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## Carbonate-Hosted Base Metal Deposits

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### 1. Introduction

Carbonate-hosted base metal sulphide deposits are discussed with reference to ore deposit mineralogy and geology, isotope geochemistry, ore fluids and ore genesis of type examples. Three main carbonate-hosted deposit types are recognized: 1. Leadville-type mineralization (LTM); 2. Sedimentary-exhalative (SEDEX); and 3. Mississippi Valley-type (MVT) deposits. The three types constitute a distinct group of deposits characterized by orebodies within carbonate host-rocks containing Pb and Zn as the major metals with variable amounts of Cu and associated by-products, including Ag, Cd, Ge, V, Ga, As, Sb, Au and In.

LTM deposits form by magmatic-hydrothermal processes associated with igneous intrusions and correspond to the carbonate-hosted high-enthalpy type of Russell & Skauli (1991) and the chimney-manto type deposits of Hutchinson (1996). The SEDEX deposits are typically characterized by syngenetic to syndiagenetic processes of mineralization at the submarine surface within sedimentary basins prior to carbonate lithification and are spatially associated with faults located within, or at the margins of, the basins. They are also known as medium-enthalpy, Irish type or clastic dominated Pb-Zn deposits (Hitzman & Beaty, 1996; Russell & Skauli, 1991; R.D. Taylor et al., 2009). In contrast, typical MVT deposits (low-enthalpy type of Russell & Skauli, 1991) are epigenetic and form at the periphery of basins in lithified carbonate rocks spatially associated with faults, structural highs and facies changes. They are commonly referred to as MVT due to the occurrence of classic districts in the Mississippi River drainage basin of the USA (Leach et al., 2010). Both SEDEX and MVT deposits form from formation waters derived from sedimentary basins with high heat flows.

#### 1.1 LTM deposits

LTM deposits are high temperature ( $>200^{\circ}$ ) carbonate-hosted Pb-Zn-Ag deposits distinctly different from MVT and SEDEX deposits by virtue of their temporal and spatial relationship to igneous intrusions. The fundamental diagnostic feature of this deposit type is its origin from magmatic-hydrothermal processes associated with felsic to intermediate magmatism and ore formation by replacement of carbonate rocks (Einaudi et al., 1981; Megaw et al., 1988; Thompson & Beaty, 1990). Although the type name originates in the Colorado mineral belt of the United States (Beaty et al., 1990), the type setting for these deposits is northern Mexico where the mineralization is hosted in carbonate-dominated portions of Jurassic-Cretaceous sedimentary sequences (Megaw et al., 1988).

The type of mineralization ranges from near-intrusion Cu and Zn-Pb skarns through distal Pb-Zn skarns to massive sulphide bodies hosted by limestone and dolostone cut by granite, quartz monzonite and other intermediate to felsic hypabyssal, porphyritic lithologies (Einaudi et al., 1981; Megaw et al., 1988). There is a continuous transition in most districts from skarn ores to massive orebodies beyond the skarn zones (Fig. 1).

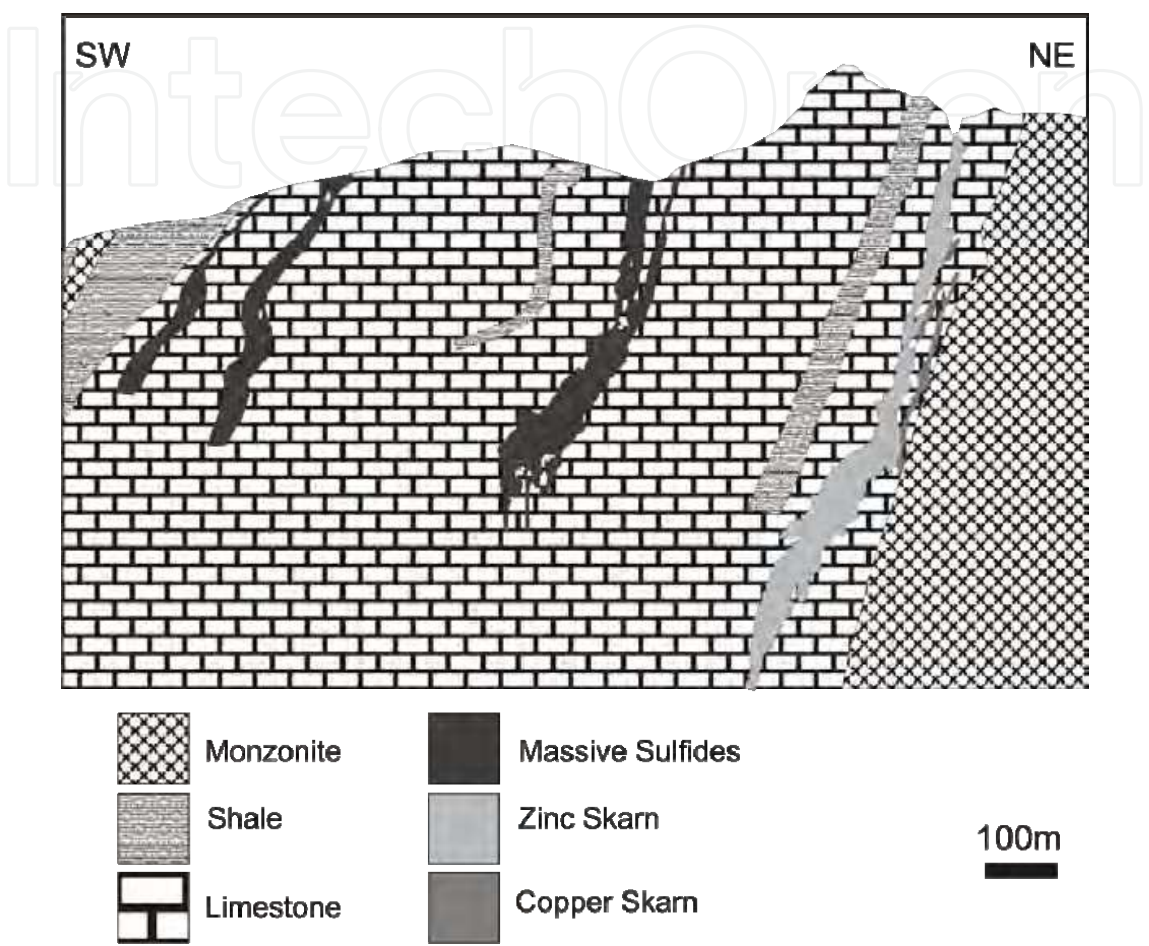


Fig. 1. Cross section of major orebodies of Providencia in Zacatecas, Mexico over a vertical interval of 1000m with concordant skarn and massive sulphide orebodies associated with a monzonite stock (modified from Megaw et al., 1988).

1.2 SEDEX deposits

Carbonate-hosted SEDEX Pb-Zn deposits are characterized by a stratiform morphology, an active tectonic setting during mineralization and low to moderate temperatures of formation (100° to 260° C). The Pb-Zn ores are associated with significant Ag and minor Cu (Hitzman & Large, 1986). The mode of occurrence of the mineralization includes cross-cutting and stratiform ores, such as in the classical Silvermines deposit in Ireland (Fig. 2), where epigenetic feeder zones occur below exhalative stratiform orebodies (Andrew, 1986a). The deposits are distinct from volcanogenic massive sulphide deposits because of a high Pb/Cu ratio and their lack of an intimate association with volcanic and volcanoclastic sequences (Turner & Einaudi, 1986). Some SEDEX deposits typically occur within marine shales or siltstones (Large, 1983) and are therefore distinct from carbonate-hosted Pb-Zn SEDEX deposits considered here.

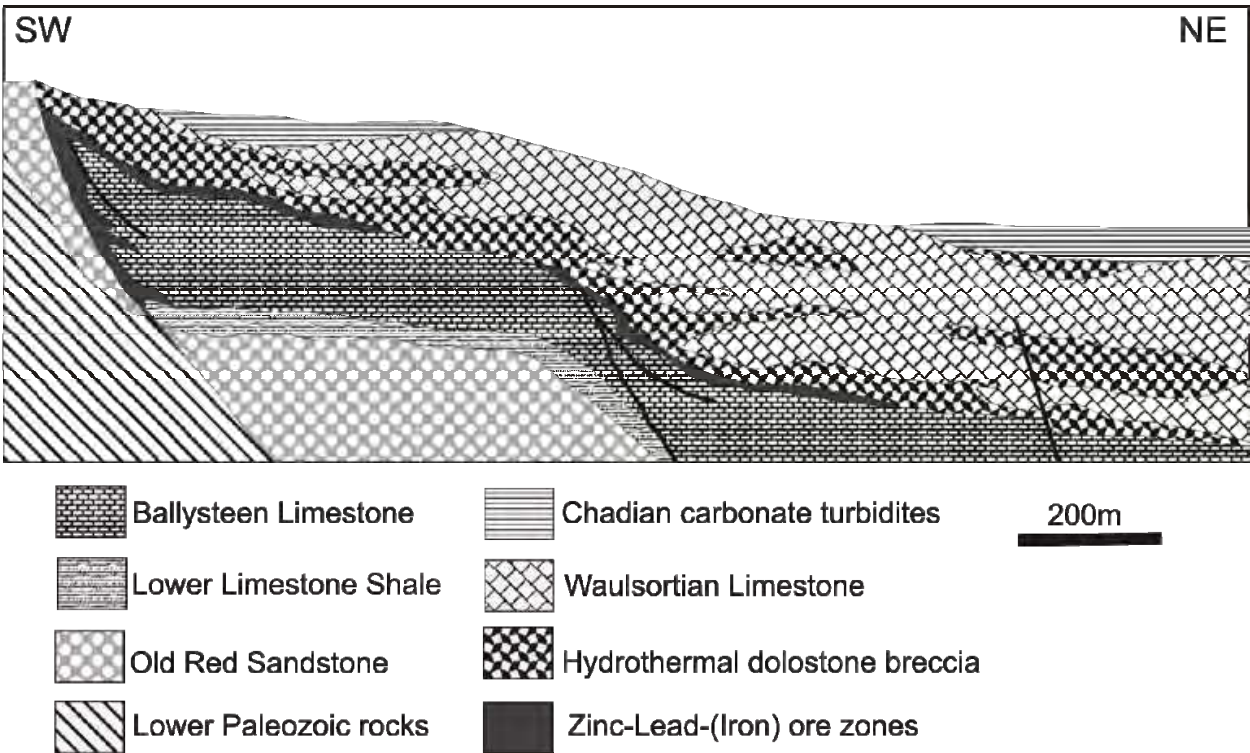


Fig. 2. Cross section of the Silvermines SEDEX deposit with an epigenetic feeder zone and stratiform ores (modified from Hitzman & Beaty, 1996).

The central Irish ore field may be considered as the type setting of carbonate-hosted SEDEX deposits. The ore field occurs in a first-order, intrashelf basin on the edge of the North Atlantic craton within Lower Carboniferous limestones (Andrew & Ashton, 1985; Hitzman & Large, 1986). The Alpine Triassic deposits of Central Europe are comparable to the Irish SEDEX deposits (Schneider, 1964; Sangster, 1976). They predominantly contain epigenetic replacement bodies and minor but extensive syngenetic stratiform orebodies in carbonate rocks (Schneider, 1964). Klau & Mostler (1986) regard the deposits as MVT based on the Pb-isotope data of Köppel (1983) which, according to them, shows no relation between magmatic rocks and mineralization. In addition, the ore lead is isotopically different from host-rock lead. However, according to Köppel (1983), basement rocks and upper Carboniferous to Permian magmatic rocks of the Southern Alps exhibit similar characteristics as the lead in the Triassic Pb-Zn deposits, whereas the lead of feldspars from Triassic volcanics shows significant differences. The syndiagenetic Pb-Zn deposits in Triassic carbonates could have obtained lead from lower crustal rocks, or material thereof, by leaching processes (Köppel, 1983).

1.3 MVT deposits

MVT deposits are stratabound, epigenetic orebodies that occur in clusters in carbonate formations of mineral districts distributed over large areas (Ohle, 1959, 1967; Heyl, 1967; Snyder, 1967). The orebodies are typically found at or near basin margins associated with domes and intrabasinal highs (Fig. 3). Like SEDEX deposits, MVT deposits are characterized by the absence of obviously associated igneous rocks, but the stratabound and often stratiform morphology of the former contrasts with the majority of MVT deposits whose morphology commonly crosscuts stratigraphy (Hitzman & Large, 1986; Sangster, 1990).



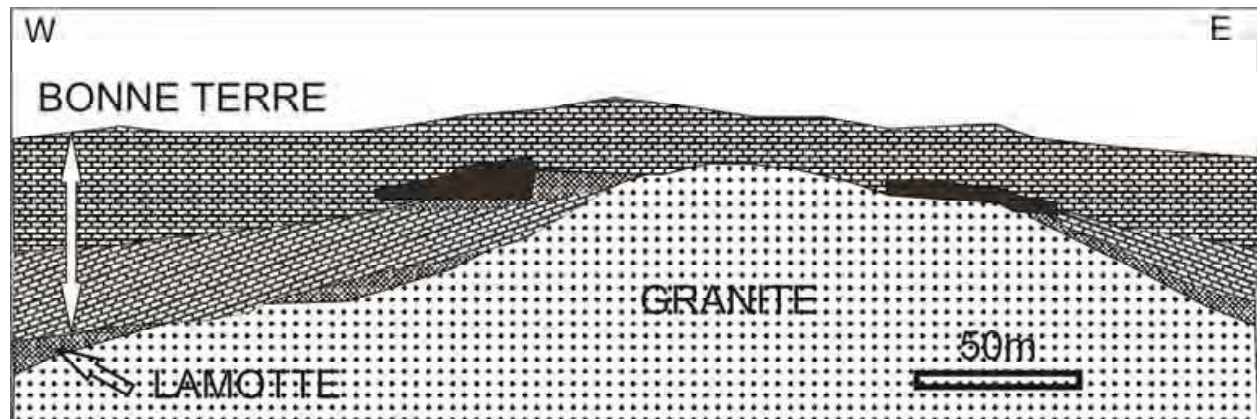


Fig. 3. Cross section through the Doe Run Mine, Southeast Missouri with ore zones (black) overlying a Precambrian granite “knob” (modified from Ohle, 1996).

Classical examples of MVT deposits are the districts of the mid-continent in the United States and the Pine Point district in Canada. However, they also occur in other districts, including the Appalachian in eastern United States, Silesia in Europe, southern and central Africa, and the Leonard shelf in Australia. They include districts varying from Zn- to Pb-dominant as well as Cu-rich deposits. With the exception of the Southeast Missouri district, which is dominantly Pb-rich, most districts are Zn-dominant and a few deposits (e.g. Kipushi and Tsumeb in Africa) contain significant amounts of Cu in addition to Zn and Pb.

## 2. Ore deposit geology

### 2.1 LTM deposits

This type of deposit is found on continental margins of orogenic belts and on the inner side of principal arcs where carbonate rocks representing miogeoclinal or stable platform depositional environments are widespread (Einaudi et al., 1981; Sawkins, 1990). The deposits are associated with granodioritic to granitic magmatism which, together with the related metallogenesis in this environment, are believed to be a function of subduction (Einaudi et al., 1981; Bookstrom, 1990). In Mexico, the mineralized districts occur within or on the margins of a thrust belt with anticlinal ranges (the Sierra Madre Oriental). The thrust belt consists of Jurassic-Cretaceous sedimentary sequences of basal continental red beds with evaporites followed by a series of shale and carbonate facies which were deformed during the Laramide orogeny. The carbonate portions of these sequences are frequently more than 3 km thick and consist of limestone with minor dolomite (Megaw et al., 1988).

The mineralization-related intrusions range from batholiths and stocks to thin dikes and sills composed of diorite, granodiorite, quartz monzonite, monzogranite, quartz latite, and rhyolite (Einaudi et al., 1981; Megaw et al., 1988; Bookstrom, 1990). In Mexico the intrusions originated from the lower crust (Ruiz et al., 1988) and their age ranges from 47 to 26 Ma (Megaw et al., 1988). Mineralization occurred during a restricted interval of the Mid-Tertiary, well after evolution of the Laramide-aged Mexican thrust belt. Large deposits like Santa Eulalia and Naica grade outward from intrusion-associated mineralization to intrusion-free ores, suggesting that districts without intrusion relationships may not have been traced to their ends (Megaw et al., 1988).

The carbonate host rock may be predominantly limestone or dolomite and there are no consistent links between ore deposition and carbonate composition, facies, organic content, or insoluble components (Megaw et al., 1988). Many deposits contain mineralization in carbonate strata within or below relatively less permeable rocks such as cherts, shales, slates and volcanic rocks, and the formation of large orebodies appears to be related to structural enhancement of permeability in the carbonate rocks (Yun & Einaudi, 1982; Megaw, et al., 1988). Complex fold and fault structures are the dominant controls in strongly folded areas, whereas simple fault-related structures are more common on fold belt margins and radial and/or concentric structural patterns related to intrusions are important controls in domal areas (Megaw et al., 1988). The controlling structures apparently acted as conduits for channeling mineralizing fluids to sites of ore deposition.

The orebodies commonly display a combination of forms that include mantos, chimneys, pods and veins (Einaudi et al., 1981; Megaw et al., 1988; Beaty et al., 1990) and are temporally and spatially associated with igneous intrusions (Fig. 1). The change in orebody morphology is caused by local variations in stratigraphy, structural patterns, travel distance of hydrothermal fluids, and depth of intrusive emplacement (Megaw et al., 1988). Podiform skarn and sulphide bodies are the deepest modes of occurrence and are irregular or equant with no particular orientation or relationship to stratigraphy. They commonly occur along intrusive, fault, and lithological contacts (Megaw et al., 1988). Typical vein deposits include Bluebell in Canada and Uchucchacua in Peru (Einaudi et al., 1981). Vein mineralization is also dominant in some major skarn deposits such as San Martin (Rubin & Kyle, 1988).

Tonnage and grade data (Megaw et al., 1988) for skarn, chimney and manto ores in seventeen districts of Mexico show a wide range of values (Fig. 4). The ore districts have an average of 11.4 million tonnes (Mt) at 11.0 wt.% Pb, 8.5 wt.% Zn, 0.7 wt.% Cu, 243 ppm Ag and 1.8 ppm Au. Santa Eulalia is the largest district with 50 Mt of ore grading 5% wt. Pb, 6.7 wt.% Zn, 0.1 wt.% Cu and 242 ppm Ag. Other major ore districts include Providencia-Concepcion del Oro (25 Mt, 2 to 20 wt. % Pb+Zn, 30 to 500 ppm Ag) in Mexico (Megaw et al., 1988), and Leadville (24 Mt, 7 wt. % Pb+Zn, 320 ppm Ag) in Colorado (Beaty et al., 1990).

With the exception of the San Carlos and Los Lamentos manto districts which are Pb-rich and contain no Zn, the average Zn/(Zn+Pb) ratio of 0.5 in the other Mexican deposits indicates equal concentrations of Pb and Zn in most of the orebodies. However, Cu values are generally low (0.7 wt. %) and only range from 0.1 to 1.6 wt % Cu. The gold grades are also typically low and ranges from 0.2 to 6 ppm Au with an average of only 1.8 ppm Au for the 9 Mexican districts for which data is available (Megaw et al., 1988). In contrast, the Ag grades are high in the majority of deposits with an average of 243 ppm Ag and a range from 14 to 600 ppm Ag with most deposits (14 out of 17) having grades >100 ppm Ag.

## 2.2 SEDEX deposits

The central Irish ore field occurs in a first-order, northerly transgressive intrashelf basin on the edge of the North Atlantic craton (Andrew & Ashton, 1985). All the known major deposits lie along basin margins adjacent to historically active basement fault zones. The major stratiform deposits at Navan, Silvermines and Tynagh occur in early Carboniferous stratigraphic successions of shallow water carbonate sediments and argillites, and deep water Waulsortian limestones overlain by carbonates and argillites deposited in latest Courcayan to Chadian stages (Philips & Sevastopulo, 1986). The carbonate succession is underlain by basal Devonian sandstones (the Old Red Sandstones) which diachronously overlie a Precambrian-Lower Paleozoic basement.

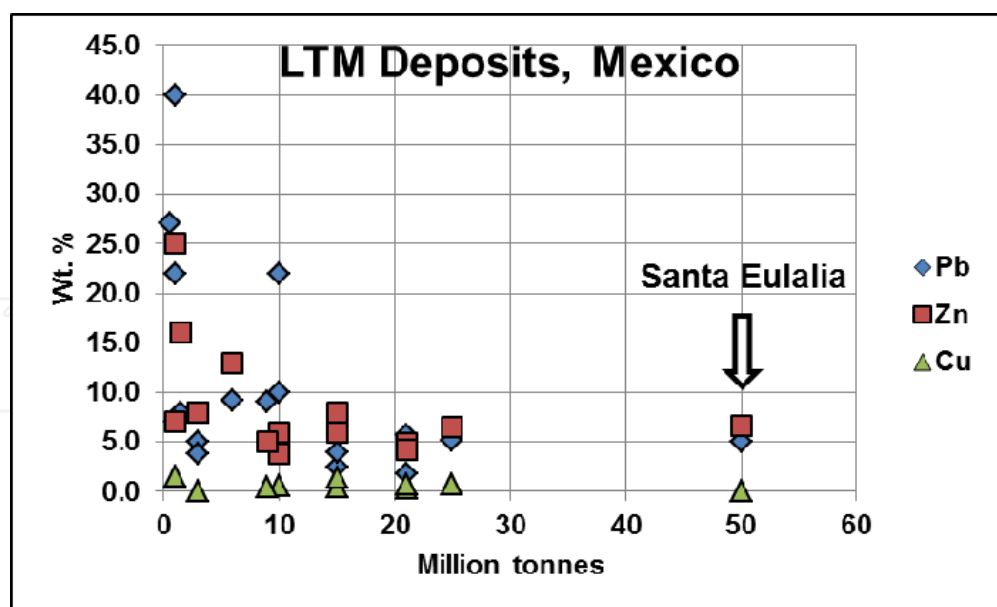


Fig. 4. Tonnage and grade data for 17 Mexican districts with skarn, chimney and manto ores based on data from Megaw et al. (1988).

There is no obvious spatial association between igneous rocks and ore deposits at Silvermines, Tynagh and Keel (Morrissey et al., 1971). A late Caledonian, post-tectonic syenite with a model lead isotopic age of 400 Ma intrudes Lower Paleozoic rocks beneath the Navan deposit, but it is not regarded as a mineralizing pluton as it is older than the mineralization age of 366 Ma (Andrew & Ashton, 1985; Ashton et al., 1986). Although thin pyroclastic beds occur at the same stratigraphic level as the most mineralized beds at Tynagh, the pyroclastic material is considered to have been derived from the Limerick volcanic centre 70 km away (Morrissey et al., 1971).

The mode of occurrence of SEDEX orebodies includes cross-cutting, epigenetic veins and breccia ores commonly regarded as feeders to overlying tabular stratiform lenses. Such a feeder-exhalative system is best developed at Silvermines (Fig. 2) where the upper stratiform ores occur at the base of and within Waulsortian carbonates (Andrew, 1986a). The mineralization is preferentially enriched immediately below siltstone and shale bands as well as in dolomitization voids and fracture systems. The thickness and distribution of the stratiform ore is related to the paleotopographic control of knolls of Waulsortian micrites (S. Taylor, 1984). Navan represents a different style of mineralization in that the orebody consists of five vertically superimposed stratiform lenses with cross-cutting veins and breccia zones within Lower Carboniferous limestones (Andrew & Ashton, 1985; Ashton et al., 1986). The mineralization is consistently restricted to non-argillaceous units, being generally best developed in micritic, oolitic, pelloidal or slightly arenaceous carbonate beds. SEDEX deposits have a spatial relationship to fault structures active during mineralization, and, in the case of Silvermines and Tynagh, during host rock deposition (Hitzman & Large, 1986). All the ore zones at Silvermines are closely related to WNW or westerly faults (Andrew, 1986a). At Navan, the mineralization is grossly located adjacent to fault intersections on the flank of an anticline (Ashton, et al., 1986). The main orebody at Tynagh was a subhorizontal wedge that extended updip of the Tynagh fault in two elongated zones separated by a barren dolomitized reef (Boast et al., 1981a; Clifford et al., 1986). In addition,

a residual deposit of oxidized and unoxidized mineralization occurred in the hanging wall of the fault in a deep post-karstification trench.

Tonnage and grade data for 28 carbonate-hosted SEDEX deposits (Fig. 5) from the data bank of Goodfellow & Lydon (2007) shows that the average deposit contains 8.9 Mt grading at 6.74 wt. % Zn, 2.51 wt. % Pb and 63 ppm Ag. The deposits are typically Zn-rich with a Zn/(Zn+Pb) ratio of 0.71.

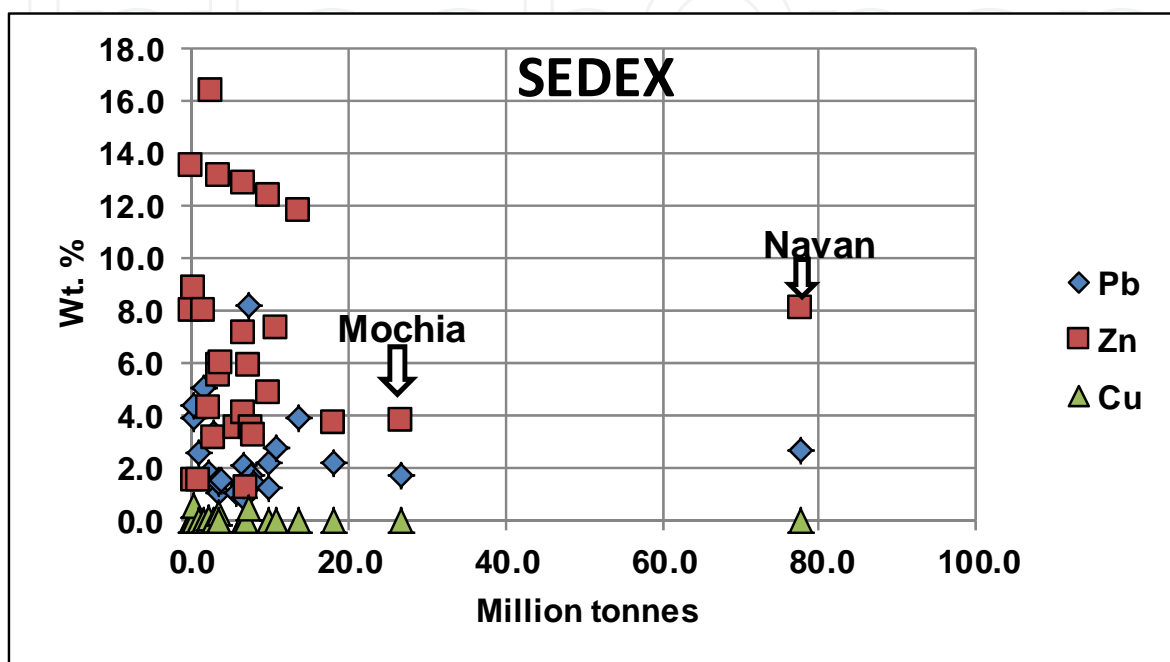


Fig. 5. Grade tonnage plot for carbonate-hosted SEDEX deposits based on data from Goodfellow & Lydon (2007).

With the exception of Navan (77.8 Mt at 8.04 wt. % Zn and 2.68 wt. % Pb) and the Palaeoproterozoic Mochia deposit in India (26.8 Mt at 3.79 wt. % Zn and 1.69 wt. % Pb) most carbonate-hosted SEDEX deposits contain less than 20 Mt of ore (Fig. 5). The Cu content of these deposits is also very low with an average of only 0.30 wt. % Cu in the four deposits for which Cu data is available. The Mehdiabad deposit in Cretaceous dolostone in Iran contains exceptionally large geological resources estimated at 218 Mt with 2.3 wt. % Pb, 7.2 wt. % Zn and 51 ppm Ag (Goodfellow & Lydon, 2007).

### 2.3 MVT deposits

MVT Pb-Zn deposits have low temperatures (100° to 150° C), uniform salinity, density and composition (Roedder, 1967, 1984) and typically occur in shallow-water platform carbonates peripheral to intracratonic basins (Sangster, 1990). The classical districts of the Upper Mississippi Valley, Tri-State and Southeast Missouri are found within the stable continental interior of the North American craton, whereas the Appalachian district occurs in an orogenic belt on the eastern margin of the continent (Hoagland, 1967, 1976; Thacker & K.H. Anderson, 1977). The mineral districts are distributed over thousands of square kilometres (Ohle, 1967) and the carbonate-hosted ore deposits occur over a stratigraphic interval of 200 million years ranging from Cambrian to Mississippian-Pennsylvanian (Ohle, 1980).



MVT orebodies are stratabound in essentially horizontal carbonates, chiefly dolomites and dolomitic limestones. They are epigenetic and typically occur within breccia bodies below unconformities (Callahan, 1967; Sangster, 1988). Zones of high permeability such as channels and troughs in algal reefs, collapse breccias, pinchouts, facies changes, bedding planes, faults and fractures are the focus of mineralization, particularly along flanks or on crests of basement highs (Fig. 3) or below unconformities. The ore-hosting breccias include discordant domes and columns that may be interconnected to concordant breccias. The breccia tops are vuggy and porous and contain mainly open-space filling mineralization while replacement mineralization is dominant near the base of the breccias (Rogers & Davis, 1977).

The regional distribution of the Southeast Missouri orebodies closely follow the pinchouts of the Lamotte Sandstone (Kisvarsanyi, 1977). Although algal reefs are also spatially associated with the mineralization, the reefs themselves are heavily mineralized only in some parts of the Viburnum Trend, and they are barren in many places. Faults seem to have been important in the Old Lead Belt where fault zone ores provided most of the lead (James, 1952). In the Tri-State district the ore occurs as elongate tabular bodies ("runs") of breccias up to 1 km or more in length which may form circular map patterns (Hagni, 1976). The dominant ore-bearing collapse breccias developed by solution enlargement of fractures along silicified dolomite-limestone contacts. In addition, flat "sheet" or blanket ore occurs in partly broken, stratified chert bodies. In the Upper Mississippi Valley the ore occurs dominantly as open-space filling in pitch-and-flat structures along bedding planes, joints and faults (McLimans et al., 1980; Heyl, 1983). The orebodies are linear, arcuate, or elliptical in plan and vary in length from 0.4 to 2 km. In the Appalachian district the ores are associated with karst breccias or reefs in dolomitic limestone at or adjacent to a dolomite-limestone interface (Hoagland, 1976).

The widespread regional distribution of MVT deposits is also observed in other districts, including the Otavi Mountainland in Namibia where regional scale ore fluid migration is indicated by the presence of Pb–Zn occurrences over 2500 km<sup>2</sup> within stratabound breccias of the Elandshoek Formation (Kamona & Günzel, 2007) as well as in central Africa (Fig. 6) where numerous prospects are associated with a few Neoproterozoic economic deposits such as Tsumeb, Kipushi, Kabwe and Berg Aukas (Kamona & Friedrich, 2007; Kampunzu et al., 2009).

Most MVT deposits are Zn-dominant as indicated by the Zn/(Zn+Pb) ratio of 0.7 in individual orebodies and districts. However, some deposits like the Viburnum No. 27 mine with 8 Mt grading 2.9 wt. % Pb and 0.2 wt. % Zn (Grundmann, 1977) and the Buick mine with >50 Mt, 8 wt. % Pb and 2 wt. % Zn (Rogers & Davis, 1977), indicate the Pb-rich nature of these ores. In contrast, sphalerite is the only ore mineral in Central Tennessee which contains 20 Mt with 5 wt. % Zn (Kyle, 1976).

Tonnage and grade data for 23 MVT deposits (Fig. 7) from Canada (Paradis et al., 2007) and Africa (Kamona & Günzel, 2007; Kamona & Friedrich, 2007; Kampunzu et al., 2009) indicate that the average MVT deposit contains 13 Mt with grades of 7.2 wt. % Zn and 3.4 wt. % Pb. The average Zn/(Zn+Pb) ratio of 0.69 is similar to that of carbonate-hosted SEDEX deposits (0.71). Copper averages 3.2 wt. % in nine of these deposits for which Cu grades are available with significant Cu grades in the Kipushi (8.0 wt. %), Tsumeb (4.42 wt. %) and Khusib Springs (10.06 wt. %) deposits. Silver contents can be considerable with a maximum of 584 ppm in the Khusib Springs deposit and an average of 96.8 ppm Ag in 11 of the deposits considered here.

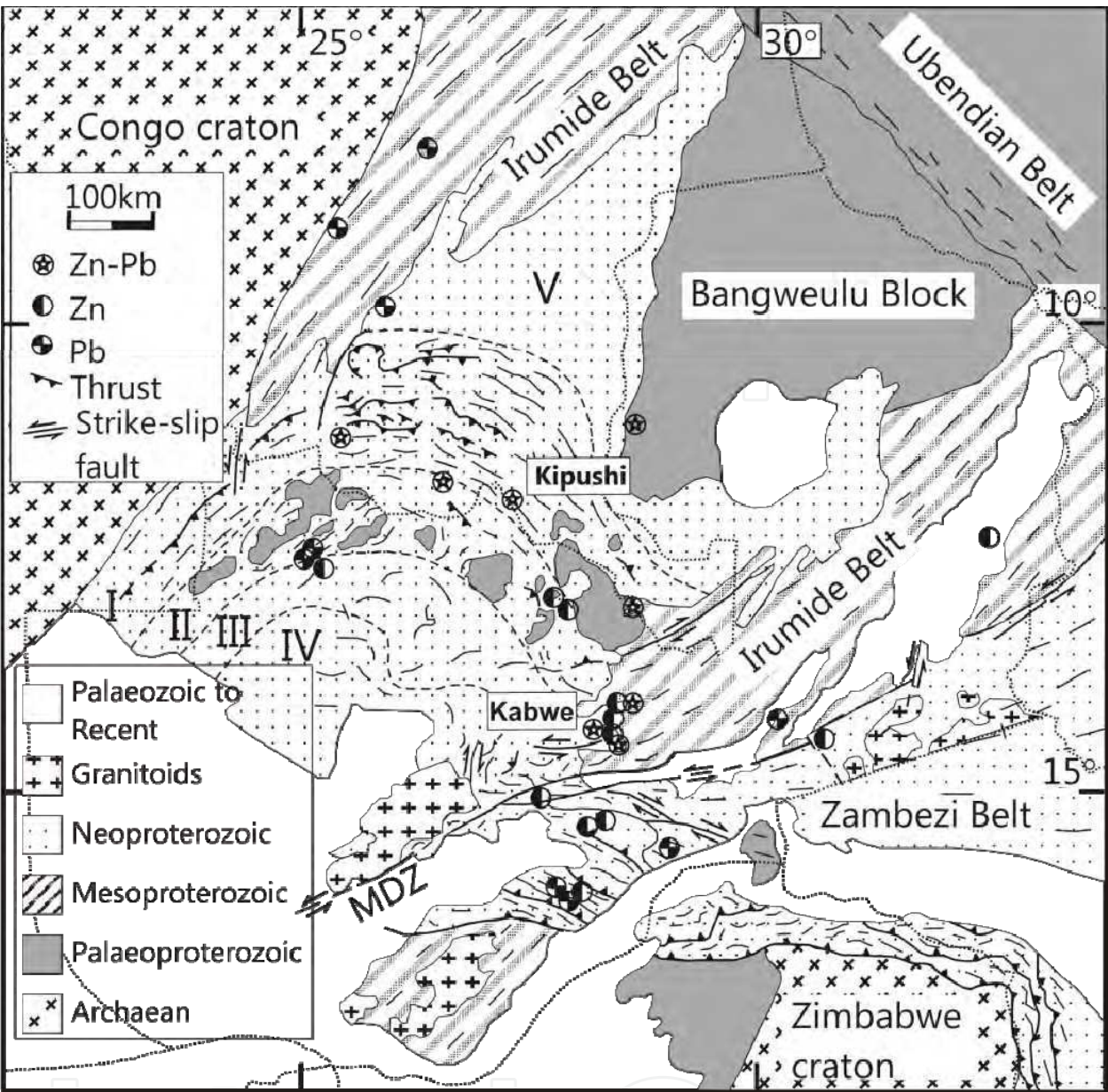


Fig. 6. Location of the Kipushi and Kabwