Models for the generation of metalliferous hydrothermal systems within sedimentary rocks, and their applicability to the Irish Carboniferous Zn-Pb deposits.

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Abstract

The applicability of various genetic models to the Irish Carboniferous Zn-Pb deposits is evaluated in the context of the geological history of the central Irish ore district, the theory of metal leaching from rocks, and the characteristics of modern hydrothermal systems. The conclusion is that the local environment of ore deposition has produced deposit characteristics that are more typical of the Sedex class in some cases, but more characteristic of the MVT class in other cases. In terms of their geological setting the Irish deposits are more closely comparable to the Sedex class of deposits. It is proposed that the ore solutions for the Irish Carboniferous Zn-Pb deposits were saline formation waters of Old Red Sandstone lithologies that had been deposited within fault-controlled troughs of the Central Midland Basin. Hydraulic sealing and thermal insulation by about 500m of semi-compacted Lower Carboniferous shale and argillaceous limestone caused these brines to become geopressured and heated to over 200°C in an environment of high heat flow related to extensional tectonism and incipient magmatic activity. The ore metals were leached from the clay minerals and iron oxide pigments of the Old Red Sandstone lithologies, and were expelled to the surface when and where the geopressured aquifers were ruptured by faulting.

Introduction

Among the ore deposit types typically hosted by sedimentary rocks are the two most important classes of Zn-Pb deposits: (a) the "Sedex", "sedimentary-exhalative", "shale-hosted" or "sediment-hosted" class of stratiform Zn-Pb deposits, and (b) the "Mississippi Valley-type" (MVT) or "carbonate-hosted" class of stratabound Zn-Pb deposits.

As noted below, both the Sedex and MVT classes of ore deposits appear to have formed from hydrothermal solutions with essentially the same chemical characteristics at temperatures of up to 250°C. Both classes of ore deposits are spatially related to sedimentary basins, and although it has been suggested that the genesis of these deposits may be related to volcanic activity, the volume of contemporaneous igneous rocks spatially associated with the deposits, even on a regional scale, is generally insignificant compared to the volume of associated sedimentary rocks. The direct derivation of the ore solutions from a magmatic source, or the derivation of the bulk of the ore metals by hydrothermal leaching of the igneous rocks themselves, would therefore seem highly unlikely in the sense of a generally applicable model. If this is the case, then the ore metals must have been derived from the spatially associated sedimentary rocks, and/or the basement on which these sedimentary rocks rest.

One of the major problems in formulating genetic models for the Sedex and MVT classes of ore deposits is to identify those processes which generate Zn-Pb metalliferous solutions at temperatures of 100-250°C within sedimentary successions or within crystalline rocks of their basement, in the absence of any large magmatic body. This article focusses on this problem and discusses it in the context of the Irish Carboniferous Zn-Pb deposits.

General features of sediment-hosted Zn-Pb deposits

Chemistry and mineralogy

Considered in terms of their chemical characteristics alone, Sedex and MVT deposits have many similarities. The main ore minerals in both cases are sphalerite and galena, and associated minerals include iron sulphides, barite and various carbonates. Copper-bearing minerals are usually rare to absent, and for the great majority of deposits the copper content is economically insignificant. The aggregate Zn:Pb ratio of ore deposits has the same range for both classes, and, insofar as available data allow comparison, fluid inclusions from deposits of both classes show the same range of salinities. These similarities in their general chemical characteristics indicate that deposits of both classes were formed from hydrothermal solutions of corresponding similar chemical compositions. In general terms, these hydrothermal solutions can be described as chloride-rich brines with salinities usually in the range of 10-20 wt.% NaCl equivalent (2M-4M NaCl), that contain zinc and lead, variable amounts of iron and barium, but little or no copper.

The two classes, however, do appear to have some distinctive mineralogical and chemical characteristics. For example, although pyrite is usually the main iron sulphide associated with ore deposits of both classes, pyrrhotite is common only in deposits of the Sedex class, whereas marcasite is more common in deposits of the MVT class. Similarly, silica (usually as chert) is commonly associated with deposits of the Sedex class, but rarely with the MVT class.

Temperature of formation

There may also be some difference in the most common temperatures of the ore forming solutions. Fluid inclusion filling temperatures for MVT deposits are most commonly in the range 100-150°C (Roedder, 1976), whereas the very sparse fluid inclusion and oxygen isotope data for the Sedex class indicates temperatures of up to 250°C or more (e.g. Gustafson and Williams, 1981; Boast et al., 1981; Samson and Russell, 1983; Nesbitt et al., 1984; Gardner and Hutcheon, 1985). However, perhaps it would be premature at the present time to assume that hydrothermal solutions responsible for deposits of the Sedex class were generally of significantly higher temperature than those responsible for deposits of the MVT class, noting that the sulphides of some MVT deposits also have filling temperatures of over 200°C (e.g. see Akande and Zentilli, 1984).

Physical characteristics

The major differences between the two classes are in their physical characteristics, such as deposit morphology, ore textures, and range of host-rock lithologies. These physical differences, as well as the chemical and/or mineralogical differences noted above, are due to the different environments of ore deposition for the two classes. Sedex class deposits were formed on the sea floor around hydrothermal vents as sulphidic muds in a variety of sedimentary environments, ranging from carbonaceous cherts of starved euxinic basins, through turbidites and greywackes of slope facies, to shallow marine carbonates and evaporites (Large, 1980, 1981 and 1983). On the other hand, deposits of the MVT class, which occur most commonly in dolomites but also in limestones (Sangster, 1976), represent open-space filling and replacement by minerals deposited from hydrothermal solutions within porous aquifers in the subsurface.

The rates, mechanisms and modes of mineral precipitation and accumulation which determine the physical and, to some extent, the mineralogical characteristics of the ore deposit, are controlled by the physical and chemical nature of the environment of ore deposition. The sea floor environment is, physically and chemically, a much more open system than a subsurface aquifer, whose open fractures and cavities may be interconnected only by the intergranular porosity. Therefore, exchange of heat and mass between the hydrothermal solution and the ambient environment can take place in greater amounts and at faster rates on the sea floor than in the subsurface. Thus, minerals like quartz or chalcedony, which require a significant decrease in temperature to precipitate from solution, are more likely to occur in Sedex deposits than MVT deposits. Similarly, the bacterial reduction of sulphate to sulphide, which requires a nutrient supply, is likely to be more efficient at the sea floor than in the subsurface. Minerals precipitated by higher rates of heat and chemical exchange at the sea floor would tend to be finer-grained than those precipitated by much lower exchange rates in the subsurface. Minerals precipitated in the ocean water column can only accumulate as concordant sediments, whereas those precipitated in the subsurface can only fill the spaces that are available. The list could be continued to account for most of the major differences between the Sedex and MVT classes of ore deposits.

Criteria such as these, on which the distinction between Sedex and MVT deposits are most commonly based, are therefore not directly related to the origins of the ore solutions, but rather to the site of ore deposition. As noted

above, insofar as can be deduced, the ore solutions for Sedex class deposits were grossly similar to those that formed MVT class deposits. The chemical composition of a natural hydrothermal solution is determined by the temperature and composite mineralogy (i.e. lithology) of the reservoir zones in which the hydrothermal solutions are generated (Ellis and Mahon, 1964; 1967). It is therefore more than likely that the ore solutions for both the Sedex and MVT classes of ore deposits were generated under similar conditions. If this is the case, then the different sites and environments of ore deposition for the two classes may be due to factors such as the timing of, and causes for, the migration of the ore solutions from the site of their generation.

Geological setting

The geological characteristics of the Sedex class of Zn-Pb deposits have been summarized by Large (1980, 1981 and 1983). Deposits of this class typically occur within tectonically controlled epicratonic or intracratonic marine basins, whose lateral dimensions usually exceed 100km. The deposits themselves are usually confined to fault-controlled third-order basins with dimensions between several hundred metres and several kilometres (Large, 1983). Faults controlling the third-order basins were active during sedimentation, and acted as channelways to focus the discharge of the ore solutions. Sporadic volcanism is often associated with the first-order basins, which suggests that Sedex deposits were formed in geotectonic provinces of anomalously high heat flow.

Notwithstanding the fact that the thickness of sedimentary rocks immediately below some deposits may be as little as a few tens of metres (e.g. Grundmann, 1977; Evans, 1977), deposits of the MVT class are also typically spatially related to sedimentary basins. However, in contrast to the intra-basinal position of Sedex class deposits, MVT class deposits, as exemplified by those of the classic areas in central USA (Fig. 1), appear to be preferentially located near the margins of the basins (Anderson and Macqueen, 1982). MVT deposits are epigenetic and were emplaced after lithification of the host rocks in pre-existing pore spaces or cavities produced by the development of breccias or karst. As discussed by Sangster (this vol.), one of the greatest problems related to the genesis of this class of ore deposits is a knowledge of the timing of the ore-forming events. Without this knowledge, the genesis of MVT deposits cannot be unequivocally related to the development or evolution of the sedimentary basins with which the deposits are spatially associated.

Genetic models
Sedex class deposits

Perhaps the most popular current opinion interprets the ore solutions for Sedex class deposits to have been formation waters derived from the sedimentary sequence underlying the deposit (Walker et al., 1977; Badham, 1981; Carne and Cathro, 1982; Lydon, 1983; Sawkins, 1984). Lydon (1983) argued that the ore solutions were connate waters of a marine sedimentary sequence undergoing a first cycle burial and compaction that had evolved into metalliferous brines due to a specific burial history. As illustrated in Figure 2 he suggested that the optimum conditions for the generation of large volumes of saline metalliferous formation waters occur where a dominantly arenaceous sequence is overlain by a dominantly argillaceous sequence,
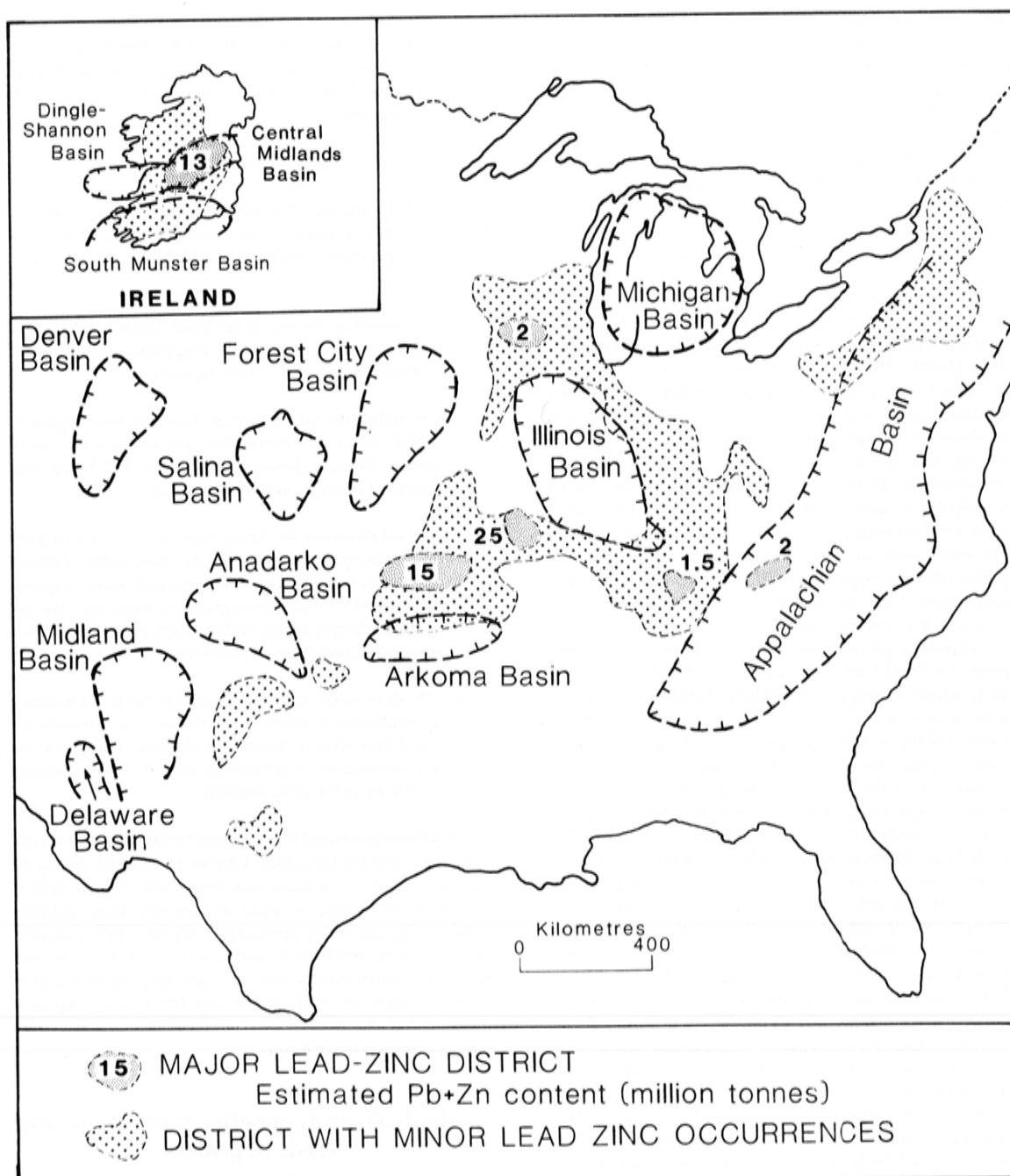
Figure 1. Simplified distribution of Mississippi Valley-type ore districts of central U.S.A. showing their spatial relation to sedimentary basins. Based on Figure 1 of Anderson and Macqueen (1982). Inset: Ireland at the same scale.

and when burial and compaction take place in a region of anomalously high heat flow. The importance of the upper argillaceous sequence is that:

(1) It acts as a thermal insulator which promotes the increase of temperature in the hydrothermal reservoir zones in the lower arenaceous sequence.

(2) It acts as a barrier of low permeability which retards the dewatering of the lower arenaceous sequence, thereby preserving high porosities and promoting geopressuring of the hydrothermal reservoir zones.

(3) It may act as a semi-permeable barrier and promote ion filtration, thereby increasing the salinity of the formation waters in the hydrothermal reservoirs.

Discharge of the ore solutions to the surface of the sedimentary pile takes place along faults, which rupture the geopressured hydrothermal reservoirs. The lateral continuity of individual layers within the concordant laminated ores, typical of most Sedex class deposits, suggests that ore precipitation took place from a brine pool that had collected within the third-order basin. Ore mineral precipitation was due to cooling of the ore solution and/or by the biogenic

557

reduction of sulphate to sulphide within the water column. In most cases it appears that the ore-forming event involved several pulses of hydrothermal discharge over a relatively short period, because the stratiform ore is confined to one stratigraphic horizon. However, in some cases where the ore deposit consists of a series of stratigraphically "stacked" individual lenses, such as in the case of the Mt. Isa deposit, it appears as if the pulses of hydrothermal discharge took place over a protracted period of time.

MVT class deposits

The observation that areas of MVT class deposits are preferentially located at the edges of sedimentary basins has led to the widespread acceptance of the basinal compaction model (Noble, 1963; Beales and Jackson, 1966). Details of this model have recently been summarized by Anderson and Macqueen (1982). In essence, this model regards the ore fluids to be saline formational waters that migrate laterally and upwards along stratiform aquifers or fault zones from the deeper parts of a sedimentary basin during its subsidence and compaction. Ore deposition occurs where a formational brine carrying metal is cooled or mixed with other solutions carrying sulphide sulphur. Stratigraphic evidence suggests that ore deposition usually takes place within a few hundred metres to a kilometre of the surface (Anderson and Macqueen, 1982).

