13.9 Sediment-Hosted Zinc–Lead Mineralization: Processes and Perspectives

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Glossary

Aquiclude An impermeable sedimentary layer that acts as a barrier to fluid flow.

Anoxia The condition of extreme oxygen depletion.

Bacteriogenic Produced by the action of bacteria, normally used in reference to the bacterial production of H_2S from seawater sulfate.

Basement The region beneath an unconformity at the bottom of a sedimentary basin, typically composed of igneous or metamorphic rocks.

Bittern The residual brine produced by the evaporation of seawater past the point at which halite precipitates.

Connate Pertaining to pore waters trapped within sediment during deposition and subsequently buried. May be expelled later due to compaction or other processes.

Convective flow Flow of fluid driven by buoyancy forces, typically due to temperature-controlled density variations.

Diachronous An equivalent process occurring at different locations and times. Normally used in reference to sedimentation, such as during marine transgression or regression, when the same sedimentary facies is deposited in different places at different times.

Epigenetic Occurring after lithification of the host rocks, normally used in reference to mineralization. In rocks that

lithify soon after deposition, such as carbonates, epigenetic textures may form near the seafloor.

Euxinia The condition of oxygen depletion (anoxia) and enrichment in sulfide.

Exhalation The venting of hydrothermal fluids into an overlying water column, normally seawater.

Feeder zone A permeable zone, typically composed of fractured or brecciated rock beneath a stratiform or stratabound mineral deposit, exploited by hydrothermal fluids.

Footwall The rocks that occur immediately beneath a stratiform or stratabound mineral deposit.

Foreland The geographic region distal from an orogenic mountain belt, located on the underriding plate.

Hinterland The geographic region proximal to an orogenic mountain belt, located on the overriding plate.

Host rock The rock immediately adjacent to mineralization.

Irish-type A zinc–lead-rich mineral deposit that formed during or soon after lithification of the host sediment (normally carbonate).

Leaching The process of normally incongruent dissolution by which a hydrothermal fluid extracts metals from a rock.

Mineral deposit An accumulation of ore minerals. Does not imply the minerals can be extracted at a profit.

Mineralization The formation of an accumulation of ore minerals by hydrothermal or other processes. This does not imply the minerals may be extracted at a profit.

Mississippi Valley-type (MVT) A zinc–lead-rich mineral deposit that formed after lithification of the host sediment (normally carbonate).

Ore An accumulation of ore minerals that may be extracted at a profit.

Ore mineral A mineral that contains one or more elements of economic interest.

Paragenesis The time sequence of formation of minerals, normally used in reference to mineralization.

Restricted basin A sedimentary basin with limited connection to the open ocean, often leading to higher degrees of evaporation and less water body mixing and oxygenation, causing anoxia.

Sedimentary exhalative (SEDEX) A zinc–lead-rich mineral deposit that formed during or soon after deposition of the host sediment (normally siltstones or mudstones).

Stratabound Contained within, and replacing or crosscutting, a defined sedimentary unit. Morphology may be variable.

Stratiform Having the gross morphology of sedimentary strata, with a very high aspect ratio of length/width to thickness. Does not imply a syngenetic origin, although syngenetic (SEDEX) deposits may have this form.

Stratiform–stratabound Having stratiform morphology but strictly stratabound within a specific sedimentary unit.

Syngenetic Occurring at the same time as deposition of the host rocks, normally used in reference to synsedimentary mineralization.

Synsedimentary Occurring at the same time as deposition of sedimentary rocks. Often used in reference to faulting or mineralization.

Thermochemical An inorganic chemical reaction requiring elevated temperatures to proceed. Normally used in reference to the reaction between organic matter and sulfate to produce H_2S.

Thermohaline Relating to both temperature and salinity characteristics of a fluid, normally used in reference to convection driven by temperature- and salinity-dependent density variations.

Topographic flow Flow of fluid driven by gravitational potential energy.

Zone refining A process by which previously deposited minerals are dissolved and reprecipitated progressively by continued hydrothermal fluid flow to produce a zoned arrangement of minerals controlled by thermal and chemical gradients.

13.9.1 Introduction

The aim of this chapter is to review the principal geologic and geochemical characteristics of the main classes of sediment-hosted zinc–lead(–silver–barite) deposits and explore current understanding of their genesis. In particular, emphasis is placed on some of the recent developments that may impact on how these deposits are viewed. These are all forms of basin-hosted mineralization and so common processes are to be expected. Another objective, therefore, is to attempt to illuminate the linkages, or otherwise, among the different styles of mineralization. Inevitably, of course, issues of classification arise and some problems with existing schemes are highlighted. In passing, it is hoped that key gaps in knowledge are identified in order to provide some suggestions for possible avenues of future research.

The two main classes of sediment-hosted ore deposits – sedimentary exhalative (SEDEX) and Mississippi Valley-type (MVT) as they are currently classified – are the focus of the chapter. Together, these contain around 48% of the global resources of zinc and 52% of the lead (Singer, 1995), so they are the most important repositories of these metals on Earth. A review of Irish-type deposits as exemplified by the carbonate-hosted ores of the Irish Midlands Basin is also presented on the basis that these deposits display a range of features that can be considered transitional between the other two classes. As such, the district provides valuable insights into the relationships and continuum of processes that might exist in basin-hosted zinc–lead deposits in general. Furthermore, a four-dimensional record of basin evolution and accompanying hydrothermal fluid flow has been preserved in Ireland that constrains many key processes better than has been possible in arguably any other basin system. To maintain focus, and in the interest of brevity, other types of sediment-hosted mineralization, such as Broken Hill-type deposits and sandstone Pb or sandstone-hosted Pb deposits, are not considered. Up front, it is important to acknowledge the key review of Leach et al. (2005), which provided an extremely valuable compilation of observations and data on which this chapter has relied extensively.

13.9.2 Sedimentary 'Exhalative' Mineralization

13.9.2.1 Introduction

Sedimentary exhalative (SEDEX) deposits are the most important class of sediment-hosted lead–zinc(–silver) deposits in terms of global resources. It has been estimated that 31% of the zinc, 36% of the lead, and 9.9% of the silver are hosted by this deposit type (Singer, 1995). The term SEDEX was first introduced by Carne and Cathro (1982) to describe laminated sulfide deposits that formed by the venting of ore fluids onto the seafloor. However, this partly genetic definition has proven to be overly restrictive and difficult to apply and so has been widened in recent literature to include explicitly a variety of stratiform and stratabound zinc–lead–silver deposits hosted by both clastic and carbonate rocks (e.g., Leach et al., 2005). This reflects the increasing awareness of the importance of subseafloor replacement as an important mechanism in the formation of these ores. As a result, the term 'SEDEX' should no longer be taken to mean that hydrothermal fluids actually vented into the overlying water column, although this may have occurred in some cases.

Many previous reviews illustrate the variety of geologic and geochemical processes attending these deposits and discuss their classification (e.g., Emsbo, 2009; Goodfellow, 2004; Goodfellow and Lydon, 2007; Goodfellow et al., 1993; Gustafson and Williams, 1981; Large, 1983; Large et al., 2002; Leach et al., 2005; Lydon, 1983, 1996), and so only a brief summary will be presented here. The aim of this chapter is to focus on the linkages or contrasts with other sediment-hosted Zb–Pb systems in an attempt to place SEDEX deposits within the wider spectrum of basin-hosted base metal mineralization. Key characteristics upon which the SEDEX classification is based are presented in Table 1, which also lists the equivalent features of the MVT and Irish-type deposits that are discussed in this chapter.

The classification of SEDEX deposits remains somewhat problematic in that there are no features that are always present that are unique to the group. Previous distinctions on the basis of the presence of finely laminated, assumed to be syngenetic, ore textures break down because of the potential for mimicry by highly selective replacement, and a division on the basis of host-rock type, although often robust, also fails in some basins where mixed successions may host ore. For example, Anarraaq, in the Red Dog SEDEX district, is thought to have formed by replacement of carbonates (Kelley et al., 2004a) and displays features more akin to Irish-type or MVT deposits. Conversely, some deposits classified as MVT show evidence for having formed in a subseafloor, syndiagenetic environment and may be quite close in age to the host sediments (e.g., Lennard Shelf deposits, Pine Point, and Gays River). Thus, Leach et al. (2005) concluded that the distinction between some SEDEX and MVT deposits can be quite subjective. The deposits that defy simple classification may be reflecting the continuum of environments and processes that can exist in natural systems. However, it may also mean that the simple descriptive characteristics that are favored in classification schemes are not sufficient to distinguish between fundamentally different modes of origin.

13.9.2.2 Tectonostratigraphic Setting

SEDEX deposits occur in two broad settings: intracontinental rifts or failed rifts; or Atlantic-type continental margins (Figure 1).

The former setting is principally represented by the giant Proterozoic mineralized basins of northern Australia (Large et al., 2005). These are currently viewed as intracontinental extensional or transtensional basins related to a subduction system far to the south in present-day central Australia. These basins contain fairly typical but very thick rift packages, dominated in the lower part by oxidized clastic rocks and minor mafic volcanics overlain by dolomites, evaporitic and ferruginous siltstones, and reduced carbonaceous and pyritic shales. Although depositional environments have been interpreted as lacustrine, isotopic studies now show that these basins were connected to some degree to the open ocean for much of their history (e.g., Brasier and Lindsay, 1998), with shallow-marine facies dominating the upper parts of the basin sequence. As such, apart from a difference in scale, they have some parallels with the Irish-type deposit setting discussed in the succeeding text. Mineralization is hosted by fine-grained dolomitic siltstone and shale that may reflect short-lived periods of accelerated tectonic subsidence or longer-lived marine transgressions.

SEDEX deposits hosted in continental-margin settings are best exemplified by the Paleozoic systems of North America, such as the Selwyn Basin and the Kuna Basin that hosts the Red Dog deposit (e.g., Goodfellow et al., 1993; Large, 1983; Lydon, 1983, 1996). The basins are typically compartmentalized into subbasins by extensional faults. As with the Proterozoic basins, the basinal sequences comprise rift- and sag-fill deposits with a basal clastic- and/or volcanic-dominated succession (rift phase), overlain by the host rocks comprising deeper water reduced siltstones, mudstones, and carbonates. However, a greater proportion of the basin fill is reduced, highlighting the importance of starved basins in which organic matter could accumulate, leading to suboxic or anoxic bottom water (Lyons et al., 2006).

In both Proterozoic and Phanerozoic deposits, locally derived fragmental sedimentary rocks are common (e.g., Goodfellow et al., 1993), related to synsedimentary faulting and fluid upwelling. Phenomena include debris flows, stratiform and discordant breccias, conglomerates, and mudflows, usually composed of rock types that occur at the same or deeper stratigraphic levels as the ore deposits (Leach et al., 2005). These emphasize the importance of synsedimentary faulting as a control of ore localization, as is also noted in the succeeding text for the Irish-type deposits.

Evidence for contemporaneous igneous activity is limited, but tuffs reflecting distal volcanism (e.g., HYC) and mafic intrusions of similar age to mineralization are known (e.g., Sullivan and Red Dog).

13.9.2.3 Structural Setting

All SEDEX deposits are localized within subbasins controlled by synsedimentary faults, with mineralization typically located in the hanging wall of second- or third-order structures (Figure 2). It is generally accepted that these fault zones provide the principal conduits for buoyant mineralizing fluids, migrating from greater depths within, or beneath, the host basin. Often, the faults are not extensively mineralized themselves, with fluid migrating into subvertical feeder fracture and breccia zones and laterally into permeable sediments, or venting into the water column (Figure 2), prior to the deposition of significant sulfide (Goodfellow et al., 1993). The subbasin

Table 1   Summary and comparison of principal characteristics of SEDEX, Irish-type, and MVT deposits

Features	SEDEX (Leach et al., 2005)	Irish-type (Wilkinson, 2003)	MVT (Leach et al., 2005)
Tectonostratigraphic setting (at the time of mineralization)	Intracontinental or failed rift basins and rifted continental margins	Carbonate ramp and extensional basins on extending continental margin	Platform carbonate sequence at flanks of basins or foreland thrust belts
Host rocks	Shales, carbonates, calcareous/organic-rich siltstones, less commonly, sandstone and conglomerate	Non-argillaceous carbonates within mixed carbonate–siliciclastic succession	Mainly dolostone and limestone, rarely sandstone in carbonate-dominant sequences
Structural controls	Synsedimentary faults controlling subbasins and associated fractures and breccias	Synsedimentary faults controlling subbasins and associated fractures and breccias	Normal, transtensional, and wrench faults and associated fractures and breccias
Ore-body morphology and controls	Single or multiple wedge- or lens-shaped, or sheeted/stratiform morphology. Hosted within, or intercalated with, preferred sedimentary horizons. May be underlain by feeder zone	Single or multiple lenses with generally stratiform but strictly stratabound morphology in preferred sedimentary horizons, sedimentary and hydrothermal breccias. May be underlain by feeder zone	Highly variable; commonly stratabound, pipes or tabular zones, locally stratiform. Veins, dissolution breccias, lithological transitions
Principal ore and gangue minerals	Sphalerite, galena, pyrite, pyrrhotite, marcasite, minor sulfosalts, chalcopyrite + calcite, siderite, dolomite, ankerite, and quartz. Barite is common to absent; apatite is sometimes common and fluorite is very rare	Sphalerite (low Fe), galena, pyrite, marcasite, minor sulfosalts, chalcopyrite + dolomite, calcite, quartz. Barite is common, locally economic. Fluorite is extremely rare	Sphalerite, galena, pyrite, marcasite, minor sulfosalts + dolomite, calcite. Barite is minor to absent and fluorite is rare
Texture	Bedding-parallel, fine-grained, layered, and banded textures with or without coarser-grained brecciated, veined, fragmental, or chaotic textures	Dominated by massive sulfide but highly variable and complex textures. Mostly replacement, common veins and locally open-space filling	Coarsely crystalline to fine-grained, massive to disseminated. Replacement and open-space filling.
Trace metal content	Cu, As, Cd, Sb, Tl, Hg, Se, Bi, Ge, Ni	Cu, Cd, Ag, As, Ni, Co	Cu, Co, Ni, Ag, Sb, Cd, Ge, Ga, In
Lead isotope signature	Within-deposit homogeneity; mostly relatively unradiogenic crustal Pb	Within-deposit homogeneity; regionally variable, relatively unradiogenic crustal Pb	Within-deposit heterogeneity; crustally derived, highly radiogenic in the United States and Canada
Sulfur isotope signature	Predominantly positive; reduced seawater sulfate (BSR or TSR) in host rock or second fluid	Predominantly negative; reduced seawater sulfate (BSR) in second fluid	Predominantly positive; reduced seawater sulfate (TSR) in host rock or second fluid
Ore fluid	Low to high temperature (70–300 °C) infiltrated or connate, variably evaporated seawater	Low to moderate temperature (70–280 °C) infiltrated partially evaporated seawater	Mostly low temperature (90–150 °C) connate bittern brines or evaporite dissolution brines
Timing of mineralization	Syngenetic and/or during early diagenesis in unlithified to lithified sediment	Mostly during diagenesis, in partly and wholly lithified sediments. Minor syngenetic component	Epigenetic, tens to hundreds of millions years after host-rock deposition
Associated igneous activity	No direct association with igneous activity, but tuffs related to synchronous distal volcanism may be present	Close spatial and temporal association with volcanic activity in Limerick province	Not associated with igneous activity
Tectonic or metamorphic overprint	Weakly to intensely deformed and metamorphosed	Most deposits have some evidence of post-ore thrusting and wrench faulting	No examples recognized

BSR, bacteriogenic sulfate reduction; TSR, thermochemical sulfate reduction.

geometry can also provide a seafloor depression into which dense brines may be exhaled, thereby limiting the dispersal of metalliferous fluids. Knowledge of the geometry of controlling faults at the time of mineralization is often obscured by post-mineralization deformation as, for example, in the Red Dog district (De Vera et al., 2004).

13.9.2.4   Mineralization

Mineralization in SEDEX deposits is typified by fine-grained sphalerite and galena contained in one or more ore lenses. Zn/(Zn + Pb) ratios average about 0.7 (Leach et al., 2005).

