aspects of each of the deposits in Ireland could be placed in any of the above categories, but such classification would be neither purposeful nor instructive. The genetic link between all these deposits is that, as basin-wide marine transgression occurred in central Ireland during the early Courcayan, second order basins developed in response to tensional forces. Faults at the edges of these second order basins tapped deep-seated fluids (rich in metals but also carrying some sulphur) that ascended to replace pre-existing sulphur minerals and also to mix with metal-poor and sulphur-rich pore- or sea-water. The relative importance of syngenetic, syndimentary, diagenetic, and epigenetic processes to ore deposition depended on rate of fluid expulsion and local geological controls.

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Tables 1-4 are on the following pages.

Table 1. Sulphur isotope data of ore stage sulphides from Keel.

Sample Number	Depth m	Run No.	Mineral	$\delta^{34}\text{S}$ (‰) CDT	Comments
QPC	QPC	170-S-4	S	-3.3	Dark sphalerite
QPC	QPC	170-S-5	S	-2.0	Pale sphalerite
QPC	QPC	200-S-5	G	-7.4	
QPC	QPC	200-S-6	S	-2.8	
DDH K1					
K1-287	87.5	194-S-9	P	-13.7	
K1-665.5	202.8	193-S-5	S	-0.9	
K1-665.5	202.8	193-S-6	G	-7.1	
K1-665.5	202.8	193-S-7	S	-2.8	
DDH K5					
K5-153.4	46.8	191-S-11	S	-3.0	
K5-180	54.9	192-S-6	S	-4.9	
K5-183	55.8	186-S-2	G	+1.0	
K5-183	55.8	186-S-1	S	-4.1	
K5-183	55.8	186-S-5	G	-3.6	
K5-428	130.5	191-S-7	S	-2.8	
K5-433	132.0	191-S-9	S	-3.6	
DDH K15					
K15-836	255.4	189-S-8	P	-5.3	
K15-883.5	269.3	189-S-5	G	-7.3	
K15-883.5	269.3	189-S-6	G	-5.8	
K15-883.5	269.3	189-S-7	S	-3.2	
DDH K17					
K17-558	170.1	194-S-5	S	-4.6	
K17-585.8	178.6	194-S-4	S	-4.6	
K17-589	179.5	221-S-11	G	-4.5	
K17-623.5	179.0	194-S-3	S	-3.5	
K17-624.5	190.4	193-S-11	S	-5.6	
K17-732	223.1	194-S-8	S	-5.0	
DDH K18					
K18-346	105.5	193-S-12	S	-4.1	Vuggy pale sphalerite
K18-346	105.5	194-S-1	S	-3.4	Massive dark brown sphalerite
K18-346	105.5	194-S-2	S	-3.7	Massive dark brown sphalerite
K18-418.5	127.6	203-S-10	G	-4.0	
K18-418.5	127.6	203-S-9	S	-0.8	
K18-488.5	148.0	185-S-4	G	-5.7	
DDH K23					
K23-387.7	118.2	191-S-12	S	-0.4	
K23-421.5	128.5	192-S-1	G	-0.8	
K23-473.9	144.4	189-S-1	S	-1.1	
K23-591.1	180.2	185-S-12	S	-2.4	
DDH K24					
K24-409.7	124.9	188-S-9	S	-2.3	
K24-455.3	138.8	193-S-8	S	-2.7	
K24-455.3	138.8	193-S-9	S	-1.9	
K24-455.3	138.8	193-S-10	G	-10.0	
K24-447	136.2	185-S-1	G	-5.9	
K24-447	136.2	185-S-2	S	-1.2	
K24-447	136.2	188-S-10	G	-5.9	
K24-447	136.2	188-S-12	G	-6.6	
K24-447	136.2	192-S-4	G	-6.0	
K24-447	136.2	192-S-5	S	-1.1	
K24-453	138.1	203-S-11	G	-6.1	
K24-453	138.1	203-S-12	S	+0.5	
K24-463	141.1	184-S-11	G	-5.8	

Table 1

K24-463	141.1	184-S-12	S	-3.5
K24-473.2	144.2	185-S-3	G	-5.8
K24-473.2	144.2	185-S-11	S	-3.5
K24-473.5	144.3	189-S-2	S	+0.0
K24-475	144.8	186-S-3	G	-7.2
K24-478.2	145.6	188-S-8	S	-1.6
DDH K77				
K77-477	145.4	194-S-6	S	-4.2
K77-477	145.4	194-S-7	P	-1.5
DDH KA170				
KA170-996.5	303.7	186-S-8	G	-6.6
KA170-996.5	303.7	186-S-9	P	-26.4
KA170-996.5	303.7	186-S-10	S	-7.5
KA170-996.5	303.7	189-S-3	G	-10.1
KA170-996.5	303.7	189-S-4	S	-5.4

Table 2. Sulphur isotope data of ore stage sulphides from Moyvoughly.