A mathematical analysis of this model by Cathles and Smith (1983) led them to conclude that in order for formational waters to migrate to shallow depths and maintain temperatures in the 100-150°C range, dewatering of the basinal sediments must be episodic. A steady dewatering of the basinal sediments would not result in any significant perturbation of the normal geothermal gradient, because the slowly migrating formational waters would be cooled by normal conductive heat loss. Cathles and Smith (1983) pointed out that dewatering would be episodic if the compaction history of the basin involved the development of geopressured aquifers, from which formational waters were released only periodically, or rupture of the aquifer, such as when pore fluid pressure had increased to lithostatic pressure. These authors also pointed out that in order to form an ore deposit, formational water migration must be focussed along a few major channelways, and in order to allow for successive episodes of mineral deposition from successive dewatering pulses, the basin margins must be tectonically stable.

An alternative model to compaction-driven flow of basinal brines to the margins of sedimentary basins has recently been proposed by Garven and Freeze (1984a; 1984b) and Garven (1985). These authors suggested that the uplift of the central part of a basin to topographic elevations higher than those at the margins of the basin would create an hydraulic head that would give rise to a gravity- or topography-driven regional groundwater flow system. They calculated that the flow of formation brines from the compacted basinal sediments would be concentrated along stratal aquifers of high permeability. Even though cooling and dilution of the brines would occur *en route,* the temperature, metal content and quantity of brine arriving at the edge of the basin could be sufficient to form MVT deposits. A wedge-shaped basin containing 3km of compacted sediment could supply the margin of the basin 300km distant with brines at temperatures up to 95°C at depths of less than 1km. Higher temperatures would require a thicker and a laterally more extensive wedge of basinal sediments. Garven (1985) suggested that the ore solutions for the Pine Point ore

field were basinal brines derived from Upper Palaeozoic sediments of the Western Canada Basin that migrated in post-Cretaceous time due to the emergence of the Rocky Mountains, and that the deposits were formed over a 0.5 to 5.0Ma time span.

Discussion

The genetic model proposed by Lydon (1983) for the Sedex class differs only in a few aspects from that discussed by Cathles and Smith (1983) for the MVT class. Differences include:

(1) Ore solutions for the Sedex class deposits may have generally been at a higher temperature than those responsible for MVT class deposits.

(2) Ore solutions for the Sedex class deposits migrated mainly in a cross-stratal direction along active fault planes, whereas those responsible for MVT deposits migrated mainly along stratal aquifers.

(3) Ore solutions for the Sedex class deposits discharged and deposited minerals at the submarine surface *within* the sedimentary basin, whereas those responsible for MVT deposits migrated to shallower depths at the *periphery* of the sedimentary basin and deposited ore minerals in the subsurface.

(4) Ore deposition at a single site may have been more a continuous or fluctuating process over a relatively short time span in Sedex class deposits compared to a discontinuous or episodic process over a prolonged period in MVT class deposits.

These differences could be explained by the different levels of tectonic activity associated with the geological setting of the two classes — sedimentary basins which host Sedex class deposits formed in areas of relatively high tectonic activity, whereas those associated with the MVT deposits formed in tectonically more stable areas. Nevertheless, the important conclusion is that the currently most popular genetic models for both Sedex and MVT class deposits envisage that the ore solutions were formation brines derived from sedimentary basins.

Geological and genetic context of the Irish deposits

Deposit characteristics

The chemical and mineralogical characteristics of the Irish Carboniferous Zn-Pb deposits are typical of both the Sedex and MVT classes of deposits. The main ore minerals are sphalerite and galena, and the dominant gangue minerals include pyrite, barite and various carbonates. Collectively, the physical characteristics of the Irish deposits appear to span the spectrum of the two major classes of Zn-Pb deposits. The stratiform B Zone and Upper G Zone of the Silvermines deposit would clearly be classified as of the Sedex class, but an unusually high proportion of the sulphide in the deposit is contained in the discordant footwall feeder zones (Taylor and Andrew, 1979; Taylor, 1984). At the Tynagh deposit, although exhalative activity produced a haematite-chert iron formation, most of the ore sulphide was deposited within fractures and cavities in the substrate

(Boast et al., 1981). Ore deposition at the Navan deposit is regarded as involving the superposition of early diagenetic mineralization on synsedimentary sulphides (Andrew and Ashton, 1982, 1985; Ashton et al., this vol.). Some of the smaller deposits may also be appropriately described as being "syndiagenetic", such as the Ballinalack deposit (Jones and Bradfer, 1982) and the Tatestown deposit (Andrew, this vol.), whereas others may be more comfortably compared to the MVT class, such as the Harberton Bridge deposit (Emo, this vol.).

Geological setting

Most deposits are thought to have formed during the mid-Dinantian (Sevastopulo, 1981b). During the early part of the Dinantian, sedimentation in central Ireland was dominated by carbonates, shales and sandstones of a generally shallow water transgressive marine sequence, forming a platform-type environment immediately to the north of the rapidly subsiding South Munster Basin (Sevastopulo, 1981a). This generally northwards transgression was intermittent, if not actually interspersed with withdrawals, suggesting some degree of tectonic control to sedimentation (Philcox, 1984). Faulting in the area to the north of the South Munster Basin appears to have controlled the development of two smaller sedimentary basins, the Dingle-Shannon Basin and the Central Midlands Basin (see Inset, Fig. 1).

Subsidence of the South Munster Basin appears to have been initiated in the Mid-Devonian and continued through to at least the Namurian (Gardiner and MacCarthy, 1981). Most of the Basin fill consists of Mid-Devonian to Courceyan Old Red Sandstone lithologies (Gardiner and Horne, 1972), which attain thickness of 3km over much of the Basin (MacDermot and Sevastopulo, 1972) and over 6km in its deeper parts (Holland, 1981).

The Dingle-Shannon Basin was initiated in the Early Devonian, and accumulated over 3km of dominantly continental sediments before stabilizing by Late Devonian, when it became the site of marine shelf sedimentation (Gardiner and MacCarthy, 1981). The Basin was reactivated during the Namurian to form the Shannon Trough (Hodson and Lewarne, 1961; Gardiner and MacCarthy, 1981). The development of the Dingle-Shannon Basin seems to have been dominated by vertical tectonic movement, particularly during the Carboniferous reactivation, and it seems likely that it, as well as the South Munster Basin, developed as a rift valley in response to crustal extension (Gardiner and MacCarthy, 1981).

As discussed below and illustrated in Figure 3, the Central Midlands Basin can be defined by isopachs of the argillaceous sequence (mainly argillaceous bioclastic limestones and shales) occurring between the underlying arenaceous lithologies of the Basal Carboniferous and Old Red Sandstone and the overlying Waulsortian "reef" micrites or lithostratigraphically equivalent limestones and dolomites. The Central Midlands Basin developed in an area of active extensional tectonics (Russell, 1976; 1983; Andrew, 1985). Sporadic volcanism occurred in Ireland throughout the Devonian (Holland, 1982) and Lower Carboniferous (Sevastopulo, 1982a), but volcanic centres within the Central Midland Basin were manifest only during the Chadian-Arundian (Sevastopulo, 1982a). The thickness of the Devono-Carboniferous arenaceous sequence within the Central Midlands Basin is not known, but certainly attains thicknesses greater than those indicated by the isopach map of Sevastopulo (1972), which are based on surface sections

exposed in the Slieve Phelim-Slieve Aughty palaeohigh. Over 350m of the Devono-Carboniferous arenaceous sequence was intersected by the Trim well (Sheridan, 1972) without reaching its base. Brown and Williams (1985). interpreted gravity and magnetic data as indicating NW-trending horst and graben structures with a relief of up to 2.5km in the sub-Carboniferous rocks, but were unable to discriminate between Devonian-Carboniferous and older (Caledonian) sediments. It therefore remains a matter of conjecture as to whether development of the central Midlands Basin, like the contiguous Dingle-Shannon Basin, was initiated during the Devonian and whether it also contains several kilometres of Devonian red bed arenaceous sediments within fault-controlled troughs. However, the conjecture would seem quite plausible considering that the two basins were controlled by the same set of reactivated Caledonian faults and had similar post-Chadian subsidence histories (Sevastopulo, 1982a). The major Irish Carboniferous Zn-Pb deposits appear to be situated around the margins of the Central Midlands Basin (Fig. 3).
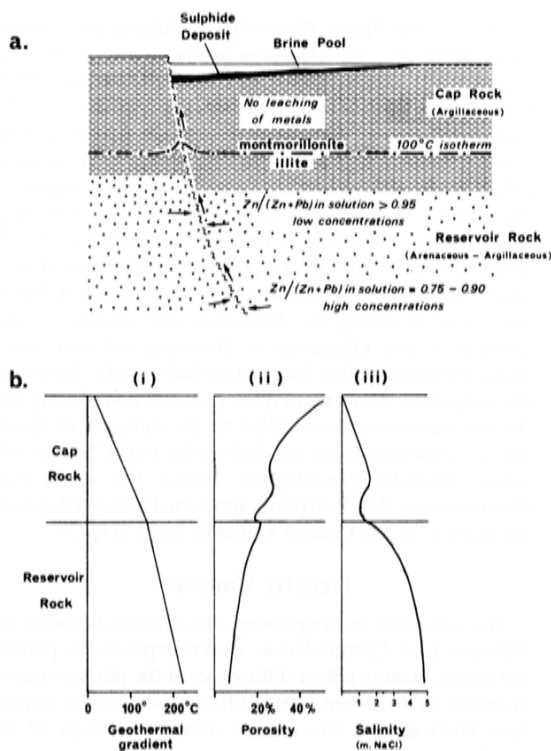
Genetic Context

The variations in morphology and textures between the different Irish Carboniferous Zn-Pb deposits, as pointed out above, mainly reflect differences in the physical and/or chemical environment of the different sites of ore deposition. Discussion of this topic is outside the scope of this article.

The timing of ore deposition and geographical distribution of the deposits is directly related to the factors that controlled the generation and migration of the ore-forming solutions. In view of the similarities between the Irish Carboniferous Zn-Pb deposits and deposits of the Sedex and MVT classes in general, it might be expected that some variant of the basinal formation water model would also be applicable to the Irish deposits. However, published models for the generation of the ore solutions responsible for the Irish Carboniferous Zn-Pb deposits prefer deep convection cells (Russell, 1976, 1978, 1983; Russell et al., 1981). As discussed below, there are objections to the deep convection cell model, and therefore a re-examination of the applicability of various models for the generation of the ore solutions for the Irish Carboniferous Zn-Pb deposits is warranted. The three types of model considered are:

a. The MVT class model.

b. The Sedex class model.

c. The deep convection cell model.

a. MVT class model

In applying the MVT class model to the Irish Zn-Pb deposits the scale of the geographical area to which the model applies is an important consideration. Figure 1 compares Ireland to the MVT districts of the central USA. This shows that the size of the areas containing the major Zn-Pb deposits are within the same order of magnitude in all cases. Although the quantity of ore metal contained in each district varies over an order of magnitude, the disparity is reduced by considering the quantity of metal per unit area of each district, leaving only the lead-rich district of SE Missouri as unusually metal rich. Thus, in terms of district size and quantity of ore metal, the Irish deposits are permissibly comparable to the MVT deposits of the central USA.

a.

Sulphide
Deposit

Brine Pool

Cap Rock
(Argillaceous)

*No leaching
of metals*

montmorillonite
illite

100°C *isotherm*

*Zn/(Zn+Pb) in solution > 0.95
low concentrations*

Reservoir Rock
(Arenaceous – Argillaceous)

*Zn/(Zn+Pb) in solution = 0.75 – 0.90
high concentrations*

b.

(i)   (ii)   (iii)

Cap
Rock

Reservoir
Rock

0   100° 200°C
Geothermal
gradient

20% 40%
Porosity

1 2 3 4 5
Salinity
(m. NaCl)

Figure 2. Diagram illustrating the optimum conditions for the generation of metalliferous pore waters in a sedimentary sequence undergoing burial and compaction (after Lydon, 1983).
(a) Geological relations, illustrating that a high geothermal gradient promotes temperature-dependent mineralogical transformations at relatively shallow depth which allows leaching of ore metals into pore waters. The $Zn/(Zn+Pb)$ ratio of saturated solutions will systematically decrease, but metal concentrations increase, in response to increasing temperature and increasing salinity.
(b) Vertical profiles through the section illustrated in 2(a), showing the variation with depth of the parameters illustrated. See text for further explanation.

However, in terms of the basinal compaction genetic model, as considered by Cathles and Smith (1983), a direct comparison is less compatible. The MVT deposits of central USA occur at the tectonically stable margins of basins whose average area exceeds the size of Ireland itself. For the Irish ore district to occupy a comparable geological position the only viable source basins would appear to be the South Munster Basin, the Dingle-Shannon Basin as described by Gardiner and MacCarthy (1981), and/or the Central Midlands Basin (Fig. 3). None of the Irish basins however, are comparable to the sedimentary basins of the central USA either in size or geological history. The three Irish basins were small fault-controlled basins with relatively short depositional histories, and appear to have developed semi-independently of each other. The South

Munster Basin was delimited by the positive topographic feature of the tectonically active South Irish Lineament, and the Dingle-Shannon Basin appears to have been separated from the Central Midlands Basin by the NW-trending Slieve Phelim-Slieve Aughty palaeohigh. The evolution and dewatering of the three Irish basins must therefore be considered separately, and not in terms of a single composite basin.

It is conceivable that dewatering of the 3 to 6km thickness of sediments of the South Munster Basin could have supplied formational waters of the requisite temperature, composition and perhaps quantity to have formed the Irish Zn-Pb deposits. However, it is improbable that the fluids could have migrated 100-200km laterally in a northerly direction and maintained a focussed flow. This migration path would have been at a high angle to the structural grain of the basement, the lithofacies boundaries within the Devono-Carboniferous sedimentary cover, and palaeotopographical features, all of which have a SE-NW to E-W trend (Holland, 1981; Gardiner and MacCarthy, 1981; Sevastopulo, 1981a; Philcox, 1984). It would seem to be necessary to invoke the existence of cryptic N-S basement sutures, as postulated by Russell (1968), in order to accommodate the focussed supply of ore solutions from the South Munster Basin to the central Irish ore district.

It is also conceivable that the age and thickness of the sediment-fill of the Dingle-Shannon Basin would have allowed the expulsion of formation waters by compaction during the Early Carboniferous to form the Irish Zn-Pb deposits. Migration of fluids to the central Ireland ore district would have been parallel to the structural elements within the basement and cover sediments, which obviates the major objection to a South Munster Basin source for the ore solutions. However, argument in favour of a Dingle-Shannon source for the ore solutions is weakened by consideration of a more local source in the adjacent, geologically similar, Central Midlands Basin, around which the deposits of the central Irish ore district are situated.

The MVT class model as proposed by Garven and Freeze (1984) can also be considered improbable for the Irish deposits for the same reasons as for the Cathles and Smith (1983) model. In addition, the uplift of the sediments of the South Munster Basin to elevations above those of Lower Carboniferous sediments in central Ireland did not take place until after the major ore deposits had formed. The lack of differential uplift and the small lateral extents of the Dingle-Shannon Basin and the Central Midlands Basin also negate the applicability of the Garven and Freeze (1984) model in this context.

If long distance lateral migration of the ore solutions for the Irish deposits can be ruled out, the alternative is the local derivation of the ore solutions from either a relatively shallow or a relatively deep source. The depth of the source region for the ore metals is one of the fundamental differences between the Sedex class model and the deep convection cell model.

b. Sedex class model

Arguments in favour of the applicability of a generalized Sedex class genetic model to the Irish deposits include:

(1) The spatial association of the Irish ore district with a sedimentary basin (Central Midlands Basin) that is comparable in size to the second order basins of Large (1980, 1981, 1983).
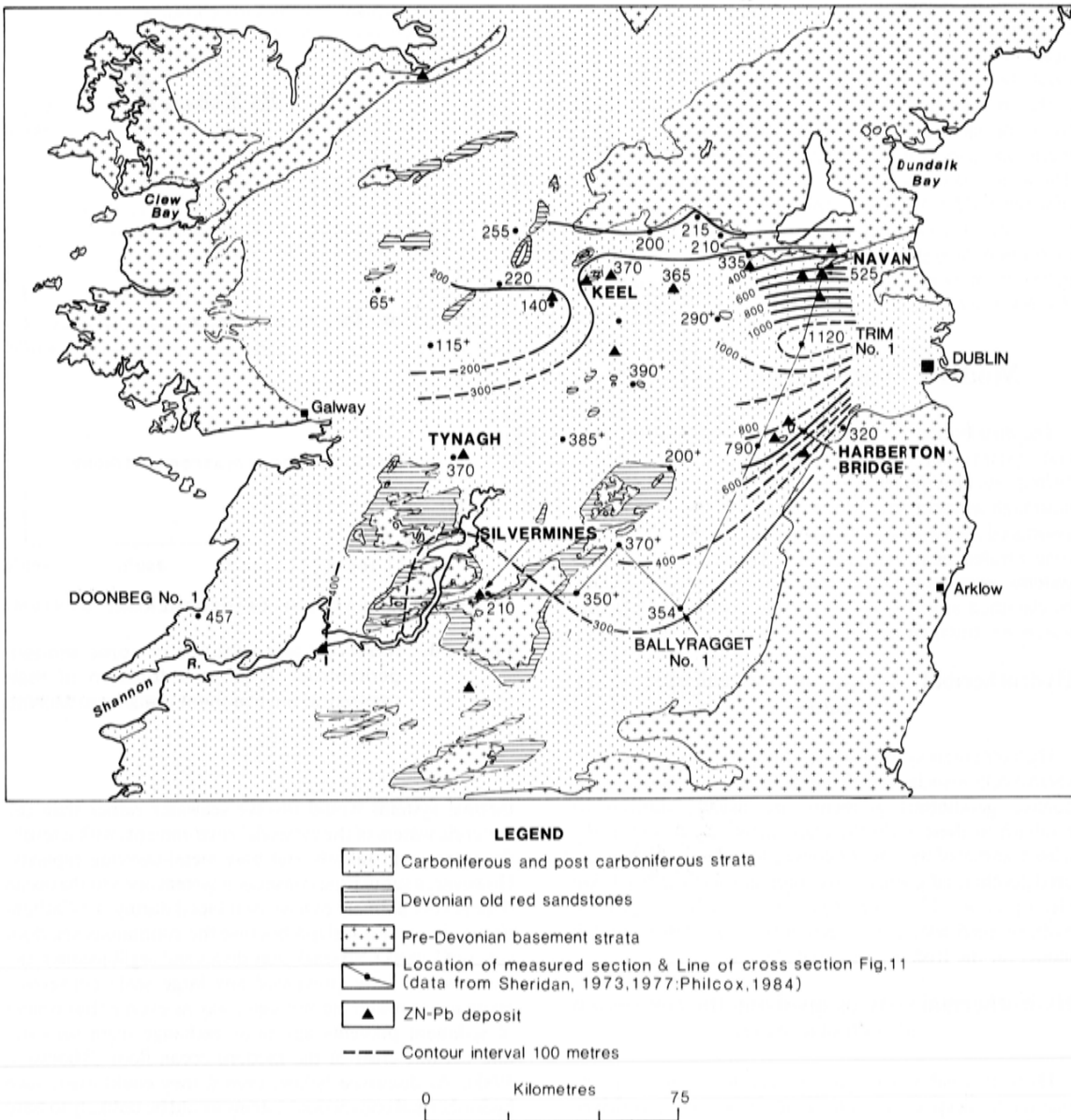
Figure 3. Map of central Ireland showing simplified geology, distribution of major Zn-Pb ore deposits, locations of measured drill hole sections (from Sheridan, 1973; 1977; Philcox, 1984), and isopachs of shale and argillaceous limestone sequence occurring between Devono-Carboniferous arenaceous litholgies and Waulsortian reef facies. Line joining drill hole locations between Silvermines and Navan refers to line of section shown in Figure 11.

(2) The subsidence of the Central Midlands Basin was probably tectonically controlled and furthermore took place in a regime of anomalously high heat flow as evidenced by sporadic or incipient volcanic activity.

(3) Most ore deposits are associated with synsedimentary faults that are presumed to have focussed the cross-stratal flow of the ore solutions.

(4) The ore-forming events, at least in the case of Silvermines and Tynagh, included a catastrophic discharge of ore solutions.

Russell (1976, 1983) considered a basin formation water model for the Irish Carboniferous Zn-Pb deposits, but rejected it mainly on the grounds that the assumed geothermal gradient and the maximum thickness of compacting sediments in adjacent basins were insufficient to account for ore solution temperatures in excess of 200°C indicated for some of the deposits.

c. Deep convection cell model

The deep convection cell model envisages the convection of seawater to depths of 15km, primarily along major fault channels associated with the incipient rifting of central and

561

southern Ireland during the Devonian and Carboniferous. It is envisaged that the convection cell was driven by the heat content of the rocks, whose geothermal gradient averaged about 35°C/km, and that the ore solutions were generated by the hydrothermal solutions scavenging metals from the metamorphosed Caledonian geosynclinal sediments and underlying crystalline basement (Russell, 1976). The main objections to the deep convection cell model are that the model appears to this author to be at variance with some observations on the characteristics of modern hydrothermal systems and constraints on the leaching of metals from rocks. The background to these objections are discussed below.

Modern hydrothermal systems

The distribution and classification of modern hydrothermal systems has been summarized by Muffler (1976a, 1976b). As also illustrated by Figure 4, he points out that most high temperature (>200°C) hydrothermal systems are associated with volcanically active zones, which in turn are concentrated near plate margins. Modern hydrothermal systems away from volcanically active zones can usually be classified as either convective circulations of meteoric waters or stratal aquifers.

Hydrothermal systems of volcanically active zones

Hydrothermal systems of this category are usually convective cells associated with young igneous intrusions. Conductive geothermal gradients are usually difficult to establish in these hydrothermally active areas due to the mass transfer of heat by the convection systems, but measured geothermal gradients are often in excess of 200°C/km (Jessop et al., 1975). Clearly, this is not the category of hydrothermal system envisaged by the deep convection cell model for the Irish deposits (see above).

Hydrothermal systems involving the convection of meteoric water

Hydrothermal systems in this category appear to be related to deep circulation along faults and are driven by the normal regional heat flow (Muffler, 1976b). Base temperatures of the hydrothermal systems are related to the regional heat flow, which in turn is usually related to the level of contemporaneous tectonic activity (see Fig. 4). For example, in the relatively tectonically inert area of the Appalachian Mountains of the eastern USA the hydrothermal systems attain surface temperatures of only 40°C, and there is no indication that their temperatures increase significantly with depth (Muffler, 1976b). In contrast, within the Basin and Range Province of the USA, which is characterized by active normal faulting and tectonic extension (Thomson and Burke, 1973) and a heat flow about twice that of the Appalachian region (Hose and Taylor, 1974), hydrothermal systems of a similar type attain temperatures of 150°C at depths of about 1.5km (Williams et al., 1976). The existence of this type of hydrothermal system gives some credence to the deeply circulating convection cell model for the Irish Carboniferous Zn-Pb deposits. However, the hydrothermal solutions of modern examples typically have low salinities and are not known to contain measurable concentrations of zinc or lead. It might be argued that in a submarine environment analogous hydro-
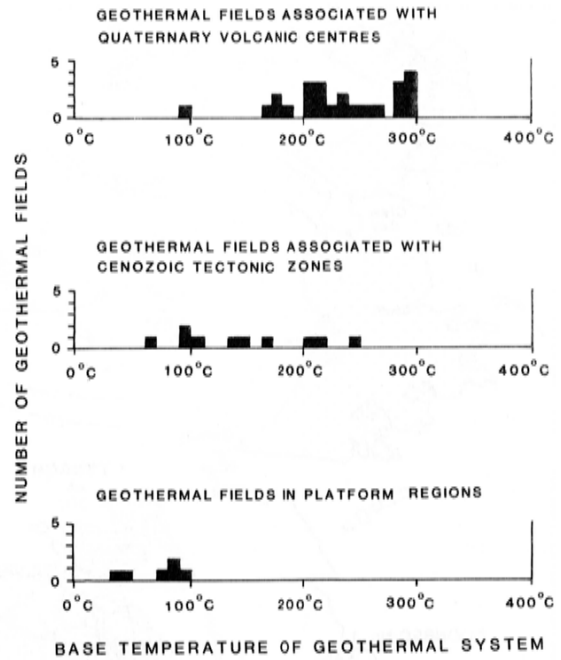

Figure 4. Reservoir temperatures of some modern geothermal fields as a function of their geological environment (data from McNitt, 1970).

thermal systems would involve seawater rather than the meteoric waters of the subaerial environment, with a resultant increase in salinity and base metal-carrying capacity. However, a submarine convection system open to the ocean floor is very unlikely to have developed during the Carboniferous in central Ireland because the continuous sea-floor cover of Lower Carboniferous shales and argillaceous limestone would have prevented any large scale convection involving seawater, in the same way as even a thin veneer of sediment prevents any mass exchange from seawater into oceanic crust of the modern ocean floor (Thomson, 1983). As discussed below, even if they could exist, such hydrothermal convection systems would be unlikely to have leached any significant zinc or lead from the metamorphosed sediments or crystalline rocks of the basement.

Stratal, hydrothermal systems

Muffler (1976) divides stratal hydrothermal systems into those that are hydrostatically pressured and those that are geopressured. The Pannonian Basin of Hungary is an example of the former. It consists of a tectonically active, sediment-filled, fault-controlled, Tertiary basin, with a geothermal gradient of 45°C to 70°C/km, and contains stratal hydrothermal aquifers to temperatures of 180°C within about 3km of the surface (Boldizsar and Korim, 1976; Ottlik et al., 1981). The prime examples of geopressured hydrothermal aquifers are found in the Gulf Coast Basin of the southern USA. The basin consists of up to 15km of sediments that are still undergoing compaction (Jones, 1970). Although near-surface geothermal gradient appear to be normal (20°C to 40°C/km), at depths of 1.5km or greater both pressures and temperatures may rise dramatically, with pore fluid pressures approaching lithostatic values and geothermal gradients of up to 100°C/km or

more (Jones, 1970; 1975). The geopressured aquifers occur beneath low-permeability shale, which acts both as a thermal insulator and as a barrier to the upward escape of the pore waters. Characteristically, the waters in these geopressured aquifers are not meteoric but consist both of connate water and water released from the dehydration of clay minerals.

Chemistry of modern hydrothermal systems

The most outstanding chemical characteristic of modern hydrothermal solutions is that their major cationic compositions, and to a large extent also their major anionic compositions, are determined by chemical equilibrium with rock-forming mineral assemblages of the hydrothermal reservoirs (Ellis and Mahon, 1964, 1967). This characteristic is so invariable, that the chemical compositions of hydrothermal solutions are routinely used as surprisingly accurate geothermometers to indicate reservoir temperatures (White, 1970).

The great majority of modern hydrothermal systems do not contain any significant quantities of dissolved metals. Modern hydrothermal systems that contain significant concentrations of dissolved zinc appear to be of one of two types:

1. Convection cells involving the circulation of seawater through basaltic rocks (e.g. black smoker vents of the East Pacific Rise, Red Sea brines). The hydrothermal solutions of this type also invariably contain significant copper but little lead.

2. Highly saline stratal aquifer systems in which there is no significant natural recharge and discharge of the hydrothermal reservoir and are therefore presumably geopressured (e.g. Salton Sea (Skinner et al., 1967; Helgeson, 1968), oil field brines of central Mississippi (Carpenter et al., 1974) and Alberta (Billings et al., 1969)). Systems of this type occur in relatively young sedimentary rocks, and the solutions usually also contain significant lead, but only subordinate concentrations of copper.

Thus, by simple analogy with modern hydrothermal systems, additional objections to the deep convection cell model can be raised. Except for some examples that flow through basalts, a characteristic of modern convective hydrothermal solutions is that concentrations of zinc and lead are below 1ppm. No surface discharge of any hydrothermal solutions from convection systems are regarded to have originated from depths as great as 15km. In the light of evidence from the modern ocean floor, the submarine recharge of large volumes of water through a blanket covering of argillaceous sediments (Fig. 7.8, Russell, 1973) is improbable.

The question as to why only some types of hydrothermal systems appear capable of leaching and mobilizing metals in significant concentrations and the factors that control the concentration of specific metals in the hydrothermal solutions are discussed below.

Leaching of metals from rocks

Most genetic models for hydrothermal ore deposits, including that by Russell (1976; 1983), assume that the ore solutions simply "scavenge" or "dissolve" the ore metals

from the rocks through which the hydrothermal solutions have flowed, but have paid little attention to the process of leaching itself.

Distribution of trace metals in rocks

Metals can be scavenged from rocks only by elution of those metals which have become loosely bound on the surfaces of compounds with high adsorption capacities or minerals with high cation exchange capacities (Kinniburgh and Jackson, 1981). Amongst the compounds of geological interest are hydrated metal oxides, particularly those of iron and manganese which commonly coat grains of other minerals such as quartz in the case of red sandstones (Zielinski et al., 1983). Some immature organic compounds may also be important. Minerals with a high cation exchange capacity are generally those with a disordered layer structure, of which montmorillonite is a prime example. These minerals can theoretically be leached of a high proportion of their trace metal content by exchange with suitable cations without rapid exhaustion of the leaching capacity of the solution, but the subject has not been studied in detail (Kinniburgh and Jackson, 1981).

In most lithologies, only a very small proportion of the total amount of zinc or lead occurs as loosely-bound adsorptions on the surfaces of mineral grains. The great proportion of these trace metals occur as diadochic substitutions for essential elements of the crystal structure of rock-forming minerals. For example, zinc most commonly substitutes for iron and manganese (Wedepohl, 1972) whereas lead most commonly substitutes for potassium (Wedepohl, 1974).

Mechanisms of leaching trace metals from rocks

As can be deduced from laboratory leaching experiments on rocks and minerals (e.g. Foster, 1973), solution leaching of metals that occur as diadochic substitutions can take place only during destruction of the host mineral by dissolution or during conversion of the host mineral into a "secondary alteration" mineral. This destruction of the host mineral in the presence of an aqueous solution can be considered to take place for one of two reasons:

(1) Chemical disequilibrium between the host mineral and the aqueous solution (mineral:solution disequilibrium).

(2) Instability of the host mineral or mineral assemblage at the given temperature and pressure with respect to another mineral or mineral assemblage (i.e. mineral:mineral disequilibrium as in thermal metamorphic reactions).

Leaching reactions that produce low concentrations of trace metals in the product solution

Natural hydrothermal solutions cannot achieve high concentrations of these trace metals in solution by a simple attack (mineral:solution disequilibrium) on the rocks through which they flow, because the solution reaches chemical equilibrium with the rock before it destroys sufficient quantities of primary minerals to give trace metal concentrations in solution above 1ppm (Lydon, 1983). This point is illustrated by Reactions 1 and 2 of Table 1, which shows some reactions involving potassium minerals and aqueous solutions due to mineral:solution disequilibrium. For simplicity in these order of magnitude calculations it is assumed that activity coefficients for all species are unity,

563

that the primary mineral in all cases contains 50ppm trace metal, and that no trace metal enters the product mineral phase. The water:rock (w/r) ratio may be defined as the weight of a given aliquot of solution divided by the weight of solid reactants with which it has chemically exchanged.

Reaction 1 describes the acid leaching of 1 mole of K-feldspar (278.32g) by an aqueous solution of pH 4, and exemplifies the case where the reactive component of the reactant solution is at a low concentration. Reaction 2 describes the albitization of K-feldspar by a 4M NaCl solution, and exemplifies the case where the reactive component of the reactant solution is at a high concentration. The same results are of course achieved by ignoring the concept of the 'excess solution" and considering the reactions as closed systems. In a closed system at 100°C, Reaction 2, for example, would stop after only a little more than 6% of the K-feldspar had reacted, because the solution would have achieved a Na^+/K^+ ratio in solution of $10^{1.8}$ and be in equilibrium with a K-feldspar-albite assemblage, but the concentration of trace metal in solution and the w/r ratio of the system would be the same as calculated in Table 1.

The same exercises can be repeated with the same result for any other chemical reaction due to mineral:solution disequilibrium involving common rock-forming minerals and a solution whose composition is within the range of natural hydrothermal solutions. It is of course possible to identify theoretical mineral:solution reactions to predict high concentrations of metal in the leachate. For example, using the same set of assumptions, the reverse of Reaction 2 (the conversion of albite to K-feldspar by a 4M KCl solution) would give a result of about 48ppm metal in solution. Applicability of this reaction to natural hydrothermal systems would require an extremely unusual circumstance, such as the selective dissolution of only the sylvite component of an evaporite sequence by fresh water to supply the reactant solution. There is a natural restraint to the range of major cationic ratios permissible in natural hydrothermal systems, because the range of common rock-forming mineral assemblages, with which all natural subsurface waters quickly equilibrate (Helgeson, 1970), is extremely limited. Therefore, the extent of chemical exchange between a given aliquot of solution and a given weight of rock due to mineral:solution disequilibrium is limited to that necessary to change the cation ratios buffered by one mineral assemblage to the ratios buffered by another mineral assemblage. It is suggested that this is one of the main reasons that most hydrothermal solutions do not contain significant concentrations of trace metals.

Leaching reactions that produce high concentrations of trace metals in the product solution

One of the few natural circumstances under which a mineral:solution disequilibrium can produce high concentrations of trace metals in solution is the case when hydration alone causes destruction of a primary mineral assemblage. The essential reactant in this case is the water itself, so in reactions of this type a solution will not lose its reactive capacity. The most important rock types susceptible to this type of alteration are basalt or ultramafic rocks. For example, Lydon (1981) calculated that by reaction with just 3.2% its weight of water, a basalt could be completely converted into a greenschist facies assemblage of albite-chlorite-epidote-actinolite. In a basaltic rock containing 50ppm leachable metal and with 20% porosity, the pore water could achieve concentrations of over 1500ppm trace

metal during such hydration reactions. It is suggested that it is because leaching of metals from a basalt can be achieved by reactions involving only hydration that the only modern hydrothermal convection systems that contain significant base metal concentrations are those that occur in basaltic rocks.

Reaction 3 (Table 1) describes the thermal metamorphism of illite into a muscovite-chlorite-pyrophyllite-quartz assemblage and exemplifies the case of host mineral destruction due to mineral:mineral disequilibrium in the presence of an aqueous solution. Since the reaction does not depend on the supply of any components from solution but does involve the destruction of the primary mineral, the reaction and concomitant leaching of metals can proceed at very low w/r ratios and produce high concentrations of metal in solution. For example, at 200°C and 10% porosity, if the illite of Reaction 3 contained 50ppm leachable trace metal, the concentration of trace metal in the pore solutions could reach 1 638ppm.

Solution concentrations in excess of 1 000ppm trace metals, such as zinc and lead, are usually only possible if the aqueous solution also contains a component for which the metal has a high affinity i.e. a complexing agent such as chloride. Unless the metals are held in solution mainly as metal complexes, under most natural subsurface conditions of pH, pO_2 and pS_2 below 300°C, zinc and lead become saturated with respect to a zinc or lead mineral respectively at concentrations of less than 1ppm. Even if high concentrations of a complexing agent are present, the concentration of metal in solution may be limited by saturation with respect to a mineral phase of the metal, so that any excess metal that is leached will precipitate as a trace secondary mineral or will be incorporated into secondary rock-forming minerals of the hydrothermal reservoir. Under these circumstances the concentration of metal in solution is determined by the solubility of the metallic mineral, the concentration of the complexing agent, the temperature and pressure.

Metal leaching constraints on the generation of ore-forming hydrothermal solutions

To explain the specific metal ratios and metal associations of various classes of hydrothermal ore deposits, it has been suggested by Hodgson and Lydon (1977) and Lydon (1983) that ore-forming hydrothermal systems, as opposed to "normal" hydrothermal systems, are those that become saturated with respect to the ore metals at the site of generation of the hydrothermal solutions. This view contrasts with the commonly-held view that the ore metals are scavenged from a large volume of source rock to produce solutions with relatively low metal concentrations, and that the ore solution becomes saturated with respect to the ore minerals only at the site of ore deposition.

Thus, based on the discussions in this section of the paper, in order for a hydrothermal solution to achieve concentrations of tens of ppm or more of ore metals, the hydrothermal system must have the following characteristics:

(1) The rocks of the hydrothermal reservoir must meet at least one of the following three mineralogical criteria:

  a. They contain a high concentration of elutable ore metals, such as those loosely bound in iron oxide coatings on grains of red sandstones.

REACTION 1

$$KAlSi_3O_8 \ (\text{K-feldspar}) \ + \ H^+ \ + \ 0.5H_2O \ \rightleftarrows \ 0.5Al_2Si_2O_5(OH)_4 \ (\text{Kaolinite}) \ + \ SiO_2 \ (\text{Quartz}) \ + \ K^+$$

	K-feldspar	H⁺	0.5H₂O	Kaolinite	Quartz	K⁺
Mass in grams:	278.32	1.01	9.01	129.08	120.16	30.10
Mass Balance:	14mg trace metal (50ppm leachable metal)	10⁴kg reactant solution at pH 4	0.32kg excess reactant solution (to fulfill constraint)	0mg trace metal	0mg trace metal	14mg trace metal in >10⁴kg product solution 0.0001m K

Constraint: Log(K⁺/H⁺)⩽4.5 at 100 C for Kaolinite stability in solution saturated with respect to Quartz

Result: < 0.0014ppm trace metal in product solution
w/r ratio 36000:1

REACTION 2

$$KAlSi_3O_8 \ (\text{K-feldspar}) \ + \ Na^+ \ \rightleftarrows \ NaAlSi_3O_8 \ (\text{Albite}) \ + \ K^+$$

	K-feldspar	Na⁺		Albite	K⁺
Mass in grams:	278.32	22.99		262.21	39.10
Mass balance:	14mg trace metal (50ppm leachable metal)	0.25kg reactant solution 4m Na	15.77kg excess reactant solution 4m Na (to fulfill constraint)	0mg trace metal	14mg trace metal in 16.02kg product solution 3.94m Na 0.06m K

Constraint: Log (Na/K)⩾1.8 at 100 C for Albite stability in solution saturated with respect to Quartz

Result: : < 0.9ppm trace metal in product solution
w/r ratio 58:1

REACTION 3

$$1.0 \ \text{Illite} \ \rightleftarrows \ 0.6 \ \text{Muscovite} \ + \ 0.05 \ \text{Chlorite} \ + \ 0.2 \ \text{Pyrophyllite} \ + \ 0.7 \ \text{Quartz}$$

	1.0 Illite	0.6 Muscovite	0.05 Chlorite	0.2 Pyrophyllite	0.7 Quartz	
Mass in grams:	383.93	239.0	29.20	72.07	45.07	
Mass balance:	19mg trace metal (50ppm leachable metal)	0mg trace metal	0mg trace metal	0mg trace metal	0mg trace metal	19mg trace metal in 11.6g product solution (see constraint)

Constraint: Rock of S.G. 2.8, 10% porosity, at 200 C ~ 383.93g of rock contains 11.6g pore solution

Formulae:

Illite	$K_6Mg_{.35}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	Quartz	SiO_2
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$		

Result: 1638ppm trace metal in product pore solution
w/r ratio 1:33

Table 1. Some chemical reactions involving the transformation of potassium minerals, illustrating various controls on the concentration of trace metals leached from these minerals in the product solution.

b. They consist of a primary mineral assemblage that may be converted to a secondary mineral assemblage by hydration alone, such as in the case of basaltic or ultramafic rocks.

c. They consist of mineral assemblages that are susceptible to mineral:mineral disequilibrium at the temperature and pressures of the hydrothermal reservoir. The prograde transformations of disordered clay mineral assemblages to ordered clays or micas is a good example.

(2) The hydrothermal solution must contain a complexing agent for which the specified metals have a strong affinity. For lead and zinc in neutral to acidic aqueous solutions the most effective complexing agent is the chloride ion.

(3) The w/r ratio of the hydrothermal system should be less, or not much greater, than unity. Otherwise, the metal concentration in solution will be much less than that of the source rock and too dilute to form a large hydrothermal ore deposit.

565

The convection cell model proposed by Russell (1976, 1983) and Caulfield (this vol.) for the generation of ore solutions for the Irish Carboniferous Zn-Pb deposits is thus unlikely for several reasons. Rocks of the pre-Devonian basement do not meet any of the criteria for ore-forming hydrothermal reservoirs listed above, because they consist of lithologies that were deformed and metamorphosed to varying degrees prior to the Carboniferous, which presumably resulted in the occlusion of intergranular porosity and the production of mineral assemblages stable above 200°C. Because of the mineral: mineral stability of such assemblages at the temperature of generation of the ore solutions, any significant metal leaching of the pre-Devonian basement rocks would have required retrograde metamorphism *via* metasomatic reaction with the hydrothermal solutions. This leaching mechanism would not have led to any significant concentration of ore metals in the hydrothermal solutions, because of the large w/r ratio required to effect the reactions. For example, for the reaction postulated in Figure 7.8 of Russell (1973) (the conversion of illite to clinochlore by the reaction of seawater magnesium), assuming the seawater contained 1350ppm magnesium and that 50ppm of metal was leached from the illite, the maximum metal concentration could not exceed 0.15ppm.

Generation of metalliferous hydrothermal solutions in sedimentary rocks

In contrast to the objections to the deep convection cell model discussed above, the model illustrated in Figure 2 meets the criteria for achieving high concentrations of lead and zinc in the hydrothermal solutions; it is in fact based, by analogy, on modern hydrothermal systems (Lydon, 1983), and can be applied to explain the distribution and chemistry of Sedex class deposits (Lydon et al., 1985). The essential details of this model and the illustration of factors that control the generation of hydrothermal solutions with the characteristics of those that formed Sedex or MVT class deposits, are conveniently considered in terms of a modern analogy.

A modern example

A prime example of a modern metalliferous hydrothermal system in sedimentary rocks is the Mississippi part of the Gulf Basin, where stratal aquifers in Cretaceous and Jurassic marine sediments at depths of greater than 6,000ft. (2000m) contain metalliferous brines. The general stratigraphy of the area is described in Figure 6. Down to the Hosston Formation, the sequence is dominated by argillaceous litholgies interlayered with subordinate arenaceous lithologies, limestones and minor evaporites. At greater depths, the sequence is dominated by arenacous lithologies with interlayered argillaceous lithologies, carbonates and evaporite lithologies. Red or purple coloured arenaceous lithologies are common, particularly in the Jurassic sequence (Dinkins, 1968).

In common with other sedimentary basins of the world undergoing a first cycle of compaction, vertical profiles of temperature, porosity and groundwater salinity through the Gulf Basin show systematic variations with depth (Burst, 1969). As illustrated in Figure 5 and Figure 2.b.(i), the increase in temperature with depth is a function of the geothermal gradient. "Normal" geothermal gradients in the Gulf Coast Basin are 20-40°C/km, but within geopressu-
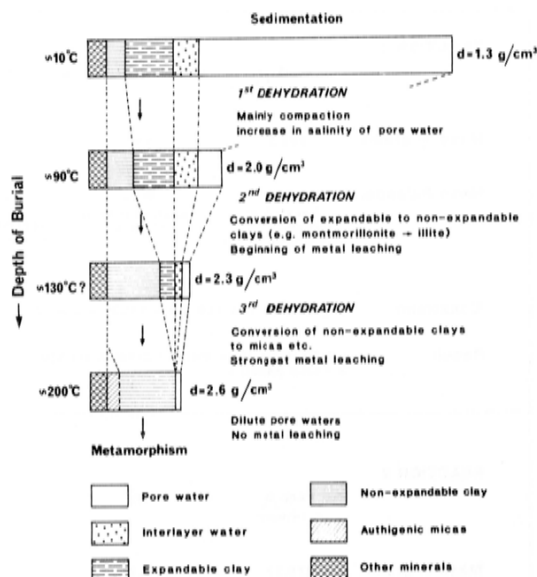

Figure 5. Schematic illustration of the change in marine shale bulk composition during burial, compaction and dehydration. (After Burst, 1969).

red argillaceous sequences the geothermal gradient may exceed 100°C/km (Jones, 1970). The reason for this is that an argillaceous layer of low permeability is an effective thermal insulator, not only because it prevents the upward mass transfer of heat by groundwater movement, but also because a clay layer with high water content has a low thermal conductivity (Jones, 1975).

The decrease in porosity with depth (Fig. 5 and Fig. 2.b.(i)) is due to the expulsion of pore water ("First Dehydration") as the sediments compact under the weight of the overlying sediment load. Layers of low permeability, notably argillaceous sediments, may impede the upwards cross-stratal escape of pore waters and give rise to geopressured conditions whereby pore waters within or below the argillaceous section rise above hydrostatic pressures and cause positive perturbations in the porosity profile.

The increase in salinity of pore waters with depth down to the 100°C isotherm (Fig. 2.b.(iii)) is also normal for compacting marine sediments, but there is some debate as to its cause. One point of view is that it is due to the phenomenon of "ion filtration" (Graf, 1982). The pressure gradient across an argillaceous section, acting as a cap rock to a geopressured aquifer, may cause it to act as a semipermeable filter that allows the passage of water more freely than dissolved salts, thus causing an increase in salinity. An alternative point of view is that the increase in salinity with depth represents a mixing curve between less saline surface waters and highly saline formational waters being expelled from depth by the process of compaction. The origin of the highly saline groundwater could be from the dissolution of halite beds and diapirs or from connate waters generated during the formation of evaporitic lithologies.

As the temperature approaches 100°C the maturation of expandable clays to non-expandable clays (dominantly montmorillonite to illite) is greatly accelerated and results in the release of clay interlayer water amounting to as much as 15% of the compacted volume of the sediment (Burst, 1969). The action of the release of interlayer water during this "Second Dehydration" is to displace or dilute the

|	Formation	Thickness in ft.	Dominant Lithologies	Symbol in Figures 7 - 10
Lower Cretaceous	Washita - Fredericksburg Group and Upper Cretaceous Formations	+3000	Varicoloured mudstones, limestone, white sandstones; siderite nodules in Upper Cretaceous	+
	Paluxy Mooringsport	800-1500 250-300	Varicoloured mudstones, red shale, limestone, red and white sandstones	×
	Ferry Lake	100	Anhydrite	
	Rodessa	700-800	Red shale, white and micaceous sandstones	✳
	Sligo	600	Limestone	⊠
	Hosston	1200-2600	Red shale, sandstone. (Qtz. 80%, clay 15%, other 5%. Secondary muscovite, quartz, calcite, ankerite, barite, dickite. No K-feldspar)	△
Upper Jurassic	Cotton Valley Group	2500-3300	Sandstone and conglomerate (80%), red, green and dark grey shale (20%)	◇
	Haynesville	700-1400	Sandstone (60%), anhydrite (15%), dolomite (15%), limestone (10%)	
	Smackover	500-1400	Limestone (75%), sandstone (20%), dolomite (5%). (Secondary quartz, K-feldspar, anhydrite; natural gas, H_2S rich)	⊙
	Norphlet	100-200	Intercalated reddish sandstone and shale. (Secondary K-feldspar interstitial halite, local pyrite concentrations)	⊡
	Louann	?	Halite, minor anhydrite	

Figure 6. Simplified summary of stratigraphic units, south-central Mississippi (after Carpenter et al., 1974).

salinity of existing pore waters (Fig. 2.b.(iii)) and, in a geopressured aquifer, increase the porosity of the rock (Fig. 2.b.(ii)). The additional increase in porosity indicated in Figure 2.b.(ii) at the argillaceous rock/arenaceous rock interface reflects the inherent porosities of the two different lithologies. For example, in the Gulf Coast Basin, at depths of less than 6km, the porosity of sandstones is about 40% higher than those of shales (Jones, 1975). The "Third Dehydration" consists of the gradual dehydration of silicate minerals as temperature and metamorphic grade increases.

The variation with depth of the chloride content of the metalliferous brines of Mississippi is shown in Figure 7, which is a composite diagram of the analyses by Carpenter et al. (1974) of formation waters extracted from aquifers tapped by different oil wells. The different symbols represent different stratigraphic formations (see Fig. 6), which

occur at different depths in different areas. The overall pattern is an increase of chloride content with depth to over 5M chloride at about 13,000 ft. (~4000m), below which there is a dilution or no increase.

Assuming a geothermal gradient of about 40°C/km (Carpenter et al., 1984), the Second Dehydration should have been completed at a depth of about 7,000ft. (~2200m). Therefore, the analyses shown in Figure 7 down to a depth of about 13,000ft. (~4000m) are from reservoirs undergoing the Third Dehydration. Based on the authigenic mineralogy reported by Carpenter et al. (1974) (see Fig. 6), the variation in the major element: chloride ratios of the brines (Lydon, 1983), and comparison with burial metamorphism documented elsewhere (Boles, 1982), it is suggested that the main reactions of this Third Dehydration are the conversion of illite to muscovite and a concomitant albitization of other minerals.
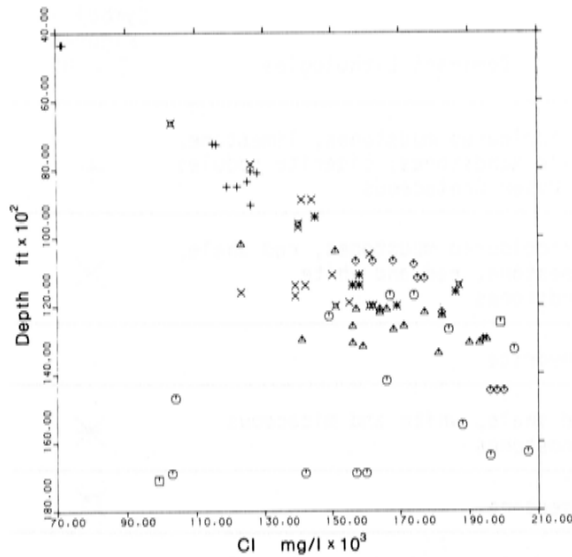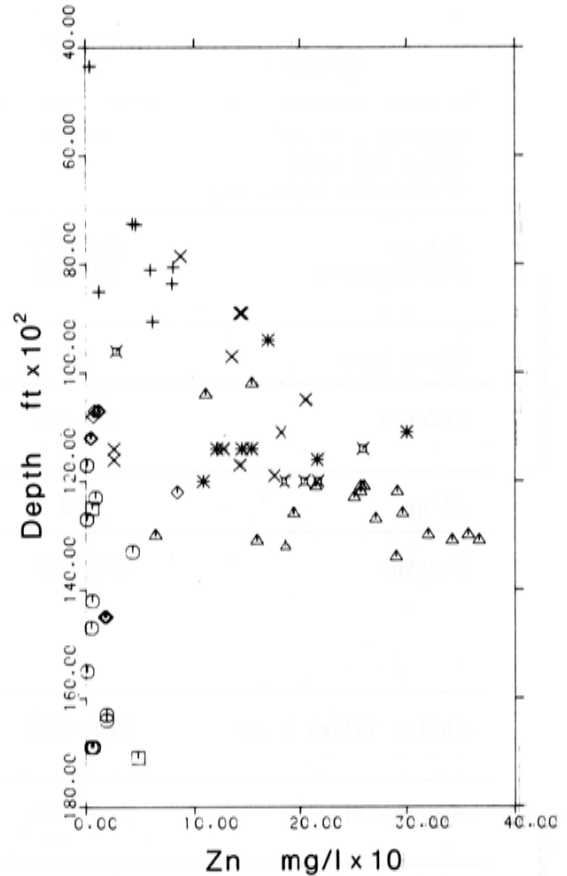
Figure 7. Mississippi oil field brines; variation of chloride content with depth. Key to symbols as in Figure 6. (data from Carpenter et al., 1974).

Factors controlling the concentration of ore metals in the Mississippi brines.

As discussed above, the mineralogical transformations associated with the Third Dehydration, coupled with the elevated temperatures and salinites and the low w/r ratios of geopressured reservoirs, provide the most favourable conditions for the leaching of metals and the generation of metal-rich pore solutions. As shown in Figure 8 for the case of zinc, this is of course exactly what has happened in the Mississippi brines. Based on the normalized concentration gradients of the various components, and assuming 20% porosity, a wet rock density of 2.3 g/cm³ and no migration of pore fluid, it is calculated that the maximum average metasomatic changes accompanying these reactions includes a gain to 1.0kg rock of 1.95g Na and losses from the rock of 2.0g Ca, 0.2g Mg, 13.5mg Zn, 4.6mg Pb, 16.0mg Fe and 2.4mg Ba.

Although it is suggested that metals were leached mainly from illite during its conversion to muscovite, the coincidence of the most metal-rich brines with the red-bed lithologies of the Hosston and Rodessa Formations (Figure 8 and Figure 6) may indicate that the leaching of metals absorbed by the iron oxide pigment is a significant factor. Shale beds themselves appear to be unfavourable candidates as source rocks for metals, since the chloride concentrations in their pore waters become very diluted during the mineralogical dehydration transformations. For example, Schmidt (1973) reported that the total dissolved salts in pore waters of shale layers in a Louisiana oil well were consistently 100,000 mg/l less than the pore waters of interbedded sandstone layers. Arenaceous beds, particularly arkoses with up to about 20% argillaceous component and an iron or manganese pigment, are theoretically the most favourable source rocks.

Samples from between 7,000ft. (~2200m) and 13,000ft. (~4000m) depths show a good correlation between zinc and chloride concentrations (Fig. 9). This suggests that the zinc is in solution mainly as chloride complexes. Furthermore, the projection of the best-fit line to this correlation indicates that detectable (>1ppm) zinc concentrations
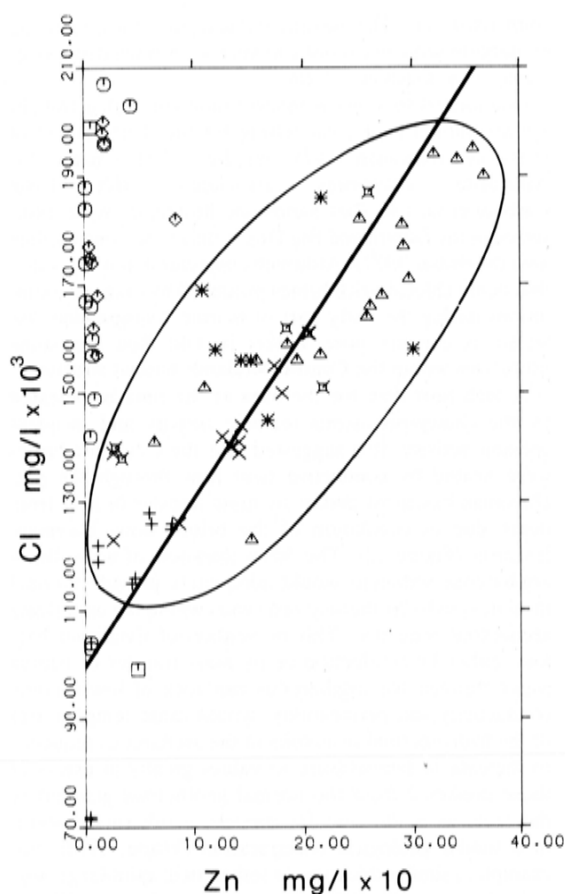

Figure 8. Mississippi oil field brines; variation of zinc content with depth. Key to symbols as in Figure 6. (data from Carpenter et al., 1974).

correspond to a chloride concentration of about 100,000mg/l, which, from the chloride profile (Fig. 7), corresponds to a depth of about 7,000ft. (~2200m) and therefore, from the assumed geothermal gradient, a temperature of about 100°C. This is close to the stoichiometric solubility of sphalerite determined by Barrett (1974) at this chloride concentration and temperature extrapolated to a pH of 5.

The correlation between zinc and lead concentrations (Figure 10) also suggests that the metalliferous Mississippi brines are saturated with respect to sphalerite and galena. The Zn:Pb ratio in solution varies from over 20:1 at the lowest metal concentrations (and lowest temperatures and chloride concentrations) to about 3:1 at the highest metal concentrations (and highest temperatures and chloride concentrations). These are exactly the ratios and trend determined experimentally for solutions saturated with respect to both sphalerite and galena (Barrett, 1974). That the brines are saturated with respect to galena is demonstrated by the precipitation of this mineral in the well-casing scale (Carpenter et al., 1974).

At depths shallower than about 7,000ft. (~2200m) the Mississippi brines do not contain significant trace metal concentrations, even though reactions associated with the Second Dehydration are presumed to have taken place. Presumably the reason for this is that at these shallower depths, the temperature and concentration of chloride in solution are too low to support detectable concentrations of lead and zinc in solutions saturated with respect to sphalerite and galena (Lydon, 1983). At Zn+Pb concentra-
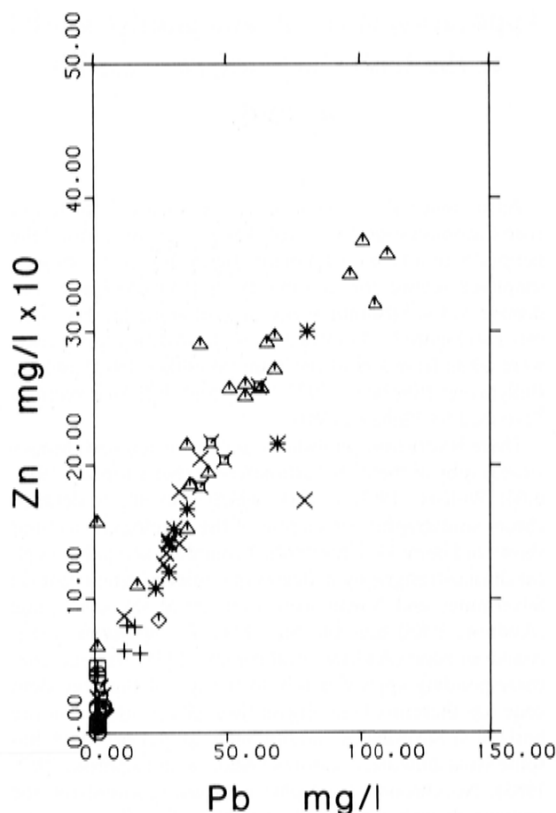
Figure 9. Mississippi oil field brines; variation of zinc content with chloride content. Key to symbols as in Figure 6. (data from Carpenter et al., 1974). Samples within enclosed area are those from aquifers situated stratigraphically above the Cotton Valley Group and do not have the high H$_2$S contents associated with the sour gas reservoir in the Smackover. Line is least-squares best fit to samples within enclosed area. (From Lydon, 1983).

Figure 10. Mississippi oil field brines; variation of zinc content with lead content. Key to symbols as in Figure 6. (data from Carpenter et al., 1974).

tions of 1ppm to 10 ppm, most brine samples do not contain detectable Pb. The reasons for this may be the increase in Zn:Pb ratio with decreasing temperature, and chloride concentration in solutions that are simultaneously saturated with respect to sphalerite and galena (Barrett, 1974) or that, as laboratory studies suggest, zinc is more easily leached than lead from argillaceous rocks by chloride solutions (e.g. Long and Angino, 1982). Whatever the reason, as indicated in Figure 2.a, the initial stages of the leaching process may produce solutions that are zinciferous but do not contain significant lead concentrations.

As discussed by Lydon (1983) several phenomena occur at, and below, the 13,000ft. (~4000m) depth, but it is uncertain whether the phenomena are interrelated. Zinc and lead concentrations are very low, which appears to be due to an increase of H$_2$S concentration, associated with a sour gas front, that supresses the solubility of sphalerite and galena. This depth also appears to correspond to a dehydration reaction (note dilution of chloride, Figure 7), which, from the change in authigenic mineralogy (Figure 6) and increase in potassium concentrations in solution,

corresponds to a conversion of muscovite and/or illite into K-feldspar. It also corresponds to a sharp decrease in sulphate but a five-fold increase in barium concentrations in solution.

Although Carpenter et al. (1974) did not report copper analyses, analysis of metalliferous brine samples from the same area revealed copper concentration to be less than 1ppm (Y. K. Kharaka, oral comm., 1985). The reason for the insignificant copper concentration is that the maximum concentration of copper in an aqueous solution saturated with respect to chalcopyrite and an iron sulphide is less than 1ppm below about 250°C (Lydon, 1983).

Using the definition of Hodgson and Lydon (1977), since the metalliferous Mississippi oil field brines are saturated with respect to sphalerite and galena, they are potential ore-forming hydrothermal solutions. Since they also contain high concentrations of barium and iron, but insignificant copper, they appear to be directly comparable in chemical composition to the ore solutions responsible for the Sedex and MVT classes of ore deposits. In fact, the migration of analogous brines upwards along the flanks of a salt dome are thought to be responsible for a deposit with characteristics of the MVT class that occurs at a depth of less than 1,000ft. (~300m) in the cap rock of the Hockley salt dome, in Cainozoic sediments of Texas (Price et al., 1983). It can be easily visualized that if similar solutions had risen to similar elevations at a location not too far distant to the south, they could have formed a deposit with characteristics of the Sedex class on the floor of the Gulf of Mexico!

Application of the stratal aquifer model to the Irish Carboniferous Zn-Pb deposits

As discussed above and illustrated in Figure 3, the major Irish Carboniferous Zn-Pb deposits are situated around the periphery of a Central Midlands Basin. Figure 11 shows a simplified section through this Basin from the Navan ore deposit to the Silvermines ore deposit along the line indicated on Figure 3. The data used in constructing this section were taken from logs of the Trim (Sheridan, 1972) and the Ballyragget (Sheridan, 1977) wells and drill hole sections described by Philcox (1984).

There is very little published data on the detailed chronostratigraphy of the Irish Carboniferous (Sevastopulo, 1982, p.66; Philcox, 1984, p. 74), which prevents a detailed chronostratigraphic correlation of the lithological sections shown in Figure 11. Unpublished conodont and palynological chronostratigraphy indicates that mineralizing events at Silvermines and Navan were initiated at the same time (Andrew, 1985) near the top of the *P. communis carina* conodont zone (Andrew, oral comm., 1985). A time line, corresponding approximately to the top of this conodont zone has therefore been drawn through the stratiform ore horizon at Silvermines and the 5-lens at Navan, which has some synsedimentary features (Andrew and Ashton, 1982; 1985). No chronostratigraphic data are reported for the sections described by Philcox (1984). The *P. communis carina* time line through the Ballyragget and Trim wells is drawn above the horizons identified by Sheridan (1972, 1977) as the lower part of the Cummings foraminifera zone 2, which according to the biostratigraphical correlations reported by Sheridan (1977, p. 118) and Sevastopulo (1979, p. 10; 1981, p. 149) is assumed to be equivalent to the *P. communis carina* conodont zone. Similarly, a time line corresponding approximately to the base of the Arundian (Cummings FZ 3) has been drawn over the top of the Waulsortian "reef" at Silvermines to approach progressively the base of the dolomite/limestone Waulsortian equivalent in the Ballyragget well (Sheridan, 1977) and at Boston Hill (Holdstock, 1982), to below the FZ 4 zone in the Trim well and above the "reef" of pre-Arundian age at Navan (Andrew and Ashton, 1982). These time lines are consistent with the diachronous nature of the lithological units which generally become younger in a northerly direction (Sevastopulo, 1982b; Andrew, 1985).

These time lines indicate that the isopach pattern of argillaceous lithologies used to define the extent of the basin in Figure 2 is largely due to basinal subsidence that took place after initialization of the ore-forming event at Silvermines and Navan. Nevertheless, the *P. communis carina* time line does indicate that at the time of ore formation the site of the Central Midlands Basin was filled by a sequence of compacting sediments, consisting of a lower arenaceous sequence of Old Red Sandstone lithologies overlain by a dominantly argillaceous sequence of shales and argillaceous limestones. This configuration, illustrated in Figure 12, embodies the fundamental requirements for the Sedex class model illustrated in Figure 2. The present average thickness of the argillaceous sequence below the *P. communis carina* time line averages about 250m over most of the area. Based on modern compaction profiles (Muller, 1967) during *P. communis carina* time, this argillaceous sequence was probably over 500m thick in its semi-

compacted state. The maximum thickness of the underlying arenaceous sequence is not known, but, as discussed above, it may be as much as 2-3 km.

Continental to shallow marine fault-controlled troughs are a common geological setting for the development of evaporites (Kinsman, 1975; Windley, 1984, Chapt. 16). Anhydrite evaporites associated with basal Carboniferous/Old Red Sandstone lithologies were intersected in the Dowra and Big Dog wells in the Leitrim-Sligo area (Sheridan, 1977). Although conjectural, it is suggested that dense chloride-rich brines produced by evaporitic conditions during the early part of marine transgression collected as connate pore waters in Old Red Sandstone lithologies within the Central Midlands basinal structure.

A high heat flow for the area at the time is indicated by the contemporaneous tectonic activity and incipient volcanic activity. It is suggested that these connate brines were heated by conductive heat flow through the pre-Devonian basement and/or by mass transfer of heat from depth due to circulation of the brines along basement fractures (Figure 12). The 500m thickness of water-laden argillaceous sediment would adequately provide thermal insulation to hydrothermal reservoirs within the underlying arenaceous sequence. This prevention of significant heat loss, either by conduction or by mass transfer of heated water through the argillaceous cap rock of low thermal conductivity and permeability, would cause temperatures of the hydrothermal reservoirs in the arenaceous sequence to increase in temperature to values greatly in excess of those predicted from the normal geothermal gradient of the area, as is the case for modern geothermal systems of a similar geological configuration (White, 1970). For example, a similar thickness of sediment in a similar geological setting caps the Salton Sea geothermal system (Younker et al., 1982), which convincingly demonstrates that a capped stratal aquifer can contain hydrothermal solutions at over 300°C within 400m of the surface, even in a subaerial environment. By analogy with modern areas of similar tectonic environment and therefore heat flow, the base temperatures of the hydrothermal systems within the subsurface of the Central Midlands Basin can therefore be expected to have ranged to over 200°C (Figure 4.).

Temperatures in this range would have allowed the thermal mineral:mineral transformations associated with the Second and Third Dehydration events to take place at shallow depth. Furthermore, the capping of the impermeable Lower Carboniferous argillaceous sequence coupled with the expulsion of clay-interlayer water can be expected to have produced geopressured conditions within the Old Red Sandstone sequence, and hence higher porosities at greater depths than those predicted from compaction curves of normally pressured compacting sedimentary sequences. As discussed above (and see Figure 2), this combination of thermal transformations of rock forming minerals at a relatively shallow depth, high porosities associated with geopressured zones, and high salinity of the pore fluids, presents the optimum conditions for the generation of large volumes of metalliferous solutions.

As in the case of the Mississippi metalliferous brines, the metals would presumably have been leached from clays and/or the iron oxide pigment of red sediments of the Old Red Sandstone lithologies. In the case of the Central Midlands Basin, however, a proportion of the metals may have been leached from rocks in the pre-Devonian basement. This is because the continuous convection of the brines within the reservoir zone (Figure 12) could serve to recharge the reactive capacity of the solutions as they

CENTRAL IRELAND

LOWER CARBONIFEROUS   UPPER DEVONIAN

MAIN LITHOLOGIES & THICKNESSES
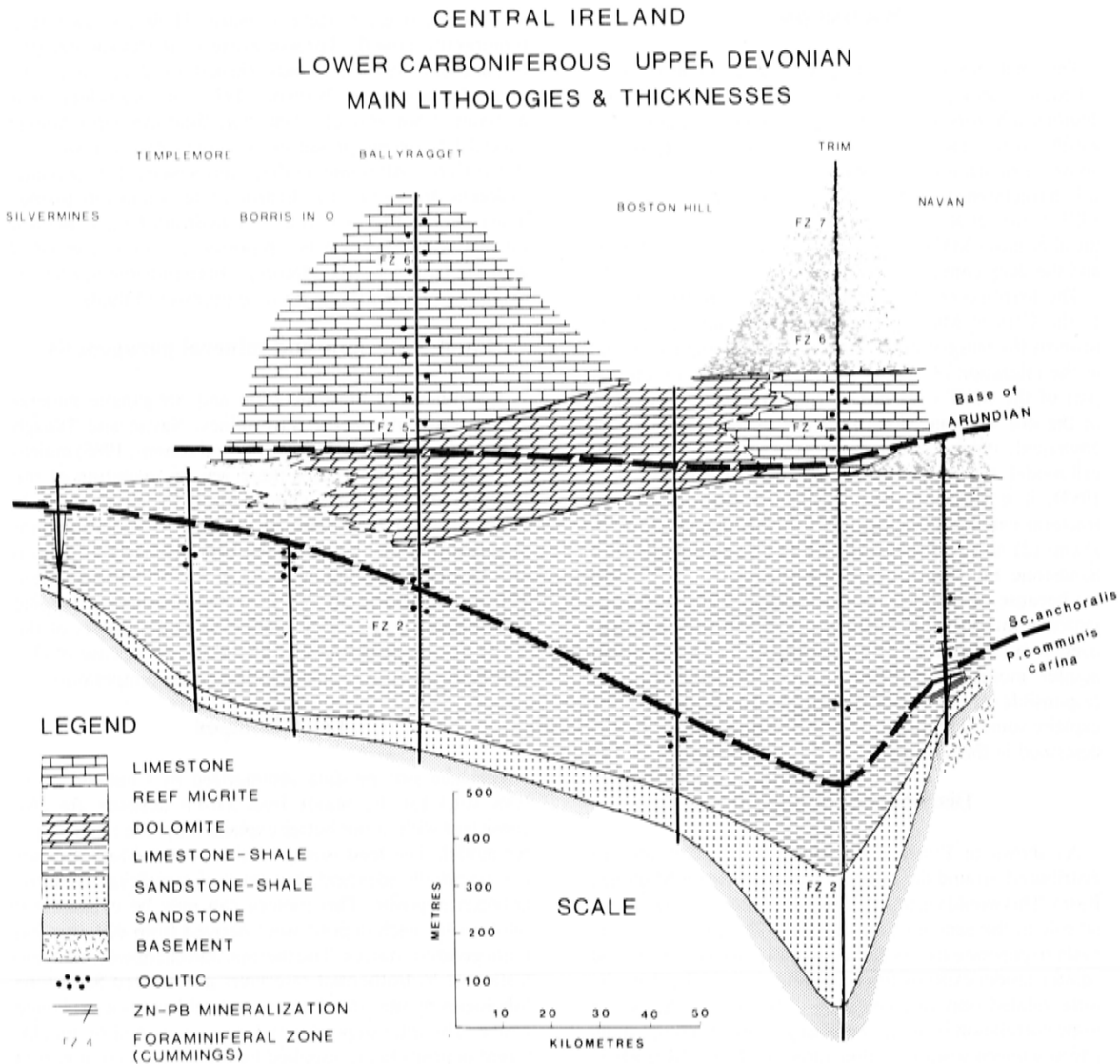
DATA FROM: SHERIDAN(1973,1977), PHILCOX(1984)

Figure 11. Correlations across the Central Midlands Basin of Ireland along the line shown in Figure 3. Drill hole sections at Trim and Ballyragget simplified after Sheridan (1972; 1977). "FZ" referes to the foraminiferal zones of Cummings. Remaining sections simplified after Philcox (1984). Lithostratigraphic correlations are those of the author. Heavy dashed lines are approximate chronostratigraphic correlations at the top of the *P. communis carina* conodont zone and base of the Arundian. See text for further explanation.

alternately equilibrated with the contrasting rock-forming mineral assemblages of the Old Red Sandstone lithologies and pre-Devonian basement respectively. This convective reflux of the brines would tend to homogenize not only the temperature but also the chemical composition of hydrothermal solutions of the same reservoir zone, and, as discussed below, give a ready explanation of the homogeneity of lead isotope ratios of individual deposits observed for the Irish deposits (Caulfield et al., this vol.).

It is suggested that, as is the case for the Mississippi metalliferous brines, metal leaching progressed until the solutions became saturated with respect to the major ore metals (Zn, Pb, Fe, Ba and Cu). However, again like the Mississippi brines, because of the low solubility of copper

sulphide minerals in a solution in equilibrium with iron sulphide below about 250°C, the Zn:Cu ratio of the solution probably remained greater than 100:1. It is also suggested that discharge of the hydrothermal solutions took place when and where a cross stratal zone of high hydraulic conductivity was provided by activation of a fault connecting the stratal aquifers to the surface or by hydrofracturing of the cap rock, and that the energy for migration of the hydrothermal solutions was provided by the hydraulic head due to geopressuring in the reservoirs. As illustrated in Figure 12, the hydrothermal solutions could flow from the Old Red Sandstone reservoirs to the surface either directly *via* the breached Lower Carboniferous argillaceous cap rock, or *via* basement faults.

571

Discussion

Thus, without over-extending scientific credibility, a stratal aquifer model appears to be consistent with the known geological history and characteristics of the Central Ireland Zn-Pb district. However, although it embodies the essentials of the model used to explain the distribution and chemical characteristics of the Sedex class of deposits (Lydon, 1983; Lydon et al., 1985), it also embodies some aspects of the alternative MVT class model (Cathles and Smith, 1983) and the deep convection cell model (Russell, 1976, 1983).

The distribution of the known deposits around the margin of the Central Midlands Basin suggests that stratal flow towards the margins of the Basin played an important role in the migration of the ore solutions, which is an integral part of the MVT class model. Similarly, convective flow of the ore solutions along fractures in the basement are envisaged, which is an integral part of the deep convection cell model, but in contrast to the model of Russell (1976, 1983), it is suggested that: (1) like modern analogues, fractures extended to a depth of only 1-3km and not up to 15km; (2) most ore metal was leached from the Old Red Sandstone lithologies and not the basement rocks; and (3) because of the impermeable barrier at the sediment-seawater interface, the waters involved in convection were connate brines and not seawater. This variant of the stratal aquifer model for the generation of the ore solutions responsible for the Irish Carboniferous Zn-Pb deposits also explains some of the more enigmatic features of the deposits described in this volume.

Distribution of deposits

As shown in Figure 3 the major Zn-Pb deposits are distributed around the periphery of the Central Midlands Basin. This would suggest that the basin played a fundamental role in the genesis of the deposits. The necessity of the basin to generate the ore solutions as required by the stratal aquifer model explains this spatial relation. If the deposits were related only to convection cells, one would expect some correlation between the timing of ore-forming events and volcanism when heat flow rates and hence hydrothermal convection should be at a maximum. More likely candidates for Irish deposits related to convection cells are those of the Cu, (Ag), (Hg) type such as Gortdrum. This is because, unlike zinc and lead, most of the trace copper in rocks occurs as trace copper sulphide minerals and thus may be directly leached to saturation concentration by simple solution attack. Modern hydrothermal systems which deposit Cu, Hg, (Ag), (As) (Sb) minerals typically have low salinity, sulphurous, carbonate-rich compositions (White, 1967), such as might be expected to be generated by hydrothermal flow through lithified argillaceous limestones.

Hydraulic jacking and hydraulic fracturing

During the course of the conference the term "hydraulic jacking" was often mentioned, especially in the context of the separation of sedimentary beds by fluid injection at the Navan deposit, which allowed the deposition of ore minerals in the resultant open space. It was also learned that a shale layer within Carboniferous rocks at the Silvermines deposits contain Silurian acritarchs, which were cited as evidence of hydraulic fracturing of basement rocks and the ejection of the lithic material during hydrothermal discharge. Hydraulic jacking requires that pore fluid pressures exceed local lithostatic pressures. Hydraulic fracturing requires that pore fluid pressures exceed the tensile strength of the rocks, which is usually 300-450 psi (2×10^3 to 3×10^3 kPa) (Grindley and Browne, 1975) or equivalent to a hydraulic head of over 300m. Pore fluid pressures cannot exceed hydrostatic pressures in a convection cell open to the surface. Alternate boiling and sealing can produce hydraulic fracturing and hydrothermal explosion phenomena in a convection cell, but hydrothermal explosion funnels and cones are not reported as being associated with the Irish deposits. However, both phenomena can be explained by the movement of geopressured fluids.

Fluid inclusions and mineral paragenesis

A synthesis of fluid inclusion and ore/gangue mineral paragenesis data on the Silvermines, Navan and Tynagh deposits by Ennex staff (Andrew, oral comm., 1985) indicates that in all three cases there was an evolution of the hydrothermal solutions characterized by an increase in temperature and decrease in salinity. A similar general temperature-salinity relation has been reported by Samson and Russell (1983) for deposits of the Silvermines area. This is the trend expected from the progressive tapping of a geopressured stratal aquifer, as saline waters of the reservoirs are progressively diluted by the release of clay interlayer water in response to increasing temperature.

Lead isotopes

The lead isotope data summarized by Caulfield et al. (this vol.) for the major Irish Zn-Pb deposits are also consistent with, if not better explained by, the stratal aquifer model. The lead isotope ratios of individual deposits are essentially identical, but there is significant variation between deposits. This pattern can only be explained if the lead for each deposit were derived from different but homogenized sources. The thermal and chemical homogenization of hydrothermal reservoirs in Old Red Sandstone lithologies by the stratal aquifer model has been explained above. The inter-deposit variation is explained by the different deposits being supplied by ore solutions of different reservoir systems (Fig. 12). However, a deep convection cell operating over an extended period of time would be expected to produce an intra-deposit variation among different generations of galena, due to the migration of the flow paths of the convection cell as old flow channels are sealed or new ones opened, and the lead is derived from different source regions at different times.

The overall trend, which apparently describes a mixing of Moinian lead with a more radiogenic source in a southerly direction, can be explained either as did Caulfield et al. in terms of a lead contribution by direct leaching of the basement (see Fig. 12) or by considering the provenance of the Old Red Sandstone, from which the stratal aquifer model assumes the bulk of the ore metals were derived. The pre-Old Red Sandstone land surface consisted of metamorphosed Lower Palaeozoic sedimentary and volcanic rocks overlying pre-Caledonian gneisses (Phillips, 1982). Because the base of Old Red Sandstone lithologies tends to be diachronous and become younger northwards, and because the main provenance direction was from the north (Holland, 1982), it would be expected that the proportion of lithic detritus in Old Red Sandstone lithologies that were derived from pre-Caledonian gneisses would increase northwards, as the level of the erosion surface in the source area deepened with time. Lead leached from Old Red
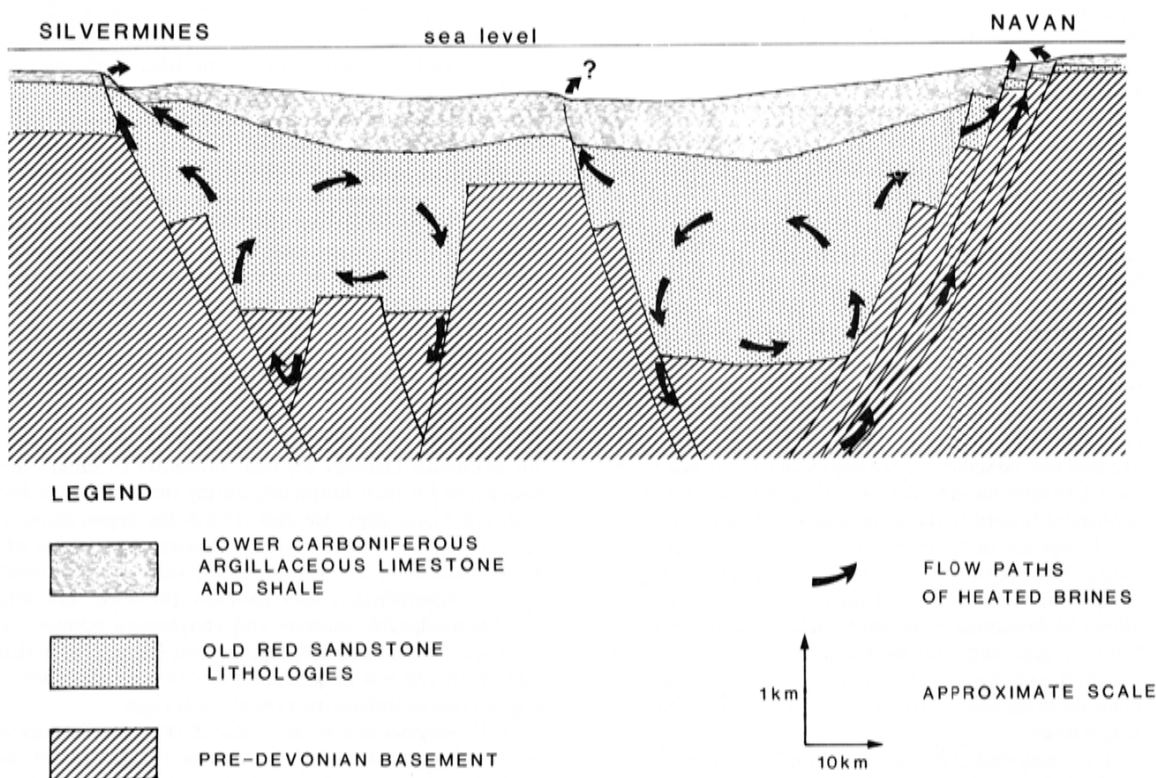
Figure 12. Schematic section across the Central Midlands Basin depicting conjectural geological relations during the time corresponding to the top of the *P. communis carina* conodont zone. Geopressured pore waters of Old Red Sandstone lithologies are residual evaporitic brines heated by conduction from the pre-Devonian basement and by convection of brines into the basement along dilatant fault zones. Lower Carboniferous argillaceous sequence provides thermal insulation and hydraulic sealing. Expulsion of brines to the surface is along tectonically active fault zones due to release of geopressure.

Sandstone lithologies would therefore be expected to reflect this progressive change in the source of clastic material northwards.

Ore deposit bulk metal ratios

The significance of ore deposit bulk metal ratios has been discussed in detail by Lydon (1983). The metal ratios and metal associations of the Irish deposits conform to the general principles established for the Sedex class of deposits. Since these geochemical patterns can only be consistently explained by assuming that the great bulk of ore and gangue minerals of a single deposit were derived from a single hydrothermal reservoir system in which the chemical composition of the ore solutions were controlled by equilibrium with the same rock-forming mineral assemblage, only the stratal aquifer model seems viable. As would be predicted from this model, maximum temperatures for the main ore event for those deposits with the highest Zn:Pb ratios (Navan) are lower than those deposits with lower Zn:Pb ratios (Silvermines, Tynagh) (Andrew, oral comm., 1985). The model might further suggest that, since the reservoirs for all three deposits were capped at approximately the same depth, and since the regional heat flow was probably approximately equal at all three localities, the reservoir for the Navan deposit was larger and less effectively sealed than the reservoirs for both the Silvermines and Tynagh deposits.

Exploration implications

The stratal aquifer model for the Irish Carboniferous Zn-Pb deposits has some interesting exploration implications. If, as in the case of the Mississippi oil field brines, it is assumed that about 15ppm ore metal has been leached from the Old Red Sandstone source rocks, then about 3×10^{11} cubic metres of source rock would be required to supply the approximately 13Mt of ore metal contained by the known Irish deposits. The area of the Central Midland Basin is about 10^{10} square metres, so derivation of this quantity of metal would require a continuous layer of source rock about 30 metres thick over the area of the basin. Since the thickness of the Old Red Sandstone lithologies is at least 5 and perhaps more than 50 times this thickness, the total metal concentrated by pore waters and released from the basin may not yet have been discovered. Deposits discovered to date occur around the edge of the basin where rock of the favourable *P. communis carina* and *Sc. anchoralis* conodont zones occur near the present surface. If the Sedex class genetic models apply to the Irish deposits then the central parts of the basin must also be considered favourable exploration target areas, though of course the thickness of younger rocks overlying the favourable time horizons presents a formidable exploration challenge.

Likewise, if the Dingle-Shannon Basin underwent a similar geological history as the Central Midlands Basin, it too may have produced conditions suitable for ore deposition of a similar type. The presence of small Zn-Pb deposits at

Courtbrown (Grennan, this vol.) and in east Clare indicate that this may have been the case. However, the same exploration problems exist as in the interior part of the Central Midlands Basin.

Conclusions

Collectively, the Irish Carboniferous Zn-Pb deposits have geological features that are characteristic of both the Sedex and MVT classes of ore deposits. Of the genetic models which have recently been proposed for these two classes of deposits, and a convection cell model proposed specifically for the Irish deposits, the stratal aquifer model for Sedex deposits explains more of the geological and geochemical features of the Irish deposits than the other two. The MVT class genetic model can be rejected on the grounds that no sedimentary basin existed in Ireland during the Carboniferous of analogous size, geological setting and geological history to those thought to be responsible for MVT deposits in North America on which the model is based. The deep convection cell model can be rejected on the grounds that it does not meet the requirements that allows hydrothermal solutions to achieve high concentrations of zinc and lead by leaching these metals from common rock types, and on the grounds that it does not conform to the characteristics shown by modern hydrothermal systems.

It is suggested that the ore solutions responsible for the Irish Carboniferous Zn-Pb deposits were generated in stratal aquifers of Old Red Sandstone lithologies, which were deposited within fault-controlled troughs during the early development of the Central Midlands Basin. These aquifers were charged with dense highly saline groundwaters during evaporitic conditions at the beginning of the Carboniferous marine transgression. Thermal insulation and hydraulic sealing by about 500m of semi-consolidated Lower Carboniferous shales and argillaceous limestone caused these brines to become heated to above 200°C in the high heat flow environment of extensional tectonism and incipient magmatic activity. Heat to the aquifers was supplied directly by conduction from the basement rocks and by reflux convection of the brines along dilatant fault zones to depths of 3km. Metals were leached mainly from the clay fraction and iron oxide pigments of the Old Red Sandstone lithologies, particularly during thermal transformations of clay minerals. Geopressuring developed by continued compaction and by the release of clay interlayer water, which tended to dilute the salinity of the formation brines as temperatures increased. The geopressured formational waters were intermittently released to the surface along fault zones during periods of tectonic activity, either directly across the Lower Carboniferous argillaceous cap rock or *via* fractured basement rocks at the margins of the basin.

The geopressured stratal aquifer model gives a consistent explanation for many features of the Irish Carboniferous Zn-Pb deposits including their spatial distribution, bulk compositions, timing of ore deposition and more enigmatic features such as fluid inclusion salinity and filling-temperature relations, hydraulic jacking and hydraulic fracturing phenomena, and lead isotope patterns.

These conclusions have implications for the broader problem of the classification of ore deposits in general. If, as this article suggests, the criteria that are commonly used to distinguish deposits of the Sedex class from deposits of the MVT class mainly reflect the siting of ore deposition

(surface versus subsurface) rather than the chemical composition and the source of the ore solutions or the timing of ore deposition, then many of the Irish Carboniferous Zn-Pb deposits cannot be strictly allocated to one class or the other. By the same token, although most of these Irish deposits have many features in common, they clearly cannot be separated as a single type that is different from deposits of either the Sedex class or the MVT class. Of course, the problem has no simple answer because the compartmentalization of classification is in inherent conflict with the continuum of process and effect in nature.

Acknowledgements

References

AKANDE, S. O. and ZENTILLI, M., 1984. Geologic, fluid inclusion, and stable isotope studies of the Gays River lead-zinc deposit, Nova Scotia, Canada. *Econ. Geol.*, v. 79, p. 1187-1211.

ANDERSON, G. M. and MACQUEEN, R. W. 1982. Ore deposit models — 6. Mississippi Valley-type lead-zinc deposits. *Geosc. Can.* v. 9, p. 108-117.

ANDREW, C. J. 1985. Tectonism, sedimentation and mineralization of the central Irish ore province (abstract). *Conference on the genesis of stratiform sediment-hosted Pb-Zn deposits*, Abstracts Volume, Stanford University.

ANDREW, C. J. and ASHTON, J. H. 1982. Mineral textures; metal zoning and ore environment of the Navan orebody, Co. Meath, Ireland. *In: Mineral Exploration in Ireland — Progress and developments 1971-1981* (A. G. Brown, ed), Ir. Assoc. Econ. Geol. p. 35-45.

ANDREW, C. J. and ASHTON, J. H. 1985. Regional setting, geology and metal distribution patterns of Navan orebody, Ireland. *Trans. Inst. Min. and Metall., (Sect. B)*, v. 94, p. B66-B93.

BADHAM, J. P. N. 1981. Shale-hosted Pb-Zn deposits: Products of exhalation of formation waters? *Trans. Inst. Min. and Metall. (Sect. B)*, v. 90, p. B70-B76.

BARRETT T. J. 1974. Solubility of galena and sphalerite in sodium chloride brines up to 90°C. Unpublished M.Sc. Thesis, University of Toronto.

BEALES, F. W. and JACKSON, S. A. 1966. Precipitation of lead-zinc ores in carbonate reservoirs as illustrated by Pine Point ore field, Canada. *Trans. Can. Inst. Min. Metall.* v. 75, (Sect. B), p. 278-285.

BOAST, A. M., COLEMAN, M. L. and HALLS, C. 1981. Textural and stable isotopic evidence for the genesis of the Tynagh base metal deposit, Ireland. *Econ. Geol.,* v. 76, p. 27-55.

BILLINGS, G. K., KESSLER, S. E. and JACKSON, S. A. 1969. Relation of zinc-rich formation waters, northern Alberta, to the Pine Point ore deposit. *Econ. Geol.,* v. 64, p. 385-391.

BOLES, J. R. 1982. Active albitization of plagiocalse, Gulf Coast Tertiary. *Am. Jour. Sci.,* v. 282, p. 165-180.

BOLDIZSAR, T. and KORIM, K. 1976. Hydrogeology of the Pannonian geothermal basin; *Proceedings 2nd United Nations Symposium on the development and use of geothermal resources, San Francisco.* United States Government Printing Office, Washington, v. 1, p. 297-303.

BROWN, C. and WILLIAMS, B. 1985. A. gravity and magnetic interpretation of the structure of the Irish Midlands and its relation to ore genesis. *J. Geol. Soc. London.* v. 142 p. 1059-1076.

BURST, J. F. 1969. Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration. *Bull. Am. Assoc. Pet. Geol.* v. 53, p. 73-93.

CARNE, R. C. and CATHRO, R. J. 1982. Sedimentary exhalative (sedex) zinc-lead-silver deposits, northern Canadian Cordillera. *Bull. Can. Inst. Min. Metall.* v. 75, p. 66-78.

CARPENTER, A. B., TROUT, M. L. and PICKETT, E. W. 1974. Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in central Mississippi. *Econ. Geol.* v. 69, p. 1191-1206.

CATHLES, L. M. and SMITH, A. T. 1983. Thermal constraints on the formation of Mississippi Valley-type lead-zinc deposits and their implications for episodic basin dewatering and deposit genesis. *Econ. Geol.* v. 78, p. 983-1002.

DINKINS Jr., T. H. 1968. Jurassic stratigraphy of Mississippi. Mississippi Geological, *Economic and Topographical Survey, Bulletin 109,* p. 9-38.

ELLIS, A. J. 1967. The chemistry of some explored geothermal systems; *In: Geochemistry of hydrothermal ore deposits* (H. L. Barnes, ed.). Holt, Rinehart and Winston, New York. p. 465-514.

ELLIS, A. J. and MAHON, W. A. J. 1964. Natural hydrothermal systems and experimental hot-water/rock interactions. *Geochim. Cosmochim. Acta,* v. 28, p. 1323-1357.

ELLIS, A. J. and MAHON, W. A. J. 1967. Natural hydrothermal systems and experimental hot-water/rock interactions (Part II). *Geochim. Cosmochim. Acta,* v. 31, p. 519-538.

EVANS, L. L. 1977. Geology of the Brushy Creek mine, Viburnum Trend, Southeast Missouri. *Econ. Geol.* v. 72, p. 381-390.

GARDINER, P. R. R. and HORNE, R. R. 1972. The Devonian and Lower Carboniferous clastic correlatives of southern Ireland. *Bull. Geol. Surv. Irel.,* No. 1, p. 335-366.

GARDINER, P. R. R. and MacCARTHY, I. A. J. 1981. The Late Paleozoic evolution of southern Ireland in the context of tectonic basins and their Transatlantic significance. *In: Geology of the North Atlantic borderlands* (J. W. Kerr and A. J. Fergusson, eds). Can. Soc. Pet. Geol., Memoir 7, p. 683-725.

GARDNER, H. D. and HUTCHEON, I. 1985. Geochemistry, mineralogy, and geology of the Jason Pb-Zn deposits, Macmillan Pass, Yukon, Canada. *Econ. Geol.,* v. 80, p. 1257-1276.

GARVEN, G. 1984. The role of regional fluid flow in the genesis of the Pine Point deposit, Western Canada Sedimentary Basin. *Econ. Geol.* v. 80, p. 307-324.

GARVEN, G. and FREEZE, R. A. 1985a. Theoretical analysis of the role of groundwater flow in the genesis of stratabound ore deposits. 1. Mathematical and numerical model. *Am. Jour. Sci.,* v. 284, p. 1085-1124.

GARVEN, G. and FREEZE, R. A. 1985b. Theoretical analysis of the role of groundwater flow in the genesis of stratabound ore deposits. 2. Quantitative results. *Am. Jour. Sci.* v. 284, p. 1125-1174.

GRAF, D. L. 1982. Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. *Geochim. Cosmochim. Acta,* v. 46, p. 1431-1448.

GRINDLEY, G. W. and BROWNE, P. L. 1975. Structural and hydrological factors controlling the permeabilities of some hot-water geothermal fields. *Proceedings 2nd United Nations symposium on the development and use of geothermal resources, San Francisco.* U.S. Government Printing Office, Washington, v. 1, p. 377-386.

GRUNDMANN JR., W. H. 1977. Geology of the Viburnum No. 27 mine, Viburnum trend, Southeast Missouri. *Econ. Geol.* v. 72, p. 349-364.

GUSTAFSON, L. B. and WILLIAMS, N. 1981. Sediment-hosted stratiform deposits of copper, lead and zinc; *Econ. Geol.,* Seventy Fifth Anniversary Volume (B. J. Skinner, ed), p. 139-178.

HELGESON, H. C. 1968. Geologic and thermodynamic characteristics of the Salton Sea geothermal system; *Am. Jour. Sci.* v. 266, p. 120-166.

HELGESON, H. C. 1970. Reaction rates in hydrothermal flow systems; *Econ. Geol.* v. 65, p. 299-303.

HODGSON, C. J. and LYDON, J. W. 1977. The geological setting of volcanogenic massive sulphide deposits and active hydrothermal systems: some implications for exploration. *Bull. Can. Inst. Min. Metall.* v. 70, p. 95-106.

HOSE, R. K. and TAYLOR, B. E. 1974. *Geothermal systems of northern Nevada.* United States Geological Survey, Open File Report, 27p.

JESSOP, A. M., HOBART, M. A. and SCLATER, J. G. 1975. The world heat flow data collection-1975. Geothermal Series Number 5, Geothermal Service of Canada, Earth Physics Branch, Ottawa, 125pp.

JONES, G. V. and BRADFER, N. 1982. The Ballinalack zinc-lead deposit, Co. Westmeath, Ireland; *In: Mineral Exploration in Ireland — Progress and developments 1971-1981* (A. G. Brown, ed). Ir. Assoc. Econ. Geol., p. 47-62.

JONES, P. H. 1970. Geothermal resources of the northern Gulf of Mexico basin. *Geothermics,* Special Issue 2, Proceedings United Nations symposium on the development and utilization of geothermal resources, Pisa, v. 2, p. 15-24.

575

JONES, P. H. 1975. Geothermal and hydrodynamic regimes in the northern Gulf of Mexico basin. *Proceedings 2nd United Nations symposium on the development and use of geothermal resources, San Francisco.* U.S. Government Printing Office, Washington, v. 1, p. 429-440.

KINSMAN, D. J. J. 1975. Salt floors to geosynclines. *Nature*, v. 255, p. 375-378.

LARGE, D. E. 1980. Geological parameters associated with sediment-hosted, submarine exhalative Pb-Zn deposits: an empirical model for mineral exploration. *Geologisches Jahrbuch*, D40, p. 59-129.

LARGE, D. E. 1981. Sediment-hosted submarine exhalative lead-zinc deposits: a review of the geological characteristics and genesis. *In: Handbook of strata-bound and stratiform ore deposits* (K. H. Wolf, ed). Elsevier, Amsterdam, v. 9, p. 469-507.

LARGE, D. E. 1983. Sediment-hosted massive sulphide lead-zinc deposits: an empirical model. *In: Mineralogical Association of Canada, Short Course Handbook vol. 8, Sediment-hosted stratiform lead-zinc deposits* (D. F. Sangster, ed.), p. 1-29.

LONG, D. T. and ANGINO, E. E. 1982. The mobilization of selected trace elements from shales by aqueous solutions: effects of ionic strength. *Econ. Geol.*, v. 77, p. 646-652.

LYDON, J. W. 1983. Chemical parameters controlling the origin and deposition of sediment-hosted stratiform lead-zinc deposits. *In: Mineralogical Association of Canada, Short Course Handbook Vol. 8, Sediment-hosted stratiform lead-zinc deposits* (D. F. Sangster, ed.), p. 175-250.

LYDON, J. W., GOODFELLOW, W. D. AND JONASSON, I. R. 1985. A general genetic model for stratiform baritic deposits of the Selwyn Basin, Yukon Territory and District of Mackenzie. *In: Current Research, Geol. Surv. Can.*, Paper 85-1A, p. 651-660.

MacDERMOT, C. V. and SEVASTOPULO, G. D. 1972. Upper Devonian and Lower Carboniferous Stratigraphical setting of Irish mineralization. *Bull. Geol. Surv. Irel.*, No. 1, p. 267-280.

NESBITT B. E., LONGSTAFFE, F. J. SHAW, D. R. and MUEHLENBACHS, K. 1984. Oxygen isotope geochemistry of the Sullivan massive sulfide deposit, Kimberley, British Columbia. *Econ. Geol.*, v. 79, p. 933-946.

McNITT, J. R. 1970. The geological environment of geothermal fields as a guide to exploration. *Geothermics*, Special Issue 2, v. 1, p. 24-31. U. N. Symposium on the development and utilization of geothermal resources, Pisa.

MUFFLER, L. J. P. 1976a. Tectonic and hydrologic control of the nature and distribution of geothermal resources. *Proceedings 2nd United Nations Symposium on the development and use of geothermal resources, San Francisco.* U. S. Government Printing Office, Washington, v. 1, p. 499-507.

MUFFLER, L. J. P. 1976b. Summary of Section II — Geology, hydrology, and geothermal systems. *Proceedings 2nd United Nations Symposium on the development and use of geothermal resources, San Francisco.* U. S. Government Printing Office, Washington, v. 1, p. xiv-lii.

MULLER, G. 1967. Diagenesis in argillaceous sediments. *In: Diagenesis in sediments* (G. Larsen and G. V. Chillingar, eds.). Elsevier, New York, p. 127-178.

NOBLE, E. A. 1963. Formation of ore deposits by waters of compaction. *Econ. Geol.*, v. 58, p. 1145-1156.

OTTLIK, P., GALFI, J., HORVATH, F., KORIM, K. and STEGANA, L. 1981. The low enthalpy geothermal resource of the Pannonian Basin, Hungary. *In: Geothermal systems: principles and case histories* (L. Rybach and L. J. P. Muffler, eds). John Wiley and Sons.

PHILCOX, M. E. 1984. *Lower Carboniferous Lithostratigraphy of the Irish Midlands*. Ir. Assoc. Econ. Geol. Dublin, 89pp.

PHILLIPS, W. E. A. 1981. The pre-Caledonian basement. *In: A geology of Ireland* (C. H. Holland, ed.), Scottish Academic Press, Edinburgh, p. 7-16.

PRICE, P. E., KYLE, J. R. and WESSEL, G. R. 1983. Salt dome related zinc-lead deposits. *In: Proceedings International Conference on Mississippi Valley Type Lead-Zinc Deposits.* G. Kisvarsanyi, S. K. Grant, W. P. Pratt and J. W. Keonig, editors, University of Missouri, Rolla, p. 558-572.

ROEDDER, E. 1976. Fluid-inclusion evidence on the genesis of ore in sedimentary and volcanic rocks. *In: Handbook of strata-bound and stratiform ore deposits* (K. H. Wolf, ed). Elsevier, Amsterdam, v. 2, p. 67-110.

SAMSON, I. M., and RUSSELL, M. J. 1983. Fluid inclusion data from Silvermines base-metal-baryte deposits, Ireland. *Trans. Instn Min. Metall. (Section B)*, Vol. 92, p. B67-B71.

SANGSTER, D. F. 1976. Carbonate-hosted lead-zinc deposits. *In: Handbook of strata-bound and stratiform ore deposits* (K. H. Wolf, ed). Elsevier, Amsterdam, v. 6, p. 447-456.

SAWKINS, F. J. 1984. Ore genesis by episodic dewatering of sedimentary basins: Application to giant Proterozoic lead-zinc deposits. *Geology*, v. 12, p. 451-454.

SCHMIDT, G. W. 1973. Interstitial water composition and geochemistry of deep Gulf Coast shales and sandstones. *Bull. Am. Assoc. Pet. Geol.*, v. 57, p. 321-337.

SEVASTOPULO, G. D. 1972. Upper Devonian and Lower Carboniferous stratigraphical setting of Irish mineralization. *Bull. Geol. Surv. Irel.*, 1, p. 267-280.

SEVASTOPULO, G. D. 1981a. Lower Carboniferous. *In: A Geology of Ireland* (C. H. Holland, ed). Scottish Academic Press, Edinburgh, p. 147-171.

SEVASTOPULO, G. D. 1981b. Economic Geology. *In: A geology of Ireland* (C. H. Holland, ed.). Scottish Academic Press, Edinburgh, p. 273-301.

SEVASTOPULO, G. D. 1982. The age and depositional setting of Waulsortian limestones in Ireland. *In: Symposium on the palaeoenvironmental setting and distribution of the Waulsortian facies*, El Paso Geological Society and the University of Texas at El Paso, p. 65-79.

SHERIDAN, D. J. R. 1972. The stratigraphy of the Trim No. 1 well, Co. Meath and its relationship to Lower Carboniferous outcrop in east-central Ireland. *Bull. Geol. Surv. Irel.* 1, p. 311-334.

SHERIDAN, D. J. R. 1977. The hydrocarbons and mineralization proved in the Carboniferous strata of deep bore holes in Ireland. *In: Proceedings of the forum on oil and ore in sediments*, Geology Department, Imperial College, London, p. 113-144.

SKINNER, B. J., WHITE, D. E. ROSE, H. J. and MAYS, R. E. 1967: Sulfides associated with the Salton Sea geothermal brine. *Econ. Geol.*, v. 62, p. 316-330.

TAYLOR, S. 1984. Structural and paleotopographic controls of lead-zinc mineralization in the Silvermines orebodies, Republic of Ireland. *Econ. Geol.*, v. 79, p. 529-548.

THOMPSON, G. 1983. Basalt seawater interaction. *In: Hydrothermal processes at seafloor spreading centres* (P. A. Rona, K. Bostrom, L. Laubier and K. L. Smith, eds), NATO conference series iv, Plenum Press, New York, v. 12, p. 225-278.

THOMSON, G. A. and BURKE, D. B. 1973. Rate and direction of spreading in Dixie Valley, Basin and Range Province, Nevada. *Bull. Geol. Soc. Am.*, v. 84, p. 627-632.

WALKER, R. N., LOGAN, R. G. and BINNEKAMP, J. G. 1977. Recent geological advances concerning the H.Y.C. and associated deposits, McArthur River, N. T. *Jour. Geol. Soc. Aust.* v. 24, p. 365-380.

WEDEPOHL, K. H. 1972. Geochemical abundances and behaviours of zinc. *In: Handbook of Geochemistry*, (K. H. Wedepohl, exec. ed.), Vol. II-3, Sections 30-D through 30-M, Springer-Verlag, Heidelberg.

WEDEPOHL, K. H. 1974: Geochemical abundances and behaviours of lead: *In: Handbook of Geochemistry*, (K. H. Wedehpohl, exec. ed.), Vol. 11-5, Sections 82-D through 82-N, Springer-Verlag, Heidelberg.

WHITE, D. E. 1967: Mercury and base-metal deposits with associated thermal and mineral water. *In: Geochemistry of hydrothermal ore deposits* (H. L. Barnes, ed.). Holt, Rinehart and Winston, New York, p. 575-631.

WHITE, D. E. 1970. Geochemistry applied to the discovery, evaluation, and exploitation of geothermal energy resources. *Geothermics*, Special Issue 2, v. 1, p. 58-80. United Nations symposium on the development and utilization of geothermal resources, Pisa.

WILLIAMS, P. B., MABEY, D. R., ZOHDY, A. A. R., ACKERMANN, H., HOOVER, D. B., PIERCE, K. L. and ORIEL, S. S. 1976. Geology and geophysics of the Southern Raft River Valley geothermal area, Idaho, U.S.A. *Proceedings 2nd United Nations Symposium on the development and use of geothermal resources, San Francisco.* United States Government Printing Office, Washington, v. 2, p. 1273-1282.

WINDLEY, B. F. 1984. *The evolving continents.* (2nd edition) John Wiley and Sons, 399p.

YOUNKER, L. W., KASAMEYER, P. W. and TEWHEY, J. D. 1982. Geological, geophysical and thermal characteristics of the Salton Sea Geothermal field, California. *Jour. Volc. Geoth. Res.*, v. 12, p. 221-258.

ZIELINSKI, R. A., BLOCH, S. and WALKER, T. R. 1983. The mobility and distribution of heavy metals during the formation of first cycle red beds. *Econ. Geol.*, v. 78, p. 1574-1589.