Sulfosalts, such as tetrahedrite, freibergite, and boulangerite, may occur proximal to feeder zones, and chalcopyrite can be a minor to significant constituent in some deposits (e.g., Red Dog, HYC, Meggen, and Rammelsberg). Silver content may be elevated and hosted by galena, sphalerite (Moore et al., 1986), and sulfosalts (Lydon, 1996), similar to its occurrence in the Irish deposits (Wilkinson et al., 2005a). Pyrite is invariably present but varies from a minor component (e.g., Red Dog, Howard's Pass, and Century) to the dominant sulfide (e.g., Cirque, Meggen, and HYC). Pyrrhotite occurs in some Proterozoic deposits (Mt. Isa and Sullivan), implying more reducing and/or higher-temperature conditions.
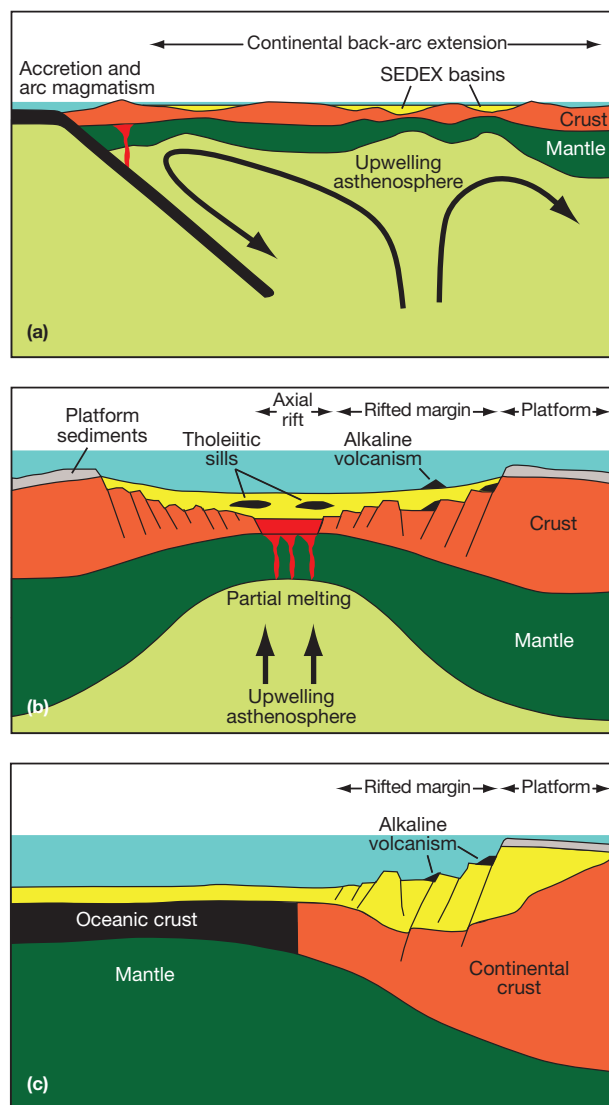
Figure 1 Tectonic settings for the formation of SEDEX zinc–lead deposits. (a) Intracontinental or failed rift where extensional basins are developed due to back-arc extension in overriding plate above a subduction zone (e.g., northern Australia); (b) continental rift floored by oceanic crust and filled with a thick sequence of clastic sediments (e.g., Selwyn Basin); (c) rifted passive margin (e.g., northern Alaska). Modified from Leach DL, Sangster DF, Kelley KD, et al. (2005) Sediment-hosted lead-zinc deposits: A global perspective. In: Hedenquist JW, Thompson JFH, Goldfarb RJ, Richards JP (eds.) *Economic Geology 100th Anniversary Volume, 1905–2005*, pp. 561–607. Littleton, CO: Society of Economic Geologists, Inc. With permission from the Society of Economic Geologists.

Sulfides display a variety of textures; the most characteristic are fine-grained layered and banded types, but coarser-grained brecciated, veined, fragmental, or chaotic textures are commonly observed. Grain-size coarsening may occur in response to hydrothermal recrystallization/zone refining or metamorphic overprinting. Textural relationships are critical when assessing the timing of introduction of sulfides relative to deposition and diagenesis of the host rocks, but unequivocal relationships are rare. This has led to many controversies surrounding the relative timing and depth of mineralization, as exemplified by

that surrounding the HYC deposit, Australia (Eldridge et al., 1993; Hinman, 1995; Large et al., 1998; Williams, 1978).

Ores are typically accompanied by manganiferous calcite, siderite, dolomite and/or ankerite, quartz, and sometimes barite and/or apatite. Quartz can occur in veins and patches in feeder zones and vent complexes but may also be present as chert in stratiform ore zones (Goodfellow et al., 1993). Barite content is variable, even within ore districts, and it can predate ore mineralization, be intimately intergrown with sulfides, or occur in younger stratigraphy (Leach et al., 2005). Apatite is an unusual hydrothermal mineral that may be common in some deposits (Anarraaq, Red Dog, Gamsberg, and Howard's Pass) and, interestingly, has also been noted in the Irish-type deposits (Hitzman et al., 2002).

Hydrothermal alteration is well developed, occurring in footwall stockwork zones and forming an extensive halo to mineralization along the stratigraphic horizon(s) hosting ore. Feeder zones and the immediate halo around ore bodies are characterized by quartz veins and/or silicification, Fe–Mn carbonates, sulfides, barite, muscovite, and chlorite (Leach et al., 2005). Tourmaline is unusually well developed at the Sullivan deposit. Footwall alteration zones are not present in northern Australian examples, perhaps because the ore lenses formed in a distal position relative to the main fluid conduits (Large et al., 2005). By contrast, stratigraphically controlled Fe–Mn carbonate alteration halos, comprising a zoned distribution of Mn-siderite, Mn-ankerite, ferroan dolomite, and dolomite moving away from ore, are very well developed in these systems, extending for a few hundred meters to tens of kilometers. Fe ± Mn alteration zones are also noted in some Paleozoic SEDEX deposits, such as Meggen (Gwosdz and Krebs, 1977), and are associated with mineralization in the Irish ore field (Russell, 1974; Wilkinson et al., 2011).

SEDEX ore bodies are characteristically stratiform, mound-, wedge-, or lens-shaped, with highly variable aspect ratios. This morphological variety has been linked to the environment of formation (Leach et al., 2005). The largest lenses are hundreds or thousands of meters in lateral extent and are typically up to tens of meters thick. These are widely thought to form in brine pool environments distal to a vent complex. Multiple stacked lenses are present in some systems (e.g., Hilton) where they are intercalated with unaltered sediments, implying episodic ore-forming events. Mound- or lens-shaped ore bodies with low aspect ratios are thought to represent systems that developed close to a site of hydrothermal exhalation, more akin to volcanic-hosted massive sulfide systems (see **Chapter 13.18**).

Mineralogical and metal zoning patterns are well developed in the ore zones of SEDEX deposits (**Figure 2**). In the Selwyn Basin, feeder zones are characterized by relatively reduced assemblages of ferroan carbonate and sulfides, grading out to more oxidized facies, including barite, hematite/magnetite, and calcic carbonates (e.g., Goodfellow et al., 1993). This suggests ore fluids must have been reduced in these systems, placing important constraints on metal transport and deposition mechanisms. Moving outward from the feeder zone, deposits display decreasing Zn/Ba, Zn/Mn, Zn/Fe, Pb/Zn, Pb/Fe, Pb/Ag, and Cu/Zn + Pb ratios (Lydon, 2004), reflecting the oxidation control on mineralogy and the temperature-dependent solubility of the base metals. Similar patterns are observed in the Silvermines deposit in the Irish ore field
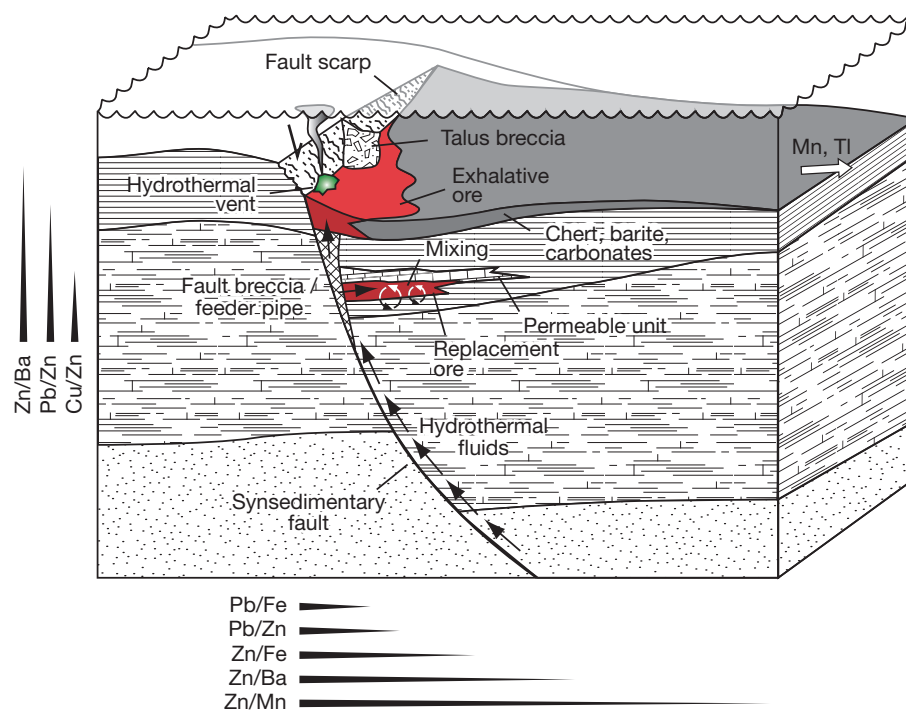
Figure 2 Cartoon model illustrating features of a typical SEDEX deposit. Variations in metal ratios laterally and vertically in the system are shown; longer bars indicate the relative dispersion of the denominator element (e.g., long bar for Zn/Mn indicates significant dispersion of Mn).

(Andrew, 1986). Vertical zonation through ore zones is also observed, with Zn/Ba decreasing upward. Pb/Zn ratios increase upward in many of the northern Australian deposits and at Red Dog (also with Zn/Fe), but in some of the Canadian deposits, and at Silvermines in Ireland, these relationships are reversed (Andrew, 1986; Lydon, 2004). Trace element zoning is most distinctive in decreasing concentrations of Mn (in carbonate) and Tl (in pyrite) along the ore horizon, with the Tl anomaly extending out as far as 20 km in the northern Australian systems (Large et al., 2005). Tl may also form an anomaly above the highest ore zones as at the Anarraaq deposit (Slack et al., 2004), reflecting waning hydrothermal activity or postmineralization redistribution. Other elements that may define a dispersion halo around SEDEX deposits include Ag, As, Ba, Bi, Ge, Hg, Ni, P, and Sb.

13.9.2.5 Fluid Sources

A major limitation in the understanding of ore-forming processes in SEDEX deposits derives from the limited, high-quality information on ore fluid properties. This is largely due to the fine-grain size of many of the minerals and postmineralization overprinting, which hinder fluid inclusion studies. Because of the near-seafloor environment of trapping inferred for most of these deposits, pressure corrections to homogenization temperatures will be small, governed by ambient seawater depth, and so, these provide a reasonable proxy for true fluid temperatures assuming that postentrapment modification has not occurred.

Of the Proterozoic systems, by far the best-studied deposit is Century in Australia. Sphalerite-bearing veins near the deposit, believed to represent a late paragenetic stage (Broadbent

et al., 1998), yielded salinities of 8.9 to 21.5 weight percent NaCl equivalent (hereafter referred to as wt%) and homogenization temperatures of 98 to 180 °C (Bresser, 1992). Inclusions in coarse-grained sphalerite from the ore zone gave homogenization temperatures of 63–159 °C and salinities of 15.4–23.3 wt% (Polito et al., 2006). Samples from other mineral occurrences in the district extend the salinity range down to 8.3 wt% and the homogenization temperature range up to 206 °C, with a broad negative correlation between the two parameters that is remarkably similar to that observed in the Irish ore field (see **Section 13.9.4.5**).

For the Paleozoic systems, probably the most reliable data are from Red Dog and from the Tom and Jason deposits in the Selwyn Basin. Fluid inclusions in ankerite from Tom yielded inferred ore-stage fluid salinities of 5.0–18.3 wt% and homogenization temperatures of 194–272 °C (Ansdell et al., 1989). Excluding just a handful of data, inclusions in quartz and carbonates from Jason gave salinities of 4.1–14.1 wt% and homogenization temperatures of 210–282 °C (Gardner and Hutcheon, 1985). These results should be treated with some caution because of the problem of proving syn-ore timing and the possibility of postentrapment modification. However, in the Jason dataset, there is little evidence for modification, and this, combined with the consistency between the two deposits, gives some confidence in the results. Slightly higher temperature, CO_2–CH_4-bearing inclusions in fluorite from Jason are excluded here because they are unlikely to represent ore-related fluids.

Fluid inclusion data from Red Dog are difficult to interpret given the strong Mesozoic overprint of the system and disagreement regarding the paragenesis of quartz (Leach et al., 2005). The most reliable data are probably from Leach et al. (2004),

who reported homogenization temperatures of 100–200 °C and salinities of 14–19 wt% from inferred primary inclusions in sphalerite.

Although many limitations remain, if the existing datasets are looked at carefully, it appears likely that the fluids that formed most if not all SEDEX deposits were moderate to high salinity (4–23 wt%), slightly to significantly higher than normal seawater, and were trapped at low to moderate temperatures (60–280 °C) in the ore-forming environment. This temperature range is consistent with estimates from sulfur isotope thermometry on coexisting sulfides. Higher fluid temperatures are possible, but the fluid inclusion evidence for this at present is ambiguous. Although there is some overlap, this range of properties generally distinguishes SEDEX ore fluids from MVT ore fluids (13–28 wt%, 70–170 °C) and is remarkably similar to the characteristics of fluids involved in mineralization in the Irish ore field (4–28 wt%, 70–280 °C). What is particularly interesting is the question of how the range of SEDEX ore fluid salinities developed – more saline than seawater but less saline than halite-saturated evaporitic brines. The implication is that fluid mixing may be involved, either in the fluid generation process or at the site of ore deposition.

Unlike MVT and Irish ore fluids (see Sections 13.9.3.5 and 13.9.4.5), few geochemical tracer studies have been carried out on the origins of water and solutes in SEDEX ore fluids. This is primarily because of the limitations of the sample material noted earlier. The source of salinity has only been constrained using fluid inclusion halogen data in one study on the Red Dog deposit. This showed that the ore fluids derived their salinity from the evaporation of seawater and were probably initially highly saline brines that were subsequently diluted at some point along their flow path (Leach et al., 2004).

Partial or strong evaporation of seawater is likely to be the source of salinity in other systems because of the lack of evidence for halite-bearing evaporitic sequences in most of the sedimentary basins hosting deposits that could have provided salt to migrating fluids. The involvement of evaporative brines is consistent with the fact that most SEDEX deposits formed within 30° of the contemporaneous equator where evaporation rates are highest (Goodfellow, 2004) and sedimentary facies indicative of evaporitic environments (at least to gypsum saturation) are common on the margins of most of the major SEDEX basin systems (Leach et al., 2005). Although a surface origin is probable, the mechanism by which these brines acquire heat and metals and how they are driven to the site of ore formation is still conjectural (see Section 13.9.2.8).

13.9.2.6 Metal and Sulfur Sources

Lead isotope data provide the strongest general constraint on the source of metals for SEDEX deposits. With few exceptions, Pb isotopes fall above the global orogen growth curve, indicating that lead is predominantly derived from crustal rocks (Leach et al., 2005). A second important general observation is that most SEDEX deposits display intradeposit homogeneity, although there may be variations from one deposit to the next within an ore district (e.g., McArthur Basin). This phenomenon is also well known from the Irish ore field (see Section 13.9.4.6) and implies that Pb has been homogenized by the hydrothermal system feeding an individual deposit or

that the source for the deposit is already homogeneous. Variability on the larger scale may reflect differences between metal source rock packages on the basin scale. Homogeneity also suggests that there is probably only one significant source for Pb, in contrast to a number of MVT deposits, where variations across the ore mineral paragenesis indicate that different sources are tapped and/or mixed at different times (see Section 13.9.3.6). Lead model ages in some cases fall quite close to host-rock ages, implying that metals are sourced from sediments within the basin; in other cases, they are significantly older or even slightly younger, reflecting lead evolution along source terrane-specific growth curves.

Strontium isotope data from barite and carbonates in SEDEX deposits show that radiogenic crustal strontium rather than seawater strontium is predominant (e.g., Goodfellow, 2004). This may be due partly to extensive isotopic exchange between evaporative brines and crustal rocks as they evolved into metalliferous ore fluids. However, much of the original marine Ca (and because of its very similar geochemical behavior, Sr) could have been lost from these fluids during evaporative gypsum precipitation. At the Red Dog main deposit, carbonates are more radiogenic than barite (Ayuso et al., 2004), consistent with an evolution from early lower-temperature barite with partly marine influence to higher-temperature mineralization associated with the introduction of greater proportions of crustal Sr. Temporal and regional heterogeneity in isotopic signatures are consistent with mixing between two Sr sources, with the radiogenic component possibly derived from underlying clastics or fractured metasedimentary basement (Ayuso et al., 2004).

The sulfide in SEDEX deposits is believed to be ultimately derived from seawater sulfate. Evidence for a seawater origin is provided by the parallel evolution of the isotopic composition of deposit sulfides and the secular seawater sulfate and sedimentary pyrite curves in the Phanerozoic (Figure 3). This shows that deposit sulfides have $\delta^{34}S$ values mostly between contemporaneous seawater sulfate and seawater−15‰, the most likely range for sulfide produced by thermochemical sulfate reduction (TSR) at around 150 °C (Kiyosu and Krouse, 1990). High rates of bacteriogenic sulfate reduction (BSR) in basins with restricted sulfate replenishment could also explain values in this range (Lyons et al., 2006). Either way, the correspondence implies that the sulfate involved is derived from connate brines or sulfate minerals from within the host-basin sequence or from contemporaneous seawater circulated down into the crust rather than from significantly older sulfate sources. Red Dog is an exception to the trend of relatively high $\delta^{34}S$ values, which, together with a proportion of the data from Howard's Pass and Aguilar, displays values so negative as to really require a significant component of the sulfide to come from BSR. In the Proterozoic, the marine sulfur isotope record is less well constrained, and there is much more overlap between sulfide produced by BSR and TSR, so it is difficult to identify mechanisms. However, the Sullivan and HYC deposits have $\delta^{34}S$ values well below the sedimentary pyrite average at the time of formation, so it would seem reasonable to infer that these deposits at least contain significant bacteriogenic sulfide.

Some deposits (e.g., HYC, Century, and Red Dog) show an evolution toward higher $\delta^{34}S$ values through the paragenesis, interpreted to reflect progressive reduction within a largely
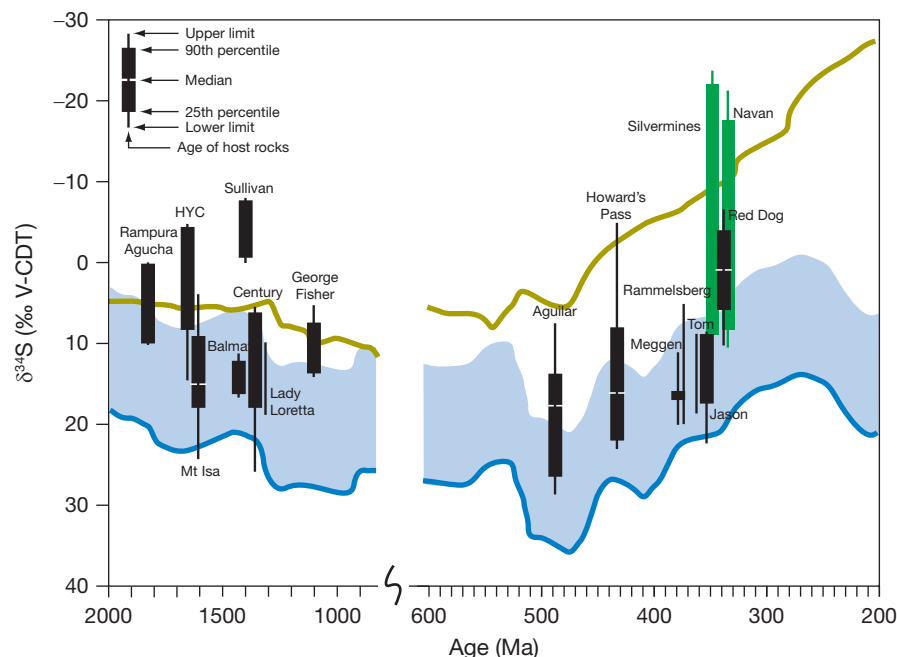
Figure 3 Diagram illustrating range and median $\delta^{34}S$ values of sulfides in a selection of SEDEX deposits plotted at their approximate host-rock/formation age compared with marine sulfate composition (blue line) and mean sedimentary pyrite composition (olive line) as produced by BSR. The blue-shaded field indicates the likely range of sulfide compositions produced by TSR of seawater-derived sulfate at 150 °C (Kiyosu and Krouse, 1990). The deposits shown in green, also positioned at their host-rock/formation ages, are Irish-type deposits for comparison. The correspondence between deposit compositions and marine sulfate evolution supports a marine sulfate origin for ore sulfides, reduced by TSR and/or BSR. Data compiled in Leach et al. (2005). Sulfur isotope curves from Farquhar et al. (2010).

closed sulfate reservoir (e.g., Large et al., 2005). However, this pattern could also be produced by a shift from earlier BSR dominance to later TSR, perhaps as fluid temperatures increased (Kelley et al., 2004b). Stratigraphic variations are also observed: HYC shows a general increase in $\delta^{34}S$ values up-section, possibly due to a Rayleigh distillation process in a closed reservoir (see Chapter 13.3), whereas at Sullivan and Howard's Pass, there is an overall decrease in $\delta^{34}S$ values upward, possibly reflecting an increasing proportion of BSR with time.

Overall, it is not clear whether sulfate and metals are transported together and sulfate reduction occurs at the site of mineralization, perhaps in a seafloor brine pool (e.g., Large et al., 2005), or whether fluid mixing is a more important process in which metalliferous but sulfur-poor brines mix with fluids enriched in H_2S in the near-seafloor environment. It is also possible that metals and reduced sulfur are transported together, but this would limit the metal transport capacity of the fluid (see Chapter 13.2) and is less effective for the production of large ore bodies.

13.9.2.7 Secular Variation in the Abundance of SEDEX Deposits

It has long been recognized that SEDEX deposits are not distributed evenly through Earth history with two main clusters, one in the Paleo-Mesoproterozoic (northern Australia, India, and Sullivan in Canada) and one in the Paleozoic (Selwyn Basin and Red Dog). The absence of SEDEX deposits in the Archean can be attributed to extremely low sulfate

concentrations in the early ocean due to the lack of sulfide weathering in a low-oxygen atmosphere (Farquhar et al., 2010; Lyons et al., 2006). This would severely limit the availability of sulfate both to seawater-derived hydrothermal fluids and to sediment pore waters or seafloor brine pools and thereby restrict the H_2S supply, whether it was produced by BSR (once sulfate-reducing bacteria had appeared at c.3.5 Ga) or TSR. The inferred increase in ocean sulfate concentrations in the Paleoproterozoic as the atmosphere became oxidized was a key stage in the development of suitable conditions for SEDEX ore genesis. Canfield (1998) suggested that, at this time, persistent oxygen deficiency in the deep ocean, coupled with rising sulfate, led to widespread BSR and the development of ocean-scale euxinia. Such conditions would have generated widespread H_2S in bottom water and underlying sediments – the perfect trap for upwelling, metalliferous ore fluids – and would have enabled the preservation of sulfide deposits once formed. Furthermore, these conditions could also have resulted in H_2S overcoming Fe fluxes to the ocean, triggering the demise of the banded iron formations. However, the limited barite content of the Proterozoic SEDEX deposits may be due to the persistence of relatively low sulfate conditions (Lyons et al., 2006).

It has been argued that episodes of SEDEX formation in the Phanerozoic also reflect periods of global ocean anoxia that could have provided ideal conditions for the accumulation and preservation of biogenically reduced sulfur in restricted basins (Goodfellow, 2004; Goodfellow et al., 1993). Although in many cases, ore sulfides are more enriched in ^{34}S than might

be expected for BSR, this can be explained by restriction of the sulfate supply and high rates of BSR in the rift basin settings characteristic of SEDEX deposits where organic matter can also be preserved (Lyons et al., 2006).

A second interesting possibility is that there may be a link to evolving ocean chemistry. Plotting the mass of Pb + Zn deposited in Phanerozoic SEDEX deposits against the sulfate and Ca^{2+} curves for seawater (Lowenstein et al., 2003) shows that the periods of dominant SEDEX mineralization approximately coincide with times when proposed $CaCl_2$-rich seas were predominant (Figure 4). The origin and even existence of $CaCl_2$ seas is controversial (e.g., Houston et al., 2011) and it is difficult to separate cause from effect, but a number of interrelated global controls have been suggested, including high seafloor spreading rates in the Silurian–Devonian, elevated sea levels, and high global volcanicity (Hardie, 1996).

There are several possible reasons why generation of brines from $CaCl_2$-rich and $MgSO_4$-depleted seawater might favor the formation of fertile ore fluids. As a result of the gypsum chemical divide in brine evolution (Hardie and Eugster, 1970), $CaCl_2$ seawater, enriched in Ca^{2+} over SO_4^{2-}, would become strongly depleted in SO_4^{2-} during gypsum precipitation to achieve low total sulfur content. Combined with the marked increase in base metal solubility with chloride content (with $[PbCl_3^-]$ increasing in proportion to $[Cl^-]^3$ in a $CaCl_2$ solution with pH buffered by a calcium silicate in a galena-saturated solution with constant $[H_2S]$; Yardley, 2005), this could yield a highly metalliferous solution. The effect would be enhanced in a sediment sequence lacking Ca or Mg silicates and carbonates, as these would tend to buffer the brine to higher pH (Yardley, 2005). The corollary of this chemistry is that an alternative source of sulfide (or sulfate) would be necessary for ore formation, at the site of mineralization.
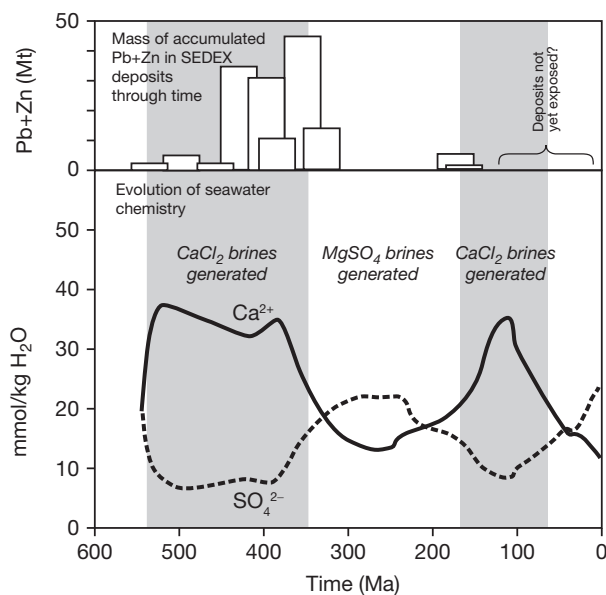

Figure 4 Mass of Pb + Zn deposited in Phanerozoic SEDEX deposits (data from Leach et al., 2001) compared with ocean chemistry (from Lowenstein et al., 2003), showing that peaks in mineralization occur at times when the oceans were conducive to production of $CaCl_2$-rich brines on continental margins.

13.9.2.8 Fluid Flow Mechanism

Given the economic significance of, and academic interest in, SEDEX deposits, it is somewhat surprising that conceptual and numerical models for large-scale fluid flow are few and remain relatively poorly constrained (Garven et al., 2001), although see Cathles and Adams (2005). In part, this is due to a lack of knowledge of the geochemistry, isotopic character, and physical properties of deep-basin or underlying basement rocks, sometimes because the original architecture has been obscured by postmineralization deformation and metamorphism. Uncertainties surrounding the properties of the ore fluids have also hindered the development of models. The consensus seems to be that in slowly subsiding extensional submarine basins, compactional and gravity effects are minimized so that the only flow mechanism that can effectively perturb normal conductive heat flow is buoyancy-driven free convection (Garven et al., 2001, 2003; Yang et al., 2004a). This mechanism is also favored by the thick, relatively permeable rift packages that are typical in the deeper parts of the basin successions that host SEDEX deposits and by the elevated heat flow that may accompany crustal extension and minor associated igneous activity (Leach et al., 2005). Additional factors that could be important are the generation of brines at surface, as suggested for the Red Dog district (Leach et al., 2004), which provide cool, dense fluids at the top of the system that encourage much faster convective overturn (Yang et al., 2004b), and the association of active and deeply penetrating normal faults in the rift basin and extending passive margin settings that can provide cross-formational permeability pathways for both descending and ascending fluids.

Numerical models have shown that convection is viable in typical SEDEX basin geometries that include permeable fault zones. In these models, some faults act as recharge faults, whereas others, typically those that penetrate the deepest, act as discharge faults and are the ultimate first-order control on the localization of ore (Garven et al., 2001, 2003; Yang et al., 2004a,b). Lateral flow tends to occur in the deep clastic aquifers, where metals are presumed to be leached. Potentially, fluids could also penetrate the basement sequences underlying the sedimentary basin if sufficient fracture permeability exists, but models generally assign very low permeability to basement so modeled fluxes are obviously low.

One question that is often not addressed explicitly in SEDEX convection models but that is an inherent part of these flow models is the importance of fluid recharge from the surface. If fluids vent at the seafloor, as the evidence in some cases suggests, then recharge of the flow system is necessary. In a submarine system, this will be from seawater or, possibly, evaporated seawater from the basin margins. Consequently, the role of 'connate basinal brines' as the ore fluids, as widely referred to in the literature, will be diminished if flow durations are such that they are flushed from the basin aquifers in the early stages of convective flow. Infiltrated, ambient surface waters will initially mix with and ultimately displace the connate waters and will become the protore fluids in the later life of the system. As emphasized by Emsbo (2009), the ongoing generation of brines at the basin margins may be essential to overcome mass balance constraints on the volumes of fluid needed to generate giant SEDEX deposits, particularly in basins where multiple episodes of mineralization occurred.

13.9.2.9   Genetic Model

The weight of evidence points toward thermohaline free convection as the primary driver of fluid flow in SEDEX ore systems (cf. Emsbo, 2009), as previously suggested for the Irish-type deposits (Wilkinson et al., 2005b). The involvement of ambient, evaporated seawater is consistent with isotopic and geochemical constraints and supported by the facies evidence for evaporitic conditions around basin margins and the development of most SEDEX deposits at paleolatitudes where high evaporation rates are prevalent. Fluids must have been capable of penetrating to sufficient depth to reach temperatures of up to ~200 °C in the Proterozoic systems of northern Australia and potentially greater than 300 °C in some of the Phanerozoic deposits of the United States and Canada. Temperatures of this order are supported by the marked elevation in Cu in some deposits (e.g., Rammelsberg) and sulfur isotope thermometry. Assuming only mildly elevated heat flow, this implies circulation to at least 5 and 7 km depth, respectively. In the very thick Proterozoic basins of Australia, the necessary flow pathway can be contained entirely within the basin package, and there is evidence that the oxidized clastic packages and/or volcanic rocks therein provide a good source of base metals (Cooke et al., 1998). In the Phanerozoic systems, fluid circulation is probably deeper and may penetrate into underlying basement rocks, as is the case in the Irish Midlands Basin, but at present, there are no isotopic data from SEDEX deposits to test this hypothesis.

The ubiquity of brines well above seawater salinity indicates that elevated salinity is a key requirement for the genesis of economic ore bodies. This is not surprising given the primary importance of chloride complexing for base metal transport (see Chapter 13.2). Given this, it is perplexing why highly saline brines, close to halite saturation, are relatively rare as ore fluids. It is possible that efficient convective flow systems are good at homogenizing fluids, with connate seawater at depth eventually diluting downward-penetrating brines to intermediate salinities, as suggested by the geochemistry of the Red Dog brines. This pattern is produced in some of the numerical flow models (e.g., Yang et al., 2004b). An additional possibility is that sufficient buoyancy for upward convection may only be possible for fluids that are hot enough and of low enough salinity. A simple consideration of the densities of NaCl solutions as a function of temperature shows that brines at halite saturation would need to be hotter than ~270 °C in order to displace low-temperature (<50 °C) normal seawater. Thus, if permeability structure allows very high-salinity fluids to penetrate only to moderate depth, without dilution they may not be able to convect upward. It is interesting to note that the density of the diluted brines at Red Dog, if they reached 140–190 °C (similar to the inferred ore fluid temperatures at the site of mineralization), would coincide with the density of normal cold seawater.

The ore-forming process involves the venting of the upwelling hydrothermal fluids at the seafloor or their lateral dispersion along permeable horizons within the shallow sedimentary succession (Figure 2). It is likely that mixing with resident sulfidic brines, perhaps in a brine pool, or with brines that had gravitationally infiltrated the underlying sediment (Lydon, 2004), was an important sulfide precipitation mechanism. However, good fluid inclusion or other evidence for this process is mostly lacking. It is not clear whether BSR or TSR was the most important sulfate reduction process, and both could have been involved. For the Proterozoic deposits and perhaps Red Dog, where ore fluids may have been oxidized and host rocks were rich in organic carbon, it is possible that sufficient sulfur was carried in the ore fluid and thermochemical reduction of the ore fluid by organic matter drove sulfide precipitation. However, for the reduced Phanerozoic basins, it is unlikely that sufficient sulfur would have been carried by the metal-bearing fluids, so a second source of sulfur at the site of ore deposition was probably critical.

On the larger scale, fertile basins for SEDEX deposits are long-lived, intracontinental, marine basins, developed at low paleolatitudes, within which thick, regionally extensive clastic aquifer systems developed. These are overlain by reduced, organic-rich packages that reflect episodes of restricted sedimentation and euxinia and bordered by evaporitic brine factories. Basins with these characteristics are limited in the Paleozoic but more frequent in the Proterozoic, explaining the superendowment of this era. The absence of SEDEX deposits from around 1300 to 600 Ma remains a mystery.

13.9.3   Mississippi Valley-Type Mineralization

13.9.3.1   Introduction

Mississippi Valley-type (MVT) deposits have been recognized as a distinct class of Zn–Pb deposits since the 1930s (Bastin, 1939). It has been estimated that 17% of the known global resources of zinc, 16% of the lead, and 2.9% of the silver are hosted by this deposit type (Singer, 1995). Their mode of origin – whether syngenetic, diagenetic, or epigenetic – and the origins of ore-forming fluids, metals, and sulfur were poorly constrained until modern geochronological, geochemical, and isotopic techniques began to be applied from the late 1960s onward (e.g., Brown, 1970). Despite a broad convergence of opinion on a model for MVT ore genesis, there are a number of features that remain enigmatic. One fundamental question that remains is how to explain the absence of deposits in many basins that otherwise have very similar geologic histories to well-endowed basins. Deposits are also heterogeneously distributed through time, being principally a Phanerozoic phenomenon with a major peak in the Devonian–Carboniferous.

Many previous reviews illustrate the diversity of geology attending these deposits and discuss their classification (e.g., Anderson and Macqueen, 1982; Brown, 1970; Leach and Sangster, 1993; Leach et al., 2005; Sangster, 1990; Snyder, 1967), and so, only a brief summary will be presented here. The aim of this contribution is to focus on the geochemistry that bears on their origin and relationships with other sediment-hosted Zn–Pb systems, together with recent findings that provide important constraints on ore-forming processes. Key characteristics upon which the MVT classification is based are presented in Table 1.

Classification of MVT deposits remains somewhat problematic in that, based on the criteria favored by Leach et al. (2005), some deposits classified as SEDEX show evidence for replacement of sediments in an early or burial diagenetic environment, whereas some deposits classified as MVT are thought to have formed in an early diagenetic environment and display laminated ore textures. The overlap stems from a number of the criteria used to divide the deposits, in particular: (1) the

emphasis on tectonic setting – which can be uncertain and dependent on the inferred timing of mineralization; (2) the division based on host-rock lithology – because mineralization can form in clastic or carbonate units in both deposit types; and (3) the postlithification mineralization implied in the term epigenetic – because carbonates typically lithify very quickly so they can develop 'epigenetic' textures in a near-seafloor setting.

13.9.3.2 Tectonostratigraphic Setting

MVT deposits are typically hosted in platform carbonate sequences in the foreland of orogenic belts, although some anomalous examples often included in the class are situated on the margin of active extensional basins (e.g., Lennard Shelf, Australia). The type of foreland is not considered critical to ore formation, with deposits interpreted to be associated with collisional, Andean, and transpressional orogens (Bradley and Leach, 2003). Host sequences can be up to several hundred million years older than mineralization so that, in contrast to SEDEX and Irish-type deposits, there is no requirement for a link between the tectonic environment in which the host rock formed and that in which mineralization subsequently developed. Deposits are typically associated with broad paleo-topographic highs and domal structures at the basin scale (Leach et al., 2005), thought to be related to the overall compressional environment and/or to basement highs that can play a role in forcing cross-stratal flow of fluids.