Sample Number	Depth m	Run No.	Mineral	$\delta^{34}\text{S}$	
				(‰)	Comments
DDH DM1					
DM1-66	20.1	215-S-12	P	-11.9	Diagenetic
DM1-66	20.1	216-S-1	P	-10.7	Diagenetic
DM1-106	32.3	201-S-3	G	-6.1	
DM1-106	32.3	201-S-4	S	-2.2	
DDH DM4					
DM4-81	24.7	201-S-1	G	-1.8	
DDH DM18					
DM18-115	35.1	201-S-5	S	-8.2	
DDH DM20					
DM20-61	18.6	201-S-7	G	-10.9	
DM20-61	18.6	201-S-8	S	-7.4	
DM20-67	20.4	201-S-9	S	-8.3	Dark, fine-grained
DM20-67	20.4	201-S-9	S	-11.4	Red coarse-grained
DM20-71	21.6	201-S-2	G	-10.8	
DM20-121	36.9	201-S-11	S	-5.6	
DM20-123	37.5	200-S-12	S	-9.4	
DM20-130	39.6	201-S-12	G	-10.7	
DDH DM22					
DM22-87.9	26.8	200-S-9	G	-9.6	
DM22-87.9	26.8	200-S-10	S	-13.5	
DM22-58	26.8	202-S-1	S	-9.8	
DM22-89	27.1	202-S-2	G	-11.9	
DM22-89	27.1	202-S-3	S	-12.6	
DM22-111	33.8	202-S-6	S	-7.8	
DM22-117.5	35.8	202-S-4	G	+0.4	
DM22-117.5	35.8	202-S-5	S	-6.6	
DDH DM25					
DM25-78	23.8	202-S-6	S	-9.7	
DM25-85	25.9	202-S-7	G	-10.2	
DM25-85	25.9	202-S-9	S	-10.1	
DM25-108	32.9	202-S-10	P	-15.9	
DDH DM32					
DM32-46.5	14.2	203-S-1	S	-13.1	
DM32-84	25.6	203-S-2	P	+0.5	

Table 2

DDH DM33					
DM33-45	13.7	203-S-3	P	+3.3	
DM33-152	46.3	203-S-4	G	-7.3	
DDH DM38					
DM38-50	15.2	203-S-5	P	-16.0	
DDH DM40					
DM40-75	22.9	203-S-6	P	-3.6	
DM40-96	29.3	203-S-7	S	-10.0	
DDH DM63					
DM63-253	77.1	203-S-8	S	-8.7	Very fine veinlet
DDH BD					
117-15					
BD14-26.5	8.1	221-S-9	G	-4.1	
DDH BD					
117-21					
BD21-86A	26.2	221-S-8	G	-0.9	
BD21-86B	26.2	221-S-10	G	+0.9	

Table 3. Sulphur isotope data of ore stage sulphides from Ballinalack.

Sample Number	Depth m	Run No.	Mineral	$\delta^{34}\text{S}$ (‰) CDT	Comments
DDH B21					
B21-73	22.3	205-S-6	G	-14.8	
B21-73	22.3	205-S-7	P	-26.6	
B21-82.5	25.1	197-S-7	P	-32.1	
B21-82.5	25.1	197-S-9	S	-27.7	
B21-104.5	31.9	205-S-4	S	-25.4	
B21-104.5	31.9	205-S-5	P	-34.0	
DDH B33					
B33-407.7	124.3	200-S-1	G	-30.8	
B33-407.7	124.3	199-S-6	S	-22.9	
B33-407.7	124.3	199-S-9	P	-28.4	
B33-407.7	124.3	200-S-1	G	-18.5	
B33-516.4	157.4	197-S-2	P	-18.9	
B33-522.7	159.1	198-S-6	S	-4.1	
B33-522.7	159.3	198-S-12	S	-2.9	
B33-573	174.7	198-S-7	P	-32.0	Clotted pyrite
DDH B35					
B35-342.8	104.5	205-S-3	P	-26.1	
B35-404.7	123.4	198-S-8	P	-23.2	
B35-404.7	123.4	205-S-2	P	-20.9	
B35-404.7	131.0	205-S-1	P	-20.5	
DDH B40					
B40-484	148.4	198-S-10	S	-18.5	
B40-487	148.4	199-S-1	S	-3.5	
B40-487	148.4	198-S-11	P	-30.8	
B40-537.7	163.3	196-S-5	G	-17.4	
B40-537.7	163.3	196-S-6	S	-0.2	
B40-537.7	163.3	196-S-7	P	-32.2	
B40-537.7	163.3	196-S-8	S	+0.0	
B40-537.7	163.3	196-S-9	P	-33.3	
B40-556.3	169.6	197-S-12	G	-21.3	
B40-556.3	169.6	198-S-1	S	-18.4	
B40-556.3	169.6	198-S-2	S	-25.9	
B40-556.3	169.6	198-S-3	P	-23.7	

Table 3

B40-579	176.5	199-S-5	G	-19.0	
B40-582.7	177.6	195-S-5	G	-19.1	
B40-582.7	177.6	195-S-7	G	-24.5	
B40-631.2	192.4	200-S-2	G	-21.0	
B40-631.2	192.4	199-S-10	P	-15.9	
B40-631.2	192.4	200-S-4	P	-16.0	
B40-631.2	192.4	199-S-7	S	-10.1	
B40-631.7	192.5	196-S-2	G	-20.6	
B40-631.7	192.5	195-S-4	P	-16.4	
DDH B51					
B51-562	171.3	199-S-8	S	-26.3	Muddy stylonitic sphalerite
B51-562	171.3	199-S-3	S	-22.9	
B51-562	171.3	199-S-11	P	-27.0	
B51-562	171.3	199-S-12	P	-36.4	
B51-614.2	187.2	198-S-9	P	-36.1	
B51-614.2	187.2	198-S-5	S	-23.8	
B51-864.7	263.6	196-S-10	G	-19.2	
B51-864.7	263.6	196-S-11	S	-12.8	
B51-864.7	263.6	196-S-12	P	-17.5	
B51-864.7	263.6	197-S-1	G	-15.8	
B51-865	263.7	194-S-12	G	-16.4	
B51-865	263.7	195-S-1	S	-12.1	
B51-865	263.7	195-S-2	P	-18.5	
B51-868.5	263.7	197-S-10	G	-15.0	
B51-868.5	264.7	197-S-11	S	-11.0	
B51-877	264.7	202-S-5	G	-21.7	
	267.3				
DDH B58					
B58-621.7	189.5	200-S-7	G	-18.5	
B58-621.7	189.5	200-S-8	S	-15.7	
B58-622	189.6	195-S-12	G	-22.6	
B58-622	189.6	196-S-1	P	-19.0	
B58-636	193.9	195-S-10	G	-21.0	
B58-636	193.9	195-S-11	P	-30.4	
B58-636	193.9	196-S-4	P	-31.7	

Table 4. Sulphur isotope data of ore stage sulphides from Tatetown.

Sample Number	Depth m	Run No.	Mineral	$\delta^{34}\text{S}$ (‰) CDT	Comments
DDH BF4					
BF4-38	11.6	204-S-1	S	+1.5	Stylonitic sphalerite
BF4-38	11.6	204-S-2	G	+7.8	
BF4-69	21.0	184-S-5	P	-33.9	Diagenetic pyrite
BF4-69	21.0	184-S-6	P	-32.2	Diagenetic pyrite
BF4-171.5	52.3	204-S-4	S	+7.6	
BF4-171.5	52.3	204-S-3	P	-41.8	
BF4-211.7	64.5	204-S-5	S	+10.7	
BF4-419	127.7	204-S-6	S	+10.4	
DDH BF7					
BF7-315.5	96.2	206-S-1	S	+0.1	
BF7-326.6	99.6	206-S-2	S	+4.2	
BF7-326.8	99.6	206-S-3	G	+2.1	
BF7-326.8	99.6	206-S-4	S	+3.3	
DDH BF9					
BF9-226	68.9	206-S-8	S	-17.2	
BF9-226	68.9	206-S-9	G	-18.2	
BF9-239.5	73.0	206-S-10	P	-21.9	
BF9-258.7	78.9	206-S-12	G	-14.9	
BF9-283	86.3	206-S-11	S	+8.7	

Table 4

DDH BF13					
BF13-180	54.9	164-S-4	G	+1.8	
BF13-378	115.2	205-S-11	S	+8.6	
BF13-278	115.2	205-S-12	G	-0.4	
BF13-378.2	115.3	164-S-5	G	-2.0	
BF13-378.2	115.3	164-S-6	G	+4.3	
BF13-380	115.8	171-S-4	G	+3.5	
BF13-380	115.8	171-S-5	S	+6.7	
BF13-380	115.8	171-S-6	G	+3.4	
BF13-380	115.8	171-S-7	S	+4.7	
BF13-380	115.8	204-S-10	S	+1.5	
BF13-381.5	116.3	174-S-10	G	+6.2	
BF13-382	116.4	174-S-1	G	-0.7	
BF13-387	118.0	122-S-5	G	+4.3	
BF13-387	118.0	122-S-6	G	+5.3	
BF13-387	118.0	122-S-7	G	+2.2	
DDH BF19					
BF19-39	11.9	207-S-11	S	+3.6	
DDH BF20					
BF20-155	47.2	173-S-10	P	-19.3	Framboidal
BF20-408.5	124.5	170-S-12	G	+6.0	
BF20-416.5	127.7	207-S-10	S	+9.0	
BF20-418.8	127.7	170-S-9	G	+2.0	
BF20-420	128.0	170-S-3	G	+11.9	
BF20-420.8	128.3	171-S-12	G	+6.8	
BF20-423	128.9	207-S-6	S	+10.9	
BF20-424	129.2	172-S-5	S	+9.8	
BF20-424	129.2	172-S-6	G	+9.7	
BF20-424.4	129.4	207-S-7	S	+6.2	
BF20-484	147.5	170-S-2	P	+27.4	Adjacent to a sill
DDH BF21					
BF21-73	22.3	170-S-10	G	+5.0	
BF21-73	22.3	170-S-11	G	+3.9	
BF21-73	22.3	208-S-10	S	+14.4	
BF21-81	24.7	164-S-7	G	+11.8	
BF21-81.5	24.8	123-S-4	G	+11.2	
BF21-81.5	24.8	123-S-5	G	+12.2	
BF21-81.5	24.8	208-S-8	S	+9.6	
BF21-87.2	24.8	208-S-9	S	+10.8	
BF21-87.2	26.6	207-S-8	S	+10.9	
BF21-119	26.6	207-S-9	G	+6.2	
BF21-127.2	36.3	208-S-7	S	+5.7	
BF21-130.6	38.8	208-S-6	P	-22.4	
	39.8	171-S-2	G	+7.3	
DDH BF23					
BF23-391	119.2	175-S-8	P	-21.0	Diagenetic pyrite
BF23-400	121.9	215-S-10	P	-21.4	
BF23-416.5	126.9	175-S-7	G	+0.4	
BF23-419	127.7	179-S-5	P	-4.7	
BF23-419	127.7	204-S-6	S	+10.0	
BF23-420	128.0	171-S-12	G	+5.4	
BF23-420	128.0	172-S-4	G	-5.1	
BF23-420	128.0	173-S-11	G	-2.7	
BF23-421.5	128.5	164-S-2	G	+8.6	
BF23-421.5	128.5	204-S-9	S	+5.3	
BF23-422.5	128.8	208-S-2	S	+4.9	
BF23-435	132.6	170-S-8	G	+7.5	
BF23-435	132.6	208-S-1	P	-13.4	
BF23-435	132.6	207-S-12	S	+9.6	
BF23-436	132.9	173-S-12	S	+8.5	
BF23-436	132.9	172-S-7	G	+8.2	
BF23-438	133.5	208-S-3	S	+10.0	
BF23-502	153.0	179-S-8	P	-11.5	Diagenetic pyrite

DDH BF26				
BF26-521	158.8	170-S-7	G	+10.7
BF26-527	160.6	174-S-5	G	+10.3
BF26-543	165.5	208-S-4	S	+6.0
DDH BF29				
BF29-413	125.9	171-S-3	G	-2.6
BF29-413.5	126.0	175-S-3	S	+6.4
BF29-438	133.5	172-S-8	G	+5.9
BF29-446.6	136.1	174-S-2	G	-1.2
BF29-446.6	136.1	174-S-2	S	-7.2
BF29-446.8	136.2	174-S-6	G	-2.3
BF29-446.8	136.2	174-S-7	G	+8.4
BF29-446.8	136.2	174-S-8	S	+11.4
BF29-446.8	136.2	174-S-9	S	-3.0
DDH BF29				
BF29-453.6	138.3	164-S-3	G	+11.4
BF29-482.3	147	164-S-1	G	+11.2
BF29-487.5	148.6	123-S-2	G	+12.0
BF29-487.5	148.6	123-S-3	G	+11.1
BF29-491	146.6	175-S-9	S	+7.4
BF29-491	146.6	175-S-10	G	+6.0
BF29-491	146.6	175-S-11	G	+7.4
BF29-491.7	149.9	186-S-6	G	+11.2
BF29-491.7	149.9	186-S-7	S	+12.0
BF29-492.3	150.1	171-S-1	G	+10.7
BF29-492.3	150.1	204-S-8	S	+7.6
BF29-492.3	150.1	204-S-9	P	-24.0
DDH BF50				
BF50-556	169.5	208-S-5	S	-2.0
BF50-624	190.2	207-S-1	S	-6.5
DDH BF54				
BF54-170.3	51.9	122-S-8	G	+10.9
BF54-170.3	51.9	122-S-9	G	+7.2
BF54-171	52.1	174-S-10	G	+3.0
BF54-171	52.1	174-S-11	G	+7.2
BF54-172.5	52.6	175-S-1	G	12.5