The relationship between collisional orogens and MVT deposits has been widely discussed in the literature (e.g., Bradley and Leach, 2003), and the origin of mineralization is now often linked to a series of processes that may occur in such settings (Figure 5). Key stages are (1) the development of unconformities and associated karstification due to the migration of a forebulge, (2) the formation of extensional and/or wrench faults in the stretched forebulge region, and (3) the proximity to a mountain belt and development of a regional slope toward the foreland (Figure 5). The first two factors may be involved in the generation of permeability subsequently exploited by mineralizing fluids, whereas the last features provide the conditions for large-scale fluid migration via topographically driven flow. However, these characteristics are developed as an integral part of basin evolution in this tectonic setting so that other factors must be at play to account for the generation of large MVT districts in some basins, whereas others, that have experienced a comparable history, are barren or poorly endowed.

13.9.3.3 Structural Setting

In most cases, there is a fundamental structural control on the district-scale localization of MVT deposits. Faults and associated fracture zones provide permeability pathways for fluids to migrate from regional aquifers into reactive host-rock sequences. Perhaps one exception to this general rule is where karst systems provide much of the permeability, such as in East Tennessee (Kesler et al., 1988). Not only do structures provide the opportunity for fluids to access reactive carbonates but they can also provide a connection to allow mixing between metalliferous brines and reduced sulfur-bearing fluids, or sour gas, which may be trapped in other aquifer horizons.

Faults controlling deposit locations can display normal, transtensional, or wrench displacements, interpreted to reflect local extensional stresses within far-field compressional environments. The principal faults are generally unmineralized; ore is usually located in structural dilatancy zones, pre-ore carbonate dissolution features, or favorable stratigraphic horizons nearby. These fault systems are viewed as extensional drains of large regional aquifer systems or as focused pathways for ascent of fluids in buoyancy-driven hydrothermal systems (Leach et al., 2005).

13.9.3.4 Mineralization

Mineralization typically occurs as highly variable host-rock replacement (which may preserve sedimentary banding), breccia cement and cavity- and vein-filling styles, commonly with coarse-grained components (Leach and Sangster, 1993; Leach
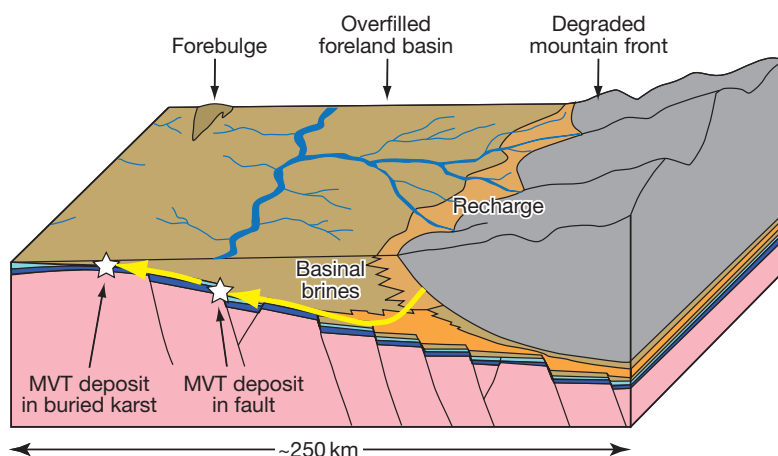
Figure 5   Tectonic setting for MVT ore genesis at the postcollisional stage of orogen development when the foreland basin has filled, creating a topographic slope toward the previously exposed forebulge region. Here, permeable carbonates provide ideal host rocks for mineralization, precipitated from connate brines migrating away from the eroding mountain belt. Redrawn from Bradley DC and Leach DL (2003) Tectonic controls of Mississippi Valley-type lead–zinc mineralization in orogenic forelands. *Mineralium Deposita* 38: 652–667.

et al., 2005; Sangster, 1990). A common characteristic is the occurrence of geopetal textures indicative of open-space growth. Sulfides are dominated by sphalerite and galena with a median Zn:Pb ratio of 3.4 (Leach et al., 2005). Additional ore minerals include pyrite, marcasite, and rare sulfides and sulfosalts containing Cu, Co, Ni, Ag, and Sb (e.g., Heyl, 1983). Associated gangue minerals are typically dolomite and calcite, with barite and fluorite locally abundant. In some cases, quartz may be present, normally in the form of fine-grained jasperoid (e.g., Brockie et al., 1968). Alteration around mineralization is predominantly in the form of dissolution and brecciation of the host rocks, accompanied in most cases by hydrothermal dolomite that either replaced host rock or precipitated in porosity or dissolution cavities. This dolomite sometimes forms a halo around deposits, such as in the Tri-State district (Leach et al., 2005). Calcite can be abundant, particularly in limestone host rocks, and authigenic K-feldspar and mica have been linked to ore-forming fluids in some districts (e.g., Hay et al., 1988).

Ore bodies are stratabound on a district scale, restricted to particular units, but are commonly highly discordant on a deposit scale. Rarely, they have high aspect ratios, more akin to the stratiform morphology of SEDEX deposits. Their highly varied forms reflect the interplay of a number of factors, including fault and sediment facies-controlled permeability and pre-ore dissolution patterns (Leach et al., 2005). Mineralization is commonly located where permeable aquifers pinch out or are intersected by faults (Cathles and Adams, 2005). A notable feature of MVT deposits is their tendency to occur as clusters of relatively small deposits in larger districts so that the economics of extraction may be dependent on having access to multiple ore bodies.

Regional geochemical anomalies have been identified in some of the carbonate sequences hosting MVT deposits (e.g., Erickson et al., 1983), attributed to long-distance flow of mineralizing solutions. However, primary metal dispersion halos may only extend a few tens of meters from individual ore bodies (Leach et al., 2010). Metal zoning patterns are notably absent in most deposits, and, where present (such as in Southeast Missouri), they are highly irregular (Hagni, 1983). This contrasts markedly with the well-developed metal zoning observed in Irish-type and SEDEX deposits.

13.9.3.5   Fluid Sources

The similarity between MVT ore solutions and oilfield brines was recognized when fluid inclusion data were first acquired from MVT ore and gangue minerals (Hall and Friedman, 1963; Roedder, 1967). Since then, numerous studies have shown that most MVT ores formed from fluids with quite a narrow range of properties. The bulk of the homogenization temperature data from sphalerite fall in the range 70–170 °C (Leach et al., 2005) if the Irish deposits and Gays River (a similar-age system that would have been close to the Irish ore field pre-Atlantic) are excluded from this class. Assuming depths of formation do not exceed a few kilometers, these values will be within a few tens of degrees of fluid-trapping temperatures. Salinities mostly range between 13 and 28 wt% with a few notable exceptions displaying lower values, including the Bou Grine salt diapir deposits, the Bleiberg deposits (considered by some to be syndiagenetic deposits and not of MVT affinity), and Upper Silesia in Poland.

The sedimentary brine character of fluid inclusions naturally led to the view of the origin of MVT deposits as a normal part of sedimentary basin evolution (Jackson and Beales, 1967). In this model, connate brines were thought to evolve into ore-forming solutions during burial and heating, extracting metals and sulfur from the rocks in which they were trapped and/or from aquifers they migrated through. Although this model is now widely implicitly or explicitly accepted in the literature (e.g., Leach and Sangster, 1993), two key problems have remained unanswered: (1) how the metals are taken up into solution to form fertile ore fluids (e.g., Sverjensky, 1986) and (2) why there are differences in solute chemistry between MVT ore fluids as trapped in fluid inclusions and typical basinal brines (Hanor, 1996). In particular, oilfield brines have low base metal content at the low temperatures of MVT ore formation, mostly below 100 ppm and commonly below 1 ppm (Hanor, 1996). Metal-poor brines are generally characterized by elevated levels of H_2S or SO_4^{2-} ($>\sim 10$ ppm and $>\sim 200$ ppm, respectively).

The source of solutes in MVT mineralizing fluids has been established by analyzing the composition of fluid inclusions in bulk samples by crush–leach methods (e.g., Kesler et al., 1996; Viets et al., 1996). Although this approach has the inherent problem of possibly mixing different generations of fluid and thereby producing data suggestive of geologic mixing trends, the results support derivation of fluids from evaporation of seawater (Figure 6). The majority of the data are consistent with moderate to strong evaporation, often past the point of halite precipitation, to yield Br-enriched bittern brines. Some
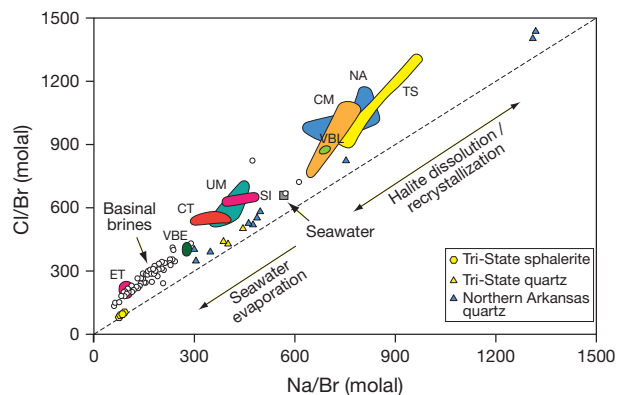

Figure 6   Halogen geochemistry of MVT fluids from the Tri-State and northern Arkansas districts measured by laser ablation ICP-MS of individual fluid inclusions (colored symbols; Stoffell et al., 2008) in quartz and sphalerite compared with bulk crush–leach results from a variety of MVT districts (colored fields; Viets et al., 1996) and basinal brine data (Carpenter et al., 1974). CM = Central Missouri, CT = Central Tennessee, ET = East Tennessee, NA = Northern Arkansas, SI = Southern Illinois, TS = Tri-State, UM = Upper Mississippi Valley, VBE = Viburnum (early), VBL = Viburnum (late). Laser ablation data indicate not only the predominance of Br-enriched bittern brines but also the presence of halite dissolution brines in some quartz-hosted inclusions. Bulk analyses from the same districts only gave halite dissolution brine signatures with the exception of Viburnum East (early). Modified from Stoffell B, Appold MS, Wilkinson JJ, McLean NA, and Jeffries TE (2008) Geochemistry and evolution of MVT mineralizing brines from the Tri-State and Northern Arkansas districts determined by LA-ICP-MS microanalysis of fluid inclusions. *Economic Geology* 103: 1411–1435.

data have Cl/Br ratios above seawater values, indicating a small component of the brines may have been derived from halite dissolution (e.g., northern Arkansas). More recent data from single-fluid inclusion analysis by laser ablation ICP-MS have clarified this picture, with results from sphalerite from northern Arkansas confirming the Br-rich bittern brine origin of primary ore fluids. These data do not require any component of halite dissolution water, so the conclusion from bulk analyses could be an artifact due to the analysis of mixed inclusion populations. Significantly, data from single inclusions in quartz from the Tri-State district revealed a less strongly evaporated signature (just past the point of halite precipitation) and evidence for a component of halite dissolution water pointing to different fluid origins for ore and gangue minerals (Stoffell et al., 2008).

13.9.3.6   Metal and Sulfur Sources

A key observation with regard to the origin of metals for MVT deposits is that the galena in many systems is enriched in radiogenic isotopes (Joplin (J)-type Pb). However, it was also noted early on that J-type lead is not present in some deposits classified as MVT, such as Pine Point, the Pennines of England, and Silesia in Poland (Heyl et al., 1974), which had Pb isotope signatures more like the SEDEX deposits of Europe. A second key point is that different deposits or districts within one basin (e.g., US midcontinent and Lennard Shelf) often have different Pb isotope signatures and/or zonation patterns. This suggests variable mixing of at least two sources of lead. In the United States, this includes a more radiogenic component thought to be derived from felsic, chemically evolved basement (Precambrian granitic rocks) and/or sediments derived from these rocks (Paleozoic sandstone aquifers such as the Lamotte Sandstone) and a less radiogenic component coming from carbonate cements and feldspars in the host rocks (Doe and Delevaux, 1972). A final important observation from the US midcontinent is that Pb and S isotopes are decoupled in some deposits and may vary throughout the mineral paragenesis in individual districts, pointing to multiple, discontinuous inputs of metals and sulfur from isotopically distinct sources (Deloule et al., 1986). Even where correlated variations between isotopes were observed, they were interpreted in terms of precipitation from several, isotopically distinct solutions (Sverjensky, 1981). The common heterogeneity of Pb isotope compositions in many MVT deposits is quite a distinctive feature that sets the class apart from SEDEX and Irish-type deposits and is perhaps one of the keys to understanding the differences in ore genetic processes between them.

New light has been shed on the origin of metals in MVT deposits from LA-ICP-MS analysis of metals in fluid inclusions. In their analyses of sphalerite-hosted inclusions, Stoffell et al. (2008) showed that these contained significantly higher metal concentrations (up to 400 ppm Pb) than those found in apparently coexisting gangue phases (up to 12 ppm Pb). This result was subsequently confirmed by Appold and Wenz (2011) and Wenz et al. (2012) in their extensive study of mineralizing fluids of the Ozark Plateau. This challenges the common assumption that intergrown phases in the same sample were formed from the same hydrothermal fluid and

suggests that sulfides were precipitated during episodic influxes of metalliferous fluids into systems that may have been non-mineralizing for much of their existence. Measured (Pb) and inferred (Zn) concentrations were at least an order of magnitude higher than most previous measurements, meaning that the fluid volumes required to form deposits are potentially much smaller and that timescales of ore formation can be much shorter than previously thought. This has important implications for models of MVT ore genesis as explored in the succeeding text.

To explain the existence of reservoirs of metal-rich brines with a Br-enriched signature, Wilkinson et al. (2009a) proposed that the development of low-pH surface brines in the US midcontinent via sulfide oxidation (Counter Benison et al., 1998) could have produced highly acidic solutions that were stored in sulfide-free rock packages, resulting in buffering to unusually high oxygen and low sulfur fugacities. Furthermore, the presence of reactive oxidized iron could remove reduced sulfur from passing fluids via sulfidation reactions (e.g., Emsbo, 2000). This environment would therefore provide optimum conditions for extraction of base metals from detrital phases at elevated temperatures. The restriction of such sedimentary packages to particular stages of basin evolution would mean that these fertile reservoirs would be quite limited in time and space and that there would only be certain stages of basin evolution when fertile brines were released from them.

This model challenges the conventional view in the literature that the solubility of base metals in chloride-rich MVT brines is reasonably well known. This view has been based on the premise of equilibrium with carbonate rocks (Plumlee et al., 1994) and either infers sulfur and redox conditions based on typical sedimentary basin conditions or estimates reduced sulfur content, assuming equilibrium with base metal sulfides and 'known' base metal concentrations (by analogy with oilfield brines). Very high base metal concentrations require very low reduced sulfur content in the ore-forming solutions (e.g., Appold and Wenz, 2011), and this in turn means that single-fluid models for metal transport and ore deposition are not viable unless the fluids are oxidized. Fluid mixing as a control of ore mineral precipitation, in which metal-rich brines mix with brines rich in H_2S at the depositional site (Anderson, 1975; Cooke et al., 2000; Corbella et al., 2004), is therefore more likely. The alternative, of local sulfate reduction at the depositional site, is possible, but deposition rates will be limited by the sulfate reduction mechanism and this process is unlikely to explain the fine-grained and dendritic textures that are indicative of rapid supersaturation. Analyses of gases in sphalerite- and gangue-hosted fluid inclusions suggest that reducing conditions prevailed during ore and gangue mineral precipitation (Wenz et al., 2012), consistent with the involvement of a reduced, H_2S-rich fluid at the site of ore deposition. Limited evidence for salinity variations in fluid inclusion data can be accounted for if the H_2S-rich fluid is also a brine.

Based on their sulfur isotope data compilation for MVT deposits, Leach et al. (2005) stated that bacteriogenically derived reduced sulfur with negative $\delta^{34}S$ is common. However, if one excludes the systems where the MVT classification is controversial (i.e., excluding Irish- and Alpine-type deposits; see
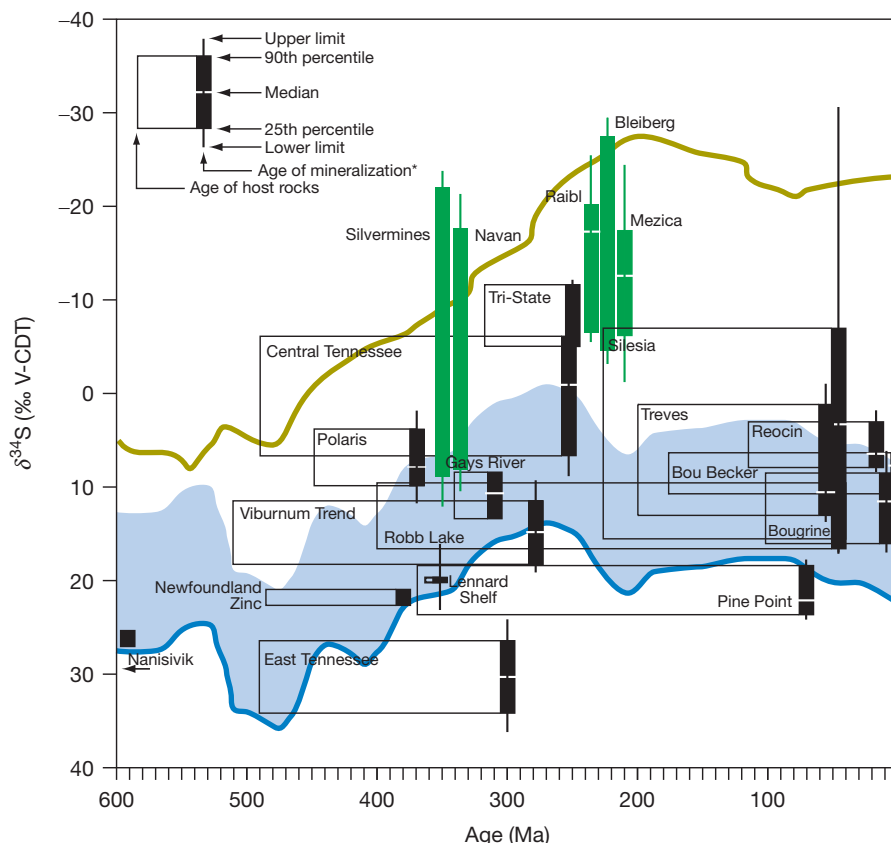
Figure 7 Diagram illustrating range and median $\delta^{34}S$ values of sulfides in a selection of MVT deposits plotted in relation to age of host rocks and inferred ages of mineralization (*as proposed by Leach et al. 2005), marine sulfate composition (blue line), and mean sedimentary pyrite composition (olive line) as produced by BSR. The blue-shaded field indicates the likely range of sulfide compositions produced by TSR of seawater-derived sulfate at 150 °C (Kiyosu and Krouse, 1990). Sulfur in most MVT deposits is consistent with an origin from seawater sulfate, reduced by TSR. The deposits shown in green, positioned at their host-rock ages, are Alpine- and Irish-type deposits that are not here regarded as MVT deposits. The predominance of BSR-derived sulfur in these systems supports a syndiagenetic origin. Data compiled in Leach et al. (2005). Sulfur isotope curves from Farquhar et al. (2010).

Section 13.9.4.1), subzero $\delta^{34}S$ values are only present in a few deposits (Figure 7). The majority of $\delta^{34}S$ data from MVT deposits are positive, widely attributed to an ultimate seawater origin involving sulfate reduction (e.g., Anderson and Macqueen, 1982).

Comparison of deposit sulfide compositions with inferred deposit age, host-rock age, and the secular seawater sulfate curve (Figure 7) shows that most MVT deposits can derive their sulfide from seawater sulfate by TSR, either directly from brines or from dissolved evaporites that were incorporated in the sedimentary basin at some time between host-rock deposition and mineralization. Production of sulfide by TSR from sulfate or sulfate-bearing fluids in the rocks hosting mineralization would appear to be most likely, given the constraints on metal and sulfur cotransport noted earlier.

There are a few anomalies in the simple pattern of involvement of sulfate derived essentially internally from the basin hosting mineralization. MVT deposits with $\delta^{34}S$ values above ambient seawater at any time between host-rock deposition and mineralization (Pine Point, East Tennessee) can only be explained by mobilization of much older, Lower Paleozoic brines if the paleomagnetic ages for these deposits quoted by Leach et al. (2001) are accepted. However, it is worth noting

that the very large time gap between the age quoted for Pine Point (71 ± 13 Ma; Symons et al., 1993) and the last time at which the requisite heavy sulfate could have been generated by a common process (mid-Devonian, ~380 Ma), would seem to make a Paleocene timing for mineralization in this deposit unlikely, and a Devonian or Carboniferous age easier to sustain. Likewise, an Acadian (Kesler and Carrigan, 2002) or even Taconic age for the East Tennessee deposits is more consistent with the sulfur isotope data.

Those deposits containing a proportion of sulfide with $\delta^{34}S$ values below the seawater−15‰ curve (Silesia, Tri-State, Central Tennessee, and Polaris) are likely to have derived a portion of their sulfur from bacteriogenically reduced sulfate, probably by reworking of sedimentary pyrite. However, in most cases, this source is unlikely to form more than about 10% of the total S.

13.9.3.7 Secular Variation in the Abundance of MVT Deposits

As noted earlier, MVT deposits are epigenetic stratabound deposits that can form in lithified carbonate host rocks of any age although they are particularly prevalent in the Phanerozoic.

The common lack of geologic constraints on timing of mineralization is compounded by the fact that they are difficult to date with isotopic methods because the minerals that typically occur contain low abundances of useful radioactive isotopes (Bradley and Leach, 2003). Paleomagnetic dating has been used as an alternative but, as well as being relatively imprecise, the ages obtained are often in disagreement with radiometric methods and geologic constraints where they exist. This has led to significant controversy in the literature (e.g., Bradley et al., 2004; Kesler and Carrigan, 2002; Kesler et al., 2004; Leach et al., 2002). Both methods suffer from problems: radiometric dating primarily due to uncertainties about the purity of ore mineral separates; paleomagnetism because of question marks over what event is being dated – primary mineralization or unrelated, later fluid flow events.

In a review of the ages of Paleozoic MVT deposits, Leach et al. (2001) pointed out that there appear to be two major episodes of ore formation, one in the Devonian–Permian and the other in the Cretaceous–Tertiary (Figure 8). These were explained in terms of a relationship between MVT ore-forming processes and supercontinent assembly cycles, namely, the formation of Pangaea and the Alpine-Laramide assimilation. A late Paleozoic peak in MVT (and SEDEX) ore genesis is well established in the literature (e.g., Barley and Groves, 1992), but the latter peak is more obscure and, in the compilation of Leach et al. (2001), is somewhat dependent on paleomagnetic ages for Pine Point, Silesia, Robb Lake, and Monarch-Kicking Horse. The first two of these have much older radiometric dates, so a Tertiary origin is by no means a given.
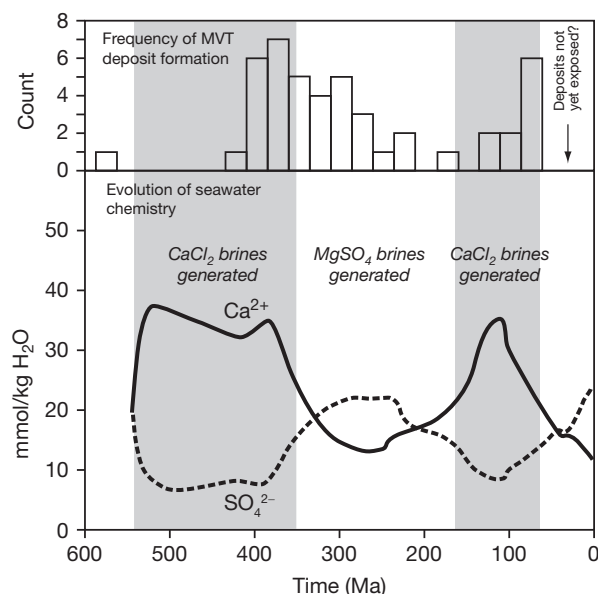

Figure 8 Frequency of Phanerozoic carbonate-hosted Zn–Pb deposits (data from Leach et al., 2001) compared with ocean chemistry (from Lowenstein et al., 2003), showing that peaks in mineralization occur following periods when the oceans were conducive to production of $CaCl_2$-rich brines on continental margins. Adapted from Farquhar J, Wu NP, Canfield DE, and Oduro H (2010) Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal VMS, SEDEX, and MVT deposits. *Economic Geology* 105: 509–533. With permission from the Society of Economic Geologists.

The predominance of MVT deposits in the Phanerozoic has been linked to the development of extensive carbonate platforms – providing the host-rock sequences – and the rise of seawater sulfate from low levels in the Proterozoic (Farquhar et al., 2010; Kesler and Reich, 2006). However, the major periods of MVT ore formation coincide with increasing sulfate rather than maximum sulfate levels (Lowenstein et al., 2003), and besides, the fluids involved in MVT ore genesis do not have to be of similar age to the deposits and may reflect the chemistry of earlier seawater-derived brines trapped within precursor basins (see Figure 7). It is interesting to note that the MVT-prone periods are immediately preceded by times in which the oceans are argued to have been dominated by $CaCl_2$ rather than $MgSO_4$ (Lowenstein et al., 2003). Thus, rather than being controlled (just) by collisional tectonics and supercontinent assembly, there may be a fundamental ocean chemistry control on the production of brines capable of evolving into fertile ore fluids, as suggested for SEDEX ore fluids (see Section 13.9.2.7).

A secular brine chemistry control on MVT deposit genesis is consistent with the fact that deposits can form in a number of tectonic settings, not just those associated with the forelands of orogenic belts (Bradley and Leach, 2003). It could also explain the lack of significant MVT deposits in some basins that would otherwise appear to meet the required source–transport pathway–trap conditions.

The general lack of MVT deposits in the Archean and Proterozoic has been commented on in several studies (e.g., Farquhar et al., 2010). Although extensive carbonate platforms were developed in the Paleoproterozoic, they are not considered to present favorable host rocks because of low permeability linked to early diagenetic dolomitization and silicification, as well as a lack of bioturbation and coarse skeletal carbonate debris (Grotzinger, 1989). Nonetheless, one might expect structurally controlled systems to be more prevalent. The operation of plate tectonics at this time also means that potential fluid drive mechanisms were available, although the transition to modern platform carbonate sedimentation and tectonics in the Neoproterozoic was suggested as the principal reason for the appearance of MVT deposits by Leach et al. (2005). An alternative possibility is that Precambrian seawater compositions did not favor the generation of metalliferous brines or sulfur-bearing, carbonate host-rock sequences. Limited data (Brennan et al., 2004) suggest that the Neoproterozoic was characterized by $MgSO_4$ seas, rather similar to the present day, and therefore perhaps not supporting low-sulfur brine generation. The first inferred rise in oceanic Ca and Cl concentrations at the start of the Cambrian coincides with the appearance of the earliest 'typical' MVT deposits.

13.9.3.8 Fluid Flow Mechanism

The presence of MVT deposits in orogenic forelands has been frequently attributed to the long-distance lateral migration of basin brines driven by gravity or topographically driven flow away from a collisional orogen (e.g., Leach and Rowan, 1986), a process that has been extensively modeled (e.g., Garven and Freeze, 1984). This widely accepted model requires a regional surface gradient from the mountain belt into the foreland region, which can only be developed in an overfilled foreland basin that has emerged above sea level (Figure 5). This

environment at the time of mineralization, with ore formation occurring at several kilometers depth in the crust beneath a terrestrial depositional system, contrasts with the submarine, near-seafloor setting (and potential involvement of contemporaneous seawater) that is argued to be the case for SEDEX and Irish-type deposits. This model is also inappropriate for deposits commonly classified as MVT but which occur in extensional basin settings, such as Reocin and Troya in Spain, the Canning Basin deposits in Australia, Toussit Bou-Becker in Morocco, and possibly Pine Point.

Numerical modeling (Appold and Garven, 1999; Appold and Nunn, 2005; Garven et al., 1993) has shown that typical temperatures of MVT ore formation can be achieved by topographic flow. The large fluid velocities generated in these models generally removes any problem with supplying the required fluid volumes. This has led to the widespread acceptance of gravity-driven flow for MVT genesis and thus the implicit genetic relationship with uplifted orogens. However, a number of complexities emerge in the models, such as the fact that multiple pore volumes of fluids are required to pass through deep-basin aquifers to advect sufficient heat to the basin margin. Consequently, if meteoric recharge occurs in the mountain belt, saline brines resident within the basin will be flushed out, placing quite narrow time constraints on the period during which discharge of elevated temperature brines is feasible (Appold and Garven, 1999). In general, an evolution from early brines to later dilute fluids is not observed, which would be an obvious prediction of the topographic flow model. One possibility is that evaporative brines were continually being produced from seawater during the period of groundwater flow and that these provided the recharge to the topographic flow system (Rowan and de Marsily, 2001). However, it is hard to envisage how ambient seawater-derived brine recharge could have taken place because this needs to occur toward the 'top' of the gravitational flow system in the region of most uplift, well above sea level. Furthermore, the requirement of a regional slope from the mountain belt to the deposits in order to maintain long-distance lateral flow precludes the existence of a marine basin and therefore makes synmineralization marine brine recharge unlikely. Nonetheless, the reduced fluid volume requirements implied by the existence of highly metalliferous fluids mean that the active period of mineralization could be tied to the early stages of topographic flow, prior to connate brine dispersal, but the heat advection problem remains.

An alternative mechanism that has received scant attention in recent literature is the possible role of basin dewatering in driving mineralizing solutions. Early calculations (Cathles and Smith, 1983) showed that gradual dewatering during compaction was not a viable mechanism to produce observed fluid temperatures at the assumed depths of ore formation. However, if pore fluid expulsion was episodic and occurred over only a very small fraction (≤1/1000th) of the basin subsidence history, then flow velocities were sufficient for adequate heat to be advected.

Arguments against this model include the relatively small (but unspecified) volumes of fluid involved and the fact that the principal aquifer along which fluids were expelled must be quite thin (also unspecified). These were considered to limit the scope for development of the widespread elevated fluid temperatures, as recorded, for example, in fluid inclusions in the US midcontinent (Coveney et al., 1987; Leach and Rowan, 1986). However, the recent measurement of orders of magnitude higher metal contents in fluid inclusions than previously considered likely allows for much smaller volumes of ore fluid to be involved in mineralization. Furthermore, the distinct geochemical character and regional heterogeneity of these metalliferous fluids (e.g., Kesler, 1996) argue for the involvement of discrete sedimentary reservoirs in their generation. As noted by Cathles and Smith (1983), many of the distinctive characteristics of MVT deposits, including the cycles of ore deposition interspersed with dissolution, rhythmically banded sphalerite, and apparent coincidence of mineralization, brecciation, and minor deformation (Ohle 1980), can be naturally accounted for by pulses of fluid expulsion. It has been suggested that the intermittent dissolution stages were caused by long periods in which influx of cooler, near-surface fluids occurred (Cathles and Smith, 1983), analogous to the barren phases of hydrothermal system evolution referred to by Stoffell et al. (2008) and Wilkinson et al. (2009a). If the upwards of 50 dewatering episodes proposed by Cathles and Smith (1983) are plausible, then the widespread observation of elevated fluid temperatures is conceptually understandable, if not quantitatively supported.

The episodic dewatering model has some interesting wider implications: for fluids to be trapped in overpressured domains, the basin must contain abundant units with very low permeability (e.g., shale); in such situations, the permeability will be so low as to preclude free convection, meaning that this mechanism is clearly separated from that which has been proposed for SEDEX and Irish-type deposits. Although there is clearly no a priori reason why this should be a requirement for an MVT flow model, distinct flow mechanisms can obviously help to explain some of the divergence in character of these deposit classes. Further modeling studies are warranted to assess whether episodic dewatering is viable, given the new knowledge of the surprisingly metal-rich and probably temporally restricted character of the ore-forming fluids.

13.9.3.9 Genetic Model

MVT systems present a difficulty when proposing a single genetic process model because of the diversity of styles and tectonic settings of deposits currently included in this class, even when controversial cases such as the Irish system are excluded.

If just the deposits formed in platform carbonates in orogenic forelands (as in the type areas of the US midcontinent) are considered, then the consensus is that continental-scale migration of brines resident in the foreland basin sequence was the primary driver of mineralization in carbonate rocks along the basin margins. Fluid inclusion data confirm that relatively low-temperature brines, similar to modern basinal brines, were involved in probably all 'typical' MVT deposits, although lower-salinity fluids were present in some systems that could be excluded from the MVT class on the grounds that they did not form in comparable environments (e.g., salt diapir deposits). However, metal contents of ore fluids are now thought to greatly exceed those measured in almost all modern brines, implicating source regions for MVT brine genesis that are atypical of basins in general. This casts some doubt on a 'normal' crustal-scale brine migration model (e.g., Bethke and

Marshak, 1990) and is in accord with the statement by Leach et al. (2001) that "in view of their restricted spatial and temporal distribution in the crust with respect to the variety of geological and geochemical controls known to form MVT lead-zinc deposits, we suggest that MVT deposits are not simply the products of the 'normal evolution' of sedimentary basins."

Many authors consider gravitational potential energy from a raised water table associated with deformation-induced topography to be the energy source for fluid flow. However, in the Ozark region, a simple northward migration away from the Ouachita Mountains does not easily account for the mineralogical (Leach et al., 2005) and fluid chemical (e.g., Shelton et al., 2009) variability observed between MVT districts in the same belt. Evidence for a northward decrease in temperatures (Bethke et al., 1988) is weak, and marked thermal anomalies exist that do not fit this pattern, such as in the Reelfoot Rift (Leach et al., 1997) and in the Upper Mississippi Valley where high heat-producing granites have been proposed as a heat source and principal fluid driver (Spirakis and Heyl, 1996).

Given the recent evidence for episodic introduction of metalliferous brines into mineralized districts (Appold and Wenz, 2011; Stoffell et al., 2008; Wenz et al., 2012; Wilkinson et al., 2009a,b), it is suggested that episodic expulsion of fluids from more proximal overpressured shale sequences should be reconsidered, as has been previously proposed (e.g., Fowler, 1994) and successfully modeled for the Lennard Shelf deposits of Australia (Garven and Wallace, 2009). Even a small sandstone reservoir within a geopressured shale (like the Abbeville area, Louisiana) could contain $4 \times 10^8 \, m^3$ of brine (Fowler, 1994), and if this contained concentrations of ~ 5000 ppm Zn (Wilkinson et al., 2009a), then 2.4 Mt Zn would be stored in this compartment. This is sufficient metal to account for 100 of the 110 MVT deposits listed in the global compilation of Leach et al. (2005). Of course, extremely efficient focusing and precipitation would be needed to deliver all of this metal to the deposit site, but, on the other hand, this simple calculation ignores the fact that if a geopressured shale ruptures, the permeable sandstone can supply much more fluid that just that which it contains, draining the surrounding shale for up to seven times its own radius.

Rapid subsidence is a requirement for the development of overpressured zones. Consequently, this model can still account for the observed temporal relationships between mineralization and orogenesis (e.g., Leach and Rowan, 1986) because of the accelerated foreland basin subsidence that will accompany encroachment of the orogenic front, particularly in the earlier phases of collision. It can also explain those MVT-like deposits that occur in extensional basins where no compressional orogen was anywhere nearby (e.g., Lennard Shelf and Nanisivik). Episodic dewatering does not exclude coincident regional topographic flow; indeed, the contradictory timescales inferred for thermal pulses linked to mineralization (tens to hundreds of thousands of years) as opposed to the lifetimes of gravity flow systems of up to tens of millions of years (Leach et al., 2001) are entirely consistent with the operation of both flow mechanisms.

Many ore precipitation models have been considered for MVT systems, including single-fluid (carrying both metals and sulfur, or with sulfide acquired at the depositional site) and fluid mixing variants (Leach et al., 2005). Numerical models generally show that fluid mixing is the most effective process for generating significant mineralization (Appold and Garven, 2000; Corbella et al., 2004; Garven and Raffensperger, 1997). The observation of high metal concentrations in ore fluids precludes significant sulfur cotransport (unless the pH was below typical crustal fluid values) so that local derivation of sulfide at the depositional site is required. Sourcing from local host rocks is possible, but it is suggested that mixing of metalliferous brines with sulfidic brines or sour gas is likely to be the key mechanism for the generation of large ore bodies. Sulfur isotope data are generally consistent with derivation of sulfur either from thermochemically reduced sulfate of similar age to the host rocks of the mineralization or from thermochemically reduced sulfate present in brines that predate host-rock deposition and that were flushed into the host-rock sequence from deeper and older aquifers.

MVT deposits are principally a Phanerozoic phenomenon, reflecting a range of factors, including the development of extensive, relatively permeable carbonate platforms, and processes linked to supercontinent assembly cycles. In addition, it is suggested that the secular evolution of seawater chemistry may have played a role in generating low-sulfur, metal-prone brines in the Cambrian–Carboniferous and Jurassic–Cretaceous that were subsequently mobilized at various times in the following ~ 100 Ma to form MVT mineralization. Climate, paleolatitude, and sea level may also have played a role, with the flooding of continental shelves by warm shallow seas in low latitudes producing the right conditions for the genesis of strongly evaporated residual brines that appear to be the predominant protore fluids.

13.9.4 Irish-Type Zn–Pb Mineralization: A Transitional Ore Type?

13.9.4.1 Introduction

The Lower Carboniferous carbonate rocks of central Ireland are host to significant Zn–Pb–Ba mineralization (~ 20 Mt contained $Zn+Pb$) that has been exploited for nearly 50 years. In terms of their origin, the deposits have always been controversial, and research in the ore field has played an important role in the development of concepts of sediment-hosted base metal ore genesis (e.g., Russell et al., 1981). Early syngenetic models, including the influential extension and convection model of Russell (1978, 1986) and the stratal aquifer model of Lydon (1986), were discounted in the 1990s by a number of authors in favor of lateral topographic flow following the MVT model (e.g., Hitzman and Beaty, 1996). The past decade has seen an evolution of ideas as new regional datasets and analytical techniques have become available.

Globally, a number of other deposits have been classified as 'Irish-type' based on a range of similarities with the type examples in the Irish Midlands (Hitzman and Large, 1986). These include Reocin and Troya (Spain), Morro Agudo (Brazil), Gays River (Nova Scotia), and Prairie Creek (Australia). The 'Alpine-type' deposits also share a range of features with the Irish style of mineralization, including predominant stratabound–stratiform morphology and the dominance of sulfide produced by BSR (Figure 7; Kucha et al., 2001). These deposits present a variably different set of features than either of the other major

classes of sediment-hosted Zn–Pb deposits discussed here but are commonly classified as of Mississippi Valley-type with the distinction being regarded as merely "a philosophical choice between splitting a broad family of MVT ores into different types based on the diversity of deposit attributes or treating diversity as a feature of MVT deposits" (Leach et al., 2005).

It is argued here that acceptance of an MVT classification for the Irish-type deposits of the Irish Midlands and, by extension, other deposits with similar characteristics, fails to appreciate adequately the range of geologic features and associated genetic processes that exist within the spectrum of sediment-hosted Zn–Pb mineralization. Further, it is believed that the Irish deposits, even based on the classification criteria of Leach et al. (2005), have as much, if not more, in common with SEDEX deposits than MVT deposits. Thus, it is considered that the Irish-type deposits are an important transitional ore type that can provide a deeper understanding of the diversity of styles and processes of mineralization within the sediment-hosted Zn–Pb class. Key characteristics upon which the Irish-type classification is based are presented in Table 1 and are discussed in depth in a number of sources (Anderson et al., 1995; Andrew, 1993; Andrew et al., 1986; Bowden et al., 1992; Hitzman, 1995; Hitzman and Beaty, 1996; Kelly et al., 2003; Wilkinson, 2003, 2010).

13.9.4.2 Tectonostratigraphic Setting

In the Lower Carboniferous, the Irish ore field was located on the southern margin of Laurussia in a passive margin setting, separated from the approaching Gondwana supercontinent by the Rheic Ocean and eastern and western arms of the Theic and Paleo-Tethys oceans (Figure 9). These were separated by the Armorican continental plate, which was bordered by opposite-facing subduction zones (Matte, 2001). At this time, the Laurussian continental margin was undergoing dextral transtensional strain as a result of oblique convergence, resulting in widespread intracontinental basin development throughout northern Europe. The onset of Variscan shortening began in central Europe in the late Devonian, as Gondwana began to collide with the south Armorican margin and continued through to the late Carboniferous–early Permian with the final collision of Gondwana–Armorica and Laurussia.

The Irish Midlands Basin initiated in the Visean as a broad area of subsidence on the Laurussian margin. It was bordered to the south by the deeper-water, extensional fault-controlled, Munster Basin (Figure 10). A diachronous, northward transgression across the Old Red Sandstone continent led to the establishment of a shallow marine ramp environment across most of south and central Ireland by the Chadian (Figure 10), and it was at this time that the host rocks for the ore deposits were laid down. A rift event at this time, linked to transtensional reactivation of Caledonian structures in the basement (approximately N–S extension), led to breakup of the Midlands into horst and graben domains, which controlled the rapid lateral facies variations that characterize the remainder of the Carboniferous subsidence history (e.g., Hitzman and Beaty, 1996). As such, there are parallels with the evolution of SEDEX basins (see Section 13.9.2.2). This rift event also coincided with the onset of episodic volcanism in the Shannon Trough (Figure 11). The late Westphalian–Stephanian (~305–310 Ma) marked the cessation of subsidence and alkaline volcanism as Variscan compression began to invert the earlier

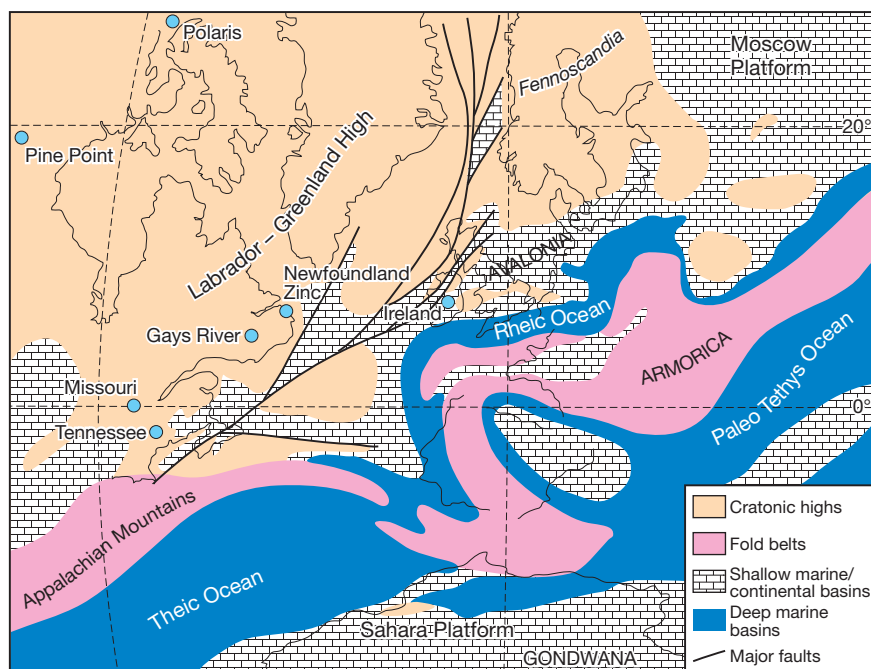**Figure 9**   Paleogeographic reconstruction of northwest Europe and northeast North America in the Lower Carboniferous showing the location of the Irish ore field and a selection of other carbonate-hosted deposits. Modified from Ziegler PA (1990) *Geological Atlas of Western and Central Europe*, 2nd edn. Amsterdam: Shell Internationale Petroleum Maatschappij B.V. With permission from The Geological Society of London.
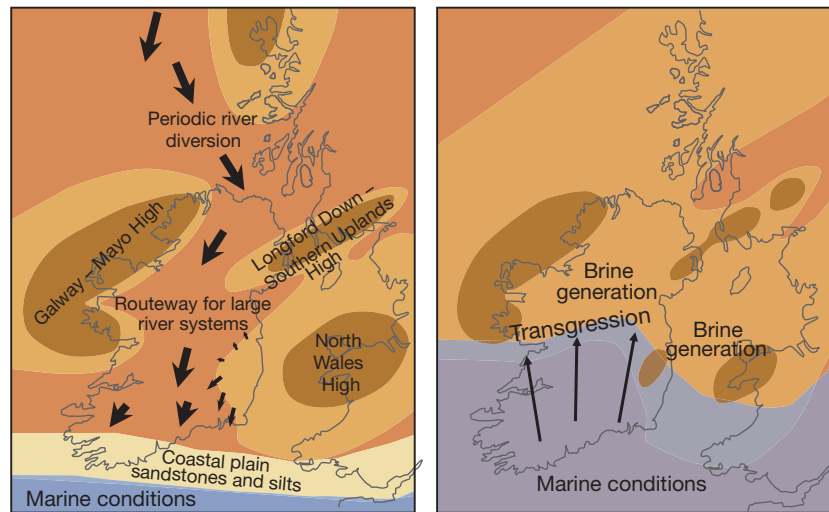
Figure 10   Paleogeographic reconstructions of Ireland and western Britain in the late Devonian (left) and early Carboniferous (right). Modified after Cope JCW, Guion PD, Sevastopulo GD, and Swan ARH (1992) Carboniferous. In: Cope JCW, Ingham JK, and Rawson PF (eds.) *Atlas of Palaeogeography and Lithofacies*, *Geological Society Memoir* 13, pp. 67–86. London: Geological Society of London. With permission from The Geological Society of London.

Figure 11   Map of Ireland showing major tectonostratigraphic elements.

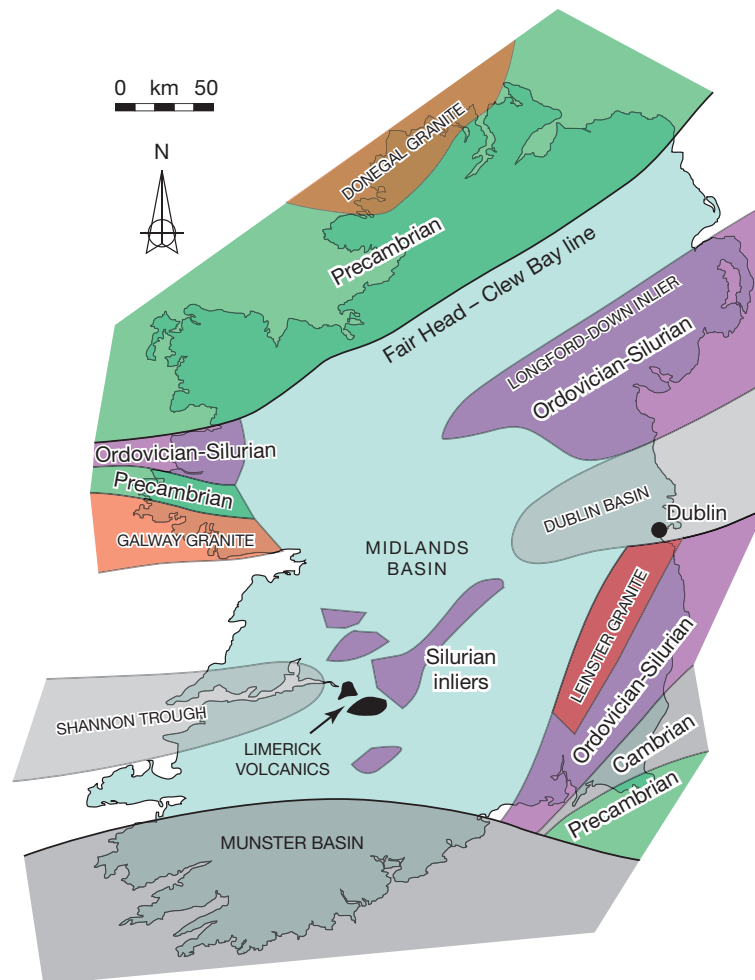basins (Woodcock and Strachan, 2012). This history highlights the short-lived nature of the Irish basin, which existed for only ~50 My. This is in marked contrast to the very long-lived and thick basinal sequences that characterize the Proterozoic SEDEX basins.

Zn–Pb mineralization is hosted by Lower Carboniferous (Dinantian) carbonate rocks, within both the Waulsortian Limestone Formation and the Navan Group – the first major non-argillaceous carbonate units in the transgressive sequence (Phillips and Sevastopulo, 1986). Beneath these rocks lie a thin package of red, terrestrial mudstones, sandstones, and conglomerates (Old Red Sandstone, ORS) that in turn unconformably overlies an eroded Lower Paleozoic volcanosedimentary succession that was deformed and underwent low-grade metamorphism in the Caledonian orogeny. A crystalline basement is inferred at depth in the Midlands area that probably comprises Grenvillian gneiss and schist to the northwest and late Precambrian, probably Avalonian, gneisses to the southeast.

The host rocks underwent early diagenesis, including extensive calcite cementation and dolomitization (Gregg et al., 2001; Lee and Wilkinson, 2002; Lees and Miller, 1995; Peace et al., 2003; Reed and Wallace, 2001; Wilkinson, 2003). It is widely considered that these processes initiated upon deposition of the carbonate sediments, with significant cementation occurring within a few tens of meters of the seafloor (e.g., Lees and Miller, 1995). Early dolomitization is pervasive in the southeastern Midlands (Gregg et al., 2001; Hitzman and Beaty, 1996; Nagy et al., 2004), possibly representing reflux dolomitization fringing the Leinster Granite massif (Figure 11). Ore-stage sulfides appear generally to postdate early marine calcite and dolomite cements and are themselves accompanied by a variety of replacive, breccia-cementing, and vein- and vug-filling calcite and dolomite, plus variable barite and minor quartz.

13.9.4.3 Structural Setting

The Irish deposits mostly developed on the margins of kilometer-scale subbasins controlled by synsedimentary faults. This paleogeography is still reflected today by the topography of the Midlands.

The geometry of the Waulsortian-hosted ore bodies is well established, controlled by a series of north- to northeast-dipping en echelon fault strands with mineralization located primarily as a series of stratiform–stratabound lenses in their hanging walls (Figure 12). The Navan deposit is more complex, sitting astride a complexly faulted anticlinorium with mineralization localized by both NW- and SE-dipping faults. The increasing recognition of low-angle faults and slides in the Navan and Lisheen (Carboni et al., 2003; Fusciardi et al., 2003) deposits confirms the intimate relationships between tectonism and sedimentation in the developing Carboniferous basins. Detailed observations show that the arising geometries have an important control on the local distribution of mineralization (Fusciardi et al., 2003).

13.9.4.4 Mineralization

Mineralization in the ore deposits principally occurs as massive sulfide displaying a complex range of textures. In subeconomic mineralization, a variety of massive, disseminated, laminated, and breccia- and vein-filling styles occur (e.g., Anderson et al., 1998; Ashton et al., 1986; Boast et al., 1981; Fusciardi et al., 2003; Hitzman et al., 2002; Lowther et al., 2003; Taylor, 1984; Wilkinson et al., 2005a). Ore minerals are dominated by sphalerite, galena, pyrite, and variable marcasite with minor chalcopyrite, tennantite, and other sulfosalts. Ore is normally associated with hydrothermal dolomite, calcite, economic to minor barite, and minor quartz. Hydrothermal alteration of
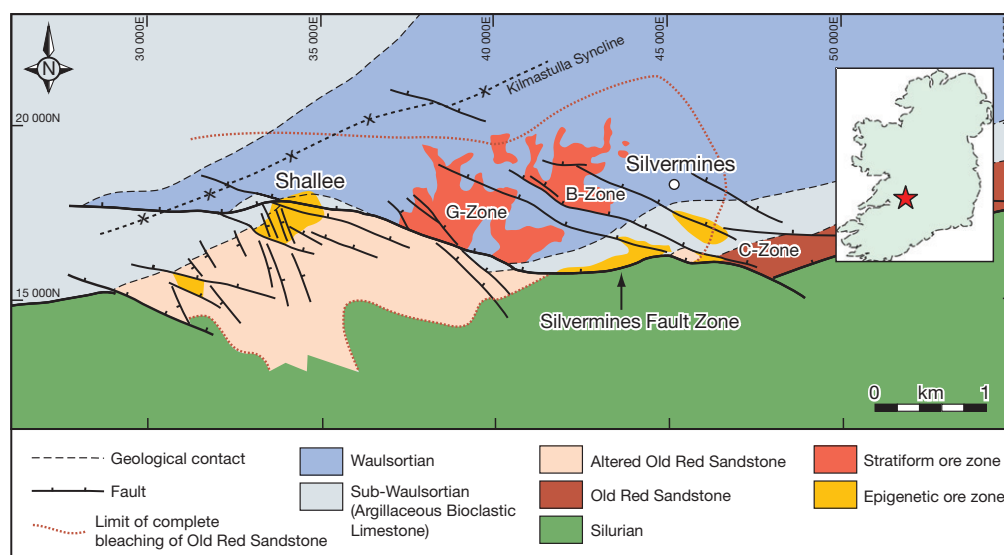
Figure 12 Simplified geologic map of the Silvermines district, in the southwest Irish Midlands, showing relationship of stratiform ore lenses to extensional faults and the axis of the Kilmastulla Syncline. Modified with permission after Andrew CJ (1986) The tectono-stratigraphic controls to mineralization in the Silvermines area, County Tipperary, Ireland. In: Andrew CJ, Crowe RWA, Finlay S, Pennell WM, and Pyne J (eds.) Geology and Genesis of Mineral Deposits in Ireland, pp. 377–417. Dublin: Irish Association for Economic Geology; Everett CE, Rye DM, and Ellam RM (2003) Source or sink? An assessment of the role of the Old Red Sandstone in the genesis of the Irish Zn-Pb deposits. *Economic Geology* 98: 31–50.

siliciclastic footwall rocks is characterized by the dissolution of hematite, development of fine-grained K-mica (which may be Li- or Ba-bearing), pyrophyllite, and, in places, hydrothermal K-feldspar overgrowth on detrital grains.

Ore bodies are broadly stratiform–stratabound and occur as single or multiple lenses hosted by permeable and/or reactive horizons within the host rocks. At Silvermines, this is a thick package of sedimentary debris flows that has been overprinted by hydrothermal activity (Andrew, 1986; Lee and Wilkinson, 2002). For the deposits of Lisheen and Galmoy, this is a breccia unit of variable thickness, located close to the base of the Waulsortian Limestone, interpreted to be of hydrothermal origin (Hitzman et al., 2002; Wilkinson et al., 2005a, 2011). At Navan, mineralization is commonly located within fractured micrites, in bioclastic grainstones having remnant porosity at the time of mineralization (Anderson et al., 1998; Peace et al., 2003), and within calcareous sandstones, in some cases below dolomitic siltstone/shale horizons that appear to have acted as aquicludes.

Metal zoning patterns are well developed in the ore bodies, typified by proximal/footwall enrichment in Cu, Ni, As, and Pb (e.g., Fusciardi et al., 2003; Wilkinson et al., 2005a). Fe-rich zones (pyrite and marcasite) typically occur at the tops of, and fringing, the ore zones. The Zn/Pb ratio increases outward and upward and also tends to increase with increasing Zn grade. An analysis of major and trace element dispersion patterns in hydrothermal alteration zones associated with ore (principally hydrothermal dolomite) showed that Ni and Ba are concentrated proximal to the thickest ore near the main faults and Mn displays a halo of enrichment on the fringes of the ore zones (Russell, 1974; Wilkinson et al., 2011). These patterns are considered to reflect the structural control of fluid flow via feeder faults and the strong chemical and thermal gradients developed as hydrothermal fluids migrated away from these conduits along the permeable host horizons. This is a characteristic feature of the Irish ores and is analogous to the zoning seen in SEDEX deposits (e.g., Goodfellow et al., 1993).

13.9.4.5 Fluid Sources

Extensive fluid inclusion studies in the Irish ore field (see Wilkinson, 2010, and references therein) show that fluid salinities range from 4 to 28 wt%, with the majority falling between 8 and 19 wt%. This variability is interpreted to be largely the result of mixing between moderate-salinity, metal-bearing fluids (the 'principal ore fluid') and low-temperature, high-salinity brines during ore formation. Homogenization temperatures range from 70 to 280 °C, with the majority falling between 130 and 240 °C and these values are considered representative of fluid temperatures at the site of ore formation (Wilkinson, 2010).

The origins of these fluids have been investigated by use of geochemical tracer studies. It was recognized several decades ago that the sulfur isotope composition of barite in the deposits ($\delta^{34}S = 14.1$–$22.6‰$; Andrew and Ashton, 1985; Boyce et al., 1983; Caulfield et al., 1986; Wilkinson et al., 2005a) was indicative of the involvement of Lower Carboniferous seawater sulfate, which declined from about 21‰ at the start of the Tournasian to about 12‰ in the late Stephanian (Kampschulte et al., 2001).

A seawater origin for the principal ore fluids was tested by analyzing the halogen composition of bulk-fluid inclusion samples using the crush–leach method. This can establish whether fluids were derived from seawater, evaporated seawater, or by dissolution of evaporites and potentially what interactions fluids from these origins might have subsequently undergone (e.g., Wilkinson, 2001). Samples included both feeder veins from beneath the deposits (Everett et al., 1999a) and gangue from within the deposits (Banks et al., 2002; Gleeson et al., 1999). The preservation of seawater Br/Cl ratios in samples that trapped primary ore fluids strongly supports a seawater origin, with elevated salinities indicative of partial (4–7 times) evaporation prior to crustal interaction (Figure 13). Samples that were dominated by higher-salinity, lower-temperature brine inclusions showed Br-enriched signatures
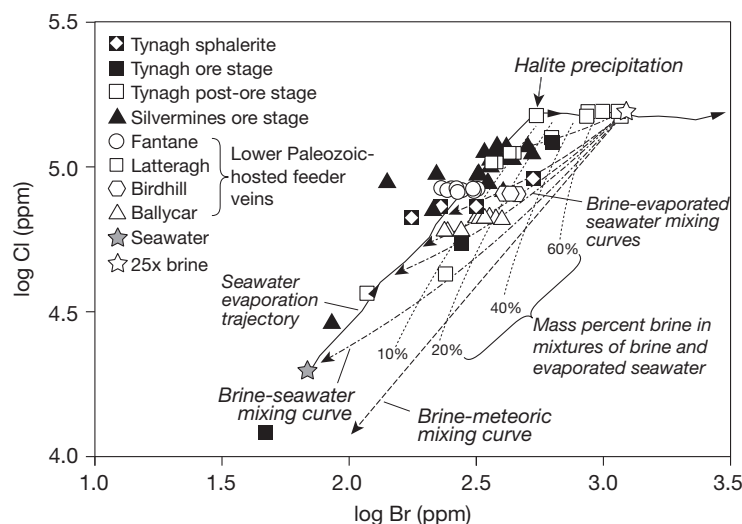

Figure 13 Halogen geochemistry of Irish fluids. Data from Everett et al. (1999b), Gleeson et al. (1999), and Banks et al. (2002). Modified from Wilkinson JJ (2010) A review of fluid inclusion constraints on mineralization in the Irish ore field and implications for the genesis of sediment-hosted Zn-Pb deposits. *Economic Geology* 105: 417–442.

indicative of evaporation past the point of halite precipitation, considered to reflect derivation from restricted or basin margin settings (Wilkinson, 2010). Evidence from the stratigraphic record in South Wales and southern England indicates the presence of restricted lagoons and hypersaline conditions at this time (Woodcock and Strachan, 2012).

The overall geochemistry of the ore solutions, including the hydrogen and oxygen isotope composition of the water, is consistent with seawater-derived fluids that underwent extensive exchange with crustal rocks at temperatures of ~ 200–$350\,°C$ (Everett et al., 1999a,b; Samson and Russell, 1987; Wilkinson, 2010; Wilkinson et al., 2005b). However, in detail, a complexity of fluid chemistry is apparent, explained in terms of a variety of evolution and mixing pathways within and beneath the host-basin sequence (Wilkinson, 2010). Significantly, the halogen–major element relationships suggest that loss of Na and Mg from the evaporated seawater occurred during crustal interaction, as observed in modern seawater hydrothermal systems and noted in hydrothermal experiments (Bischoff and Dickson, 1975; Bischoff et al., 1981). A range of elements are enriched in the principal ore fluids (in the order $Pb > Co > Fe \approx Mn > Ba \approx Zn > Li > Sr > Ca$) relative to the putative evaporated seawater precursor, consistent with the elements seen to be enriched in the ore and alteration zones and those mobilized in hydrothermal leaching experiments (Bischoff et al., 1981).

13.9.4.6   Metal and Sulfur Sources

The origin of lead (and, by inference, other metals) in the Irish ore field has been well constrained by isotope studies. Lead isotope analyses have demonstrated that there is a systematic variation in the isotopic composition of galena across the ore field (Figure 14) that mirrors the underlying Lower Paleozoic geology (Caulfield et al., 1986; Dixon et al., 1990; LeHuray et al., 1987; O'Keeffe, 1986). The variation in the Lower Paleozoic rocks is interpreted to be due to sedimentary mixing of Pb derived from weathering of the two continental blocks (Grenvillian and Avalonian) on either side of the Iapetus Ocean (Dixon et al., 1990). An alternative, that Pb was sourced from the clastic ORS, has been discounted based on its overly radiogenic signature and geologic arguments that it is unlikely to have acted as a continuous regional aquifer (Everett et al., 2003). The limited thickness of the Carboniferous basin itself and low metal content of the intrabasinal sediments rule this out as a viable source of metals on mass balance grounds (e.g., Lewis et al., 1995).

Strontium, carbon, and oxygen isotope data also point to sourcing of components from beneath the Carboniferous basin. Data from hydrothermal carbonates in the deposits fall on arrays that trend toward footwall veins and samples of Lower Paleozoic rocks (Everett, 1999; Wilkinson, 2003; Wilkinson et al., 2005b), interpreted in terms of isotopic exchange between upwelling hydrothermal fluids and the carbonate host rocks.

Assessment of the potential of Lower Paleozoic rocks as a source for metals has been investigated experimentally. Bischoff et al. (1981) carried out hydrothermal experiments on Irish graywacke samples at 200 and $350\,°C$ using both seawater and a brine. Metal extraction was highly efficient under the higher-temperature and higher-salinity conditions,
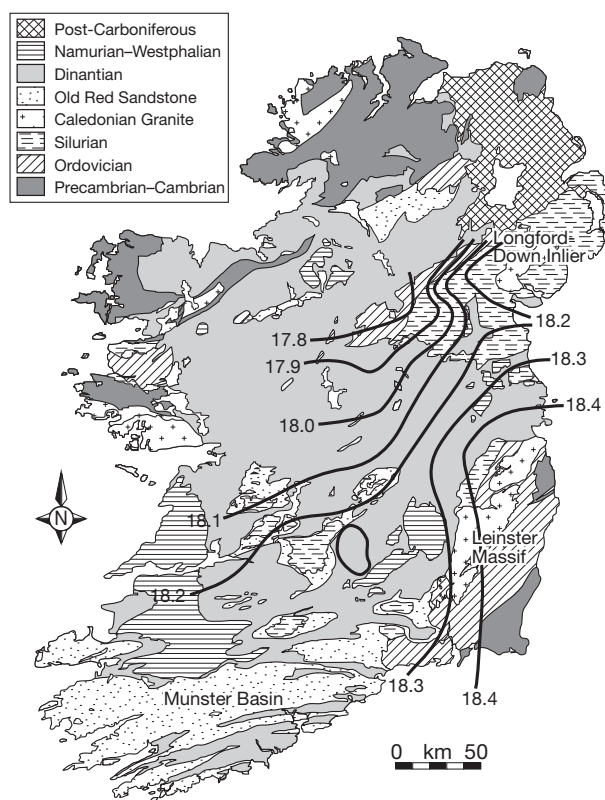

Figure 14   Contours of the average $^{206}Pb/^{204}Pb$ ratio in galena from different locations across the Midlands Basin. Modified with permission of the Society of Economic Geologists from Everett CE, Rye DM, and Ellam RM (2003) Source or sink? An assessment of the role of the Old Red Sandstone in the genesis of the Irish Zn–Pb deposits. *Economic Geology* 98: 31–50.

with significant leaching in the order $Pb > As \approx Mn > Sr \approx Ca > Zn > Cd \approx K > Co \approx Ni > Cr \approx Ba > Fe$ (Figure 15). Added to the rock were Mg and Na, as is observed in modern submarine hydrothermal systems (e.g., Bischoff and Dickson, 1975; see also Chapter 13.18). These experiments show that the graywacke–shale sequence underlying much of the Midlands Basin is a fertile source of the major and minor metals that are enriched in the ore deposits.

Although most tracers point to a Lower Paleozoic-dominated source, Nd isotope studies on hydrothermal carbonates from the Navan deposit suggest that interaction with crystalline basement occurred in this area (Walshaw et al., 2006), possibly due to its presence at shallower depth in the northern Midlands. The anomalous hydrogen isotopic composition of ore fluids from the Silvermines system could also be explained by fluid interaction with a previously deuterically altered crystalline basement (Wilkinson, 2010).

The Old Red Sandstone has been proposed as a source of metals in some models (e.g., Hitzman and Beaty, 1996; Lydon, 1986). Comparison of altered ORS samples from the Silvermines system (Figure 16) with unaltered samples shows that this footwall unit acted as a trap for hydrothermal Ca and Mn (calcite), Ba (barite), Li (probably Li-muscovite; Mallon, 1997), and Co and Cu (chalcopyrite). Pb is also variably added. This is consistent with the copper-rich (+barite and
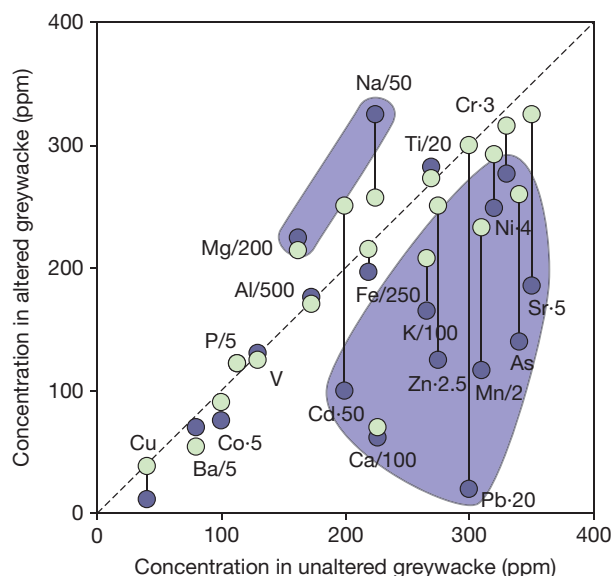
Figure 15 Results of experimental leaching of graywacke at 300 °C with seawater (light blue symbols) and brine (dark blue symbols). The shaded fields indicate the elements that are significantly added to the rock during hydrothermal interaction with brine (Na and Mg) and those extracted by the brine (Pb, Ca, Mn, As, Cd, Zn, Sr, K, Ni, and Cr). Data from Bischoff et al. (1981).
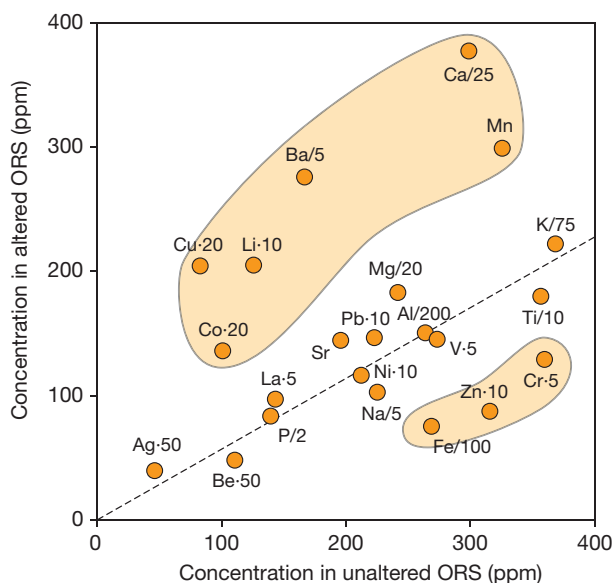

Figure 16 Comparison of altered and unaltered samples of Old Red Sandstone from the Silvermines area. The dashed line is the line of inferred no net change based on Al immobility. Shaded fields indicate elements that are significantly added to the rock during alteration (Cu, Li, Co, Ba, Ca, and Mn; above the line) and those that are removed and which could be added to the overlying mineralization (Fe, Zn, and Cr; below the line).

galena) vein mineralization that occurs in the Shallee area (Figure 12) and the characteristic zoning of the Irish deposits (feeder fault proximal Cu, Pb, and Ba). The principal elements stripped from the ORS during alteration and potentially added to mineralization from this source were Fe, Zn, and Cr.

Dissolution of grain-coating hematite is apparent from the locally intense bleaching of the sandstones, and the proportional loss of Zn and Fe suggests that Zn too was derived from oxide grain coatings. However, a mass balance estimate for the Silvermines area based on the known extent of alteration of the ORS (5000 × 2000 × 200 m) suggests that <2 to 8% of the Zn in the Silvermines ore bodies could have been derived from this source (Wilkinson et al., 2007).

The light isotopic composition of the majority of sulfide in the ore deposits has been extensively discussed in the literature (e.g., Anderson et al., 1998; Boyce et al., 1983; Caulfield et al., 1986; Fallick et al., 2001; Wilkinson, 2003; Wilkinson et al., 2005a) and is one of the very distinctive characteristics of the Irish deposits. The modal $\delta^{34}S$ of around −10‰ (e.g., **Figure 3**) is strongly suggestive (if not conclusively diagnostic) of open system bacteriogenic reduction of Carboniferous seawater sulfate. This is an important line of evidence that led to the development of early seawater convection models for mineralization (e.g., Boyce et al., 1983; Russell, 1978) and requires a close connection between the Carboniferous hydrosphere and the ore-forming environment in any viable genetic model.

13.9.4.7 Timing of Mineralization

The consensus in the recent literature is that formation of the major Irish ore bodies was due to hydrothermal fluid flow linked to limited ($\approx 5\%$) extension in the Lower Carboniferous. Based on a range of constraints, most activity appears to have occurred in the latest Courceyan–Chadian and late Chadian–Arundian stages (Hitzman and Beaty, 1996; Wilkinson et al., 2003), related to significant rifting events and concurrent volcanism (Woodcock and Strachan (2012).

Early studies of Tynagh, Silvermines, and Navan concluded that there was an exhalative component to the mineralization (Andrew, 1986; Ashton et al., 1986), and this is still considered likely by a number of authors based on the occurrence of spatially extensive finely laminated sulfides, fossils believed to be of chemoautotrophic organisms (Boyce et al., 2003), and stratiform barite (e.g., Wilkinson et al., 2003). However, extensive petrographic studies utilizing cathodoluminescence imaging have shown that the majority of ore-stage sulfides replace components of the carbonate host rocks. The depths at which replacement occurred are not well constrained, with suggestions ranging from near surface to a few hundred meters (Lee and Wilkinson, 2002; Wilkinson et al., 2005a,b, 2011) to >800 m (Reed and Wallace, 2001).

The onset of hydrothermal activity, at least in the Silvermines district, at the time of deposition of the basal Waulsortian (Courceyan) is supported by recent geochronology with a Rb–Sr isochron on sphalerite yielding a 360 ± 5 Ma age (Schneider et al., 2007). A similar Re–Os age on pyrite of 356 ± 5 Ma from the Lisheen Deposit (Hnatyshin, 2012) is also consistent with a small time gap between host-rock deposition and mineralization. The preponderance of surface-derived bacteriogenic sulfur in the majority of the deposits (Fallick et al., 2001) requires that mineralization must have developed sufficiently close to the ambient paleosurface to allow an adequate flux of sulfur to be supplied from this source (Wilkinson et al., 2003). As noted earlier, barite sulfate compositions are consistent with late Tournasian to

Visean seawater. These constraints are therefore strongly suggestive of the development of mineralization at relatively shallow burial depths.

Although arguments for mineralization in a near-seafloor environment have been widely presented, there are a number of lines of evidence to indicate that ore deposition continued during burial. For example, the predominance of hydrothermal sulfur, particularly toward the base of the Lisheen ore bodies (Wilkinson et al., 2005a), suggests that this mineralization developed at depths beyond the influence of surface sulfur input. Geologic and geochemical data suggest that the bulk of mineralization at Lisheen developed at depths of around 150 m beneath the paleoseafloor in the late Courceyan–early Chadian (Wilkinson et al., 2011). Such an extended duration of (potentially episodic) hydrothermal activity is supported by a Re–Os age of ≈ 340 Ma (Arundian) on pyrite from the Bog Zone at Lisheen (Creaser et al., 2009; Hnatyshin, 2012).

There is good geologic evidence that ore at Lisheen (Carboni et al., 2003) and at Navan (Ashton et al., 1986) is cut by thrusts related to Variscan tectonic inversion. This implies that mineralization had ceased prior to Variscan deformation at ~ 300 Ma (Wartho et al., 2006). This geologic constraint contradicts suggested paleomagnetic dates for mineralization as young as 269 ± 4 Ma at Silvermines (Symons et al., 2007). It is concluded that these young paleomagnetic ages reflect acquisition of chemical remanent magnetism during Variscan burial and fluid flow and cast doubt on the validity of this technique for dating sediment-hosted deposits of this kind (cf. Kesler and Carrigan, 2002).

13.9.4.8 Fluid Flow Mechanism

Over the past two decades, two competing models have been proposed to explain regional fluid flow and Zn–Pb mineralization in Ireland. The first invokes Variscan topography to the south of Ireland as a driver for south–north fluid flow and the ORS as a regional aquifer (Garven et al., 1999; Hitzman and Beaty, 1996; Murphy et al., 2008). This is essentially a variant of the model widely proposed for MVT deposit genesis in which mineralization is purely epigenetic, forming at moderate burial depth, in the hinterland of a major orogen. A late timing for mineralization is required for this model to be viable in Ireland because significant topography and a regional topographic surface gradient could not have existed while subsidence and marine sedimentation were occurring in the Munster Basin to the south (Figure 11). These would only have developed when continental collision and uplift occurred in the late Carboniferous. In combination with the Pb isotope data that exclude the ORS as a significant metal source and geologic factors that suggest it is unlikely to have been a continuous and permeable unit across the Midlands (Everett et al., 2003), these arguments appear to rule out this model. Evidence for a syndiagenetic timing (within ~ 10 Ma of host-rock deposition) for the bulk of mineralization is also incompatible with this interpretation.

The alternative model invokes density-driven free convection as the principal fluid flow driver, built on the original ideas of Russell (1978, 1986). A convection model satisfactorily accounts for the constraints on fluid and metal sources as outlined earlier and can explain a relatively early onset of mineralization. Evidence for sufficiently high basement permeability to allow convection comes from geophysical data that demonstrate an abundance of deep-seated Caledonian structures in the Iapetus suture zone (e.g., O'Reilly et al., 1999) and field observations of extensive brittle faults and fractures in Lower Paleozoic rocks, including the presence of veins linked to flow of mineralizing fluids (Everett et al., 1999a).

There are two recent modifications to the original Russell ore genetic model. The first is the recognition that generation of dense brines at the surface would have provided a much more efficient, thermohaline, density-driven flow system (Wilkinson et al., 2005b) that can drive an order of magnitude higher fluid fluxes than simple thermal convection alone (Yang et al., 2004b). This addresses one criticism of thermal convection, that numerical models do not produce very high flow velocities unless hydraulic conductivity and heat flow are high (e.g., 0.8 m year^{-1} with hydraulic conductivity in faults of 10 m year^{-1} and heat flow of 150 mW m^{-2}; Garven et al., 1999). A second idea is that topographic flow, largely through the Lower Paleozoic basement, could have supplemented convective flow in the Midlands later in the evolution of the system (Everett et al., 2003; Garven et al., 1999; Lewis and Couples, 1999). Such forced convection with a basement permeability flow path would still satisfy geochemical constraints but, as noted earlier, could not easily account for mineralization in the Lower Carboniferous.

13.9.4.9 Genetic Model

Synthesizing the available evidence leads to the conclusion that fluids involved in the Irish hydrothermal system were derived from ambient seawater that must have circulated to sufficient depths to have interacted extensively with Lower Paleozoic basement ($\pm$ Precambrian crystalline rocks). Depths of circulation must also have been sufficient to generate the observed ore fluid temperatures of up to 280 °C and the enrichments in metals such as Cu and Ni, which are generally mobilized at higher temperatures than Pb and Zn. Although paleogeothermal gradients are unknown, anomalous vitrinite and conodont alteration indices in rocks of the Midlands Basin (Clayton et al., 1989) suggest elevated heat flows throughout the Carboniferous, despite the lack of significant crustal extension. Although penecontemporaneous volcanism was limited, locally important submarine eruptions of basaltic, low-degree partial melts from the mantle occurred, particularly in the Limerick area (Strogen, 1995), and the recent discovery of Lower Carboniferous diatremes in the Limerick province points toward a significant role for magmatic heat in driving the hydrothermal system. Using a slightly elevated geotherm of 40 °C km^{-1} implies fluid circulation to depths of 5–7 km. Thermohaline free convection is proposed as the principal flow mechanism for the main stages of mineralization (e.g., Wilkinson et al., 2005b), with sourcing of saline fluids from the Carboniferous ocean allowing multiple pore volumes of fluids to be circulated through the upper crust in several pulses, linked to tectonic and magmatic activity, over perhaps 15 My.

The most important factor responsible for localizing the Midlands Basin ore field was the ancestral oceanic suture zone that provided deep crustal permeability for extensive hydrothermal fluid circulation and a pathway for emplacement of mantle-derived melts into the mid-crust that could have acted as an energy source. Reactivation of Caledonian

structures in this zone ultimately controlled the development of Carboniferous faults and the successor basins into which the receptive carbonate host rocks were deposited. The existence of an intensely deformed, weakly metamorphosed accretionary complex beneath the Carboniferous basins provided a fertile source of metals that was available for leaching by descending, weakly acidic, seawater-derived fluids. The shallow marine environment and climatic conditions favored the development of brines that enhanced metal leaching at depth and the establishment of surface conditions conducive to bacterial activity that were critical in producing the near-surface sulfur trap.

The processes invoked in this model have much in common with those inferred in SEDEX ore systems, in particular those where the host rocks have a significant carbonate component (e.g., Anarraaq in the Red Dog district) and even those systems transitional between sediment-hosted and volcanic-associated massive sulfide deposits, such as the Carboniferous Iberian Pyrite Belt. The recognition that many deposits classified as SEDEX may have mineralization that formed during early to late diagenesis (up to 20 My after host-rock deposition; Leach et al., 2005) places many deposits of this type into the relative time frame considered likely for the Irish Midlands. However, the fact that low-temperature, subeconomic deposits with many features akin to MVT deposits also occur in Ireland indicates that processes that form this style of mineralization were also operative. It is suggested that these have most in common with the extensional basin-hosted MVT deposits like those on the Lennard Shelf. It is therefore hard to escape the conclusion that the Irish Midlands contains deposits that form part of a continuum where the style of mineralization is a function of the depth to which fluids penetrated (and hence ore fluid temperature), the relative timing of host-rock deposition and hydrothermal activity, and the host-rock composition. These factors are in part linked, related to the series of interconnected processes occurring in an evolving basin system in an intracratonic rift or extending passive margin.

13.9.5 Discussion

13.9.5.1 Irish Deposits as Carbonate-Replacement SEDEX Systems

Consideration of the geologic characteristics and interpreted geochemical processes operating in the discussed sediment-hosted Zn–Pb deposits leads to a recognition of the following commonalities between SEDEX deposits and Irish-type deposits:

1. They formed in intracratonic submarine settings in second- or third-order basins undergoing active extensional faulting and subsidence.
2. There is an indirect temporal link with igneous activity.
3. Synsedimentary faults controlled the formation of seafloor depressions that may have trapped brines, acted as conduits for ore fluids, and generated debris flow breccias that can become mineralized.
4. Carbonate-hosted SEDEX deposits (e.g., Anarraaq) have many morphological and textural similarities to Irish-type ore bodies.
5. Ore bodies have a high aspect ratio and are dominated by fine-grained massive sulfides.
6. Replacement textures are common.

7. Well-developed lateral and vertical metal and mineralogical zoning patterns are observed, extending for kilometers to tens of kilometers from ore zones.
8. Lead isotopes are homogeneous within individual deposits.
9. Ore fluids were derived from evaporated seawater and typically reached temperatures of 200–250 °C.
10. Thermohaline convection involving infiltration of surface-derived evaporitic brines is the fluid flow model that best fits the available geochemical constraints.

Given these observations, it is clear that the Irish-type ore bodies are more akin to typical examples of the SEDEX family than to typical examples of the MVT clan. The principal similarity that the Irish-type ore bodies have with MVT deposits is that they are carbonate-hosted, but, as noted earlier, this is a poor classification criterion for sediment-hosted deposits given that classic shale-hosted SEDEX camps can include carbonate-hosted deposits, and many SEDEX deposits are hosted by carbonate-rich mudstones or siltstones. The most striking differences between Irish-type deposits and SEDEX deposits are the host-rock depositional environment (shallow ramp carbonates rather than deeper-water shales) and perhaps the overwhelming predominance of BSR in the former (e.g., Figure 3). Why the Irish system is so productive in terms of sulfide generation has yet to be satisfactorily explained, although the presence of low Fe carbonates will have helped to minimize H_2S sequestering by pyrite formation.

The presence of late-stage MVT-like deposits in Ireland complicates the picture. Although their tectonostratigraphic setting is more like the extensional basin-hosted deposits of the Lennard Shelf, the properties of fluids and sulfide involved in their genesis are consistent with the typical MVT model. Consequently, it appears to be possible for a transition to occur from higher-temperature SEDEX-like convection with subseafloor deposition of ore in a bacteriogenic H_2S trap to a lower-temperature flow regime, which did not involve BSR as a source for sulfide. This hints at the possibility that the SEDEX process is self-organizing, with seafloor venting or seeping, delivering a significant nutrient flux that could cause large increases in primary productivity and boost BSR rates (cf. Emsbo, 2009). In Ireland, the remarkable development of the Waulsortian mudbank facies could also be attributed to high bacterial productivity related to hydrothermal activity. As convection systems waned, the sulfide production factory would also shut down, dealing a double blow to continued mineralization, with minor TSR providing the small amounts of late sulfide to the small MVT occurrences. The appearance of MVT deposits in the late history of other basins, or even synchronously with SEDEX mineralization (e.g., Nelson et al., 2002), suggests that there is more to learn about the relationships between carbonate-replacement Zn–Pb mineralization (whether 'true' MVT or not) in, or proximal to, basins in which SEDEX ore-forming processes were operative.

13.9.5.2 Key Factors in the Genesis of SEDEX Deposits

Several factors are identified as critical for the formation of large SEDEX deposits:

1. Low paleolatitude and the development of evaporitic environments along basin margins. This provides the brine recharge to enable a multipass convective system to operate,

thereby efficiently stripping metals from deeper source rocks. It also increases flow velocities by introducing dense, cool brines at the top of the system, thus increasing discharge temperatures.

2. Deep-rooted synsedimentary faults that enable surface-derived brines to penetrate to significant depths and attain temperatures >100 °C and to allow buoyant, metalliferous brines to flow back to the surface.

3. Laterally extensive, thick, permeable clastic packages in the basin sequence, providing sufficient available metal for leaching by migrating/convecting brines and containing reactive iron to sequester reduced sulfide to maximize metal transport.

4. Anoxic subbasins with low sediment supply allowing organic carbon to accumulate, enhancing H_2S production to make an efficient sulfur trap, and providing topographic lows to contain exhaled brines.

5. Periods of Earth history when $CaCl_2$ seas existed, favoring the generation of low-sulfide brines via evaporation, which could then evolve into highly metalliferous ore fluids during convective circulation and with lowered marine sulfate concentrations enhancing the survival of H_2S produced by BSR in the sediments hosting ore.

13.9.5.3 Key Factors in the Genesis of MVT Deposits

Critical ingredients for the formation of large MVT deposits are suggested to be:

1. Low paleolatitude prior to mineralization and the generation of bittern brines produced by evaporation of seawater past the point of halite precipitation.

2. The burying of these brines within, or the migration into, oxidized clastic packages containing reactive iron to sequester reduced sulfide, where metals could be effectively leached to produce highly metalliferous ore fluids.

3. Release of these brines at a later stage along a focused flow path, either by collapse of overpressured compartments or by topographically driven flushing of the basin.

4. Local accumulations of H_2S-rich brines or sour gas to act as traps for migrating metalliferous brines and permeability pathways to allow the two fluids to mix.

5. Periods of Earth history following times when $CaCl_2$-rich seas had existed, so that exceptionally low-sulfide brines produced via evaporation were evolving into highly metalliferous solutions within sedimentary basins and were ready and waiting for mobilization by MVT flow systems.

13.9.5.4 Outstanding Questions

Although the SEDEX deposits in many ways present quite a unified class in terms of process, there are clearly some marked differences between the supergiant Proterozoic systems and the generally smaller Phanerozoic deposits that are yet to be fully understood. Scale issues regarding the size and longevity of the Proterozoic rift basins are one factor, and another is the inference that most of the Phanerozoic deposits generated reduced rather than oxidized ore fluids based on the mineralogy of the deposits and the source basin stratigraphy (Cooke et al., 2000). Given the size of deposits formed from oxidized fluids, should exploration be focused in Phanerozoic basins containing extensive oxidized rift packages? The reason for the absence of discoveries in such systems – perhaps with the exception of Red Dog – is unclear.

For very deep basins, there is probably no need to appeal to fluid flow outside the basinal domain. However, studies of the Irish ore field tell us that extensive flow through fractured basement is feasible and that low-grade metamorphic rocks, especially metagraywacke and shale, can be extremely fertile source rocks for ore metals. At present, however, it is difficult to recognize evidence for fluid flow within basement.

A major limitation in the understanding of SEDEX systems is the limited amount of data on basic ore fluid properties, let alone ore fluid chemistry. It is remarkable that the inferences on the origins and flow paths of fluids come from such a restricted dataset, with much of this work being done before the development of some of the new analytical tools. For example, more data need to be acquired from single, paragenetically constrained fluid inclusions to avoid many of the uncertainties that plague conventional bulk analytical techniques. However, to do this with the sort of material available in these systems is a major challenge.

In the MVT systems, the involvement of basement rocks is again controversial, but there does appear to be some correspondence between MVT systems where fluid temperatures reach higher values than normal (>200 °C, e.g., Tennessee and Upper Mississippi Valley) and isotopic and mineralogical evidence suggesting that basement interaction occurred (e.g., Grant and Bliss, 1983). The appearance of highly metalliferous brines at certain stages of basin evolution has now been quite widely documented in the US midcontinent, but it would be useful to know if these unusual fluids are a characteristic feature of all MVT ore systems.

A revisit of episodic expulsion compaction models is needed to evaluate the impact of new knowledge of the metal content of ore fluids. Much smaller volumes of brine than previously thought will be necessary to make large deposits so that release of fertile fluid from quite a small proportion of the basin fill could be sufficient to make an ore body.

The recognition of the ubiquitous importance of partially or strongly evaporated seawater in the formation of all types of sediment-hosted Zn–Pb deposits is one of the major advances in the field in the past decade. The suggestion here that $CaCl_2$-rich seas may favor the generation of unusually fertile ore fluids for both SEDEX and MVT systems is worthy of further analysis. However, a better understanding of how such brines migrate in the subsurface is needed, requiring improved models that can properly simulate mixing and dispersion processes involving variable salinity fluids. Major breakthroughs in the understanding of how SEDEX, Irish, and MVT systems work lie in wait for those with the tools to tackle such complex mathematical simulations and with the drive to go and seek the geochemical and isotopic evidence of brine passage in the rocks.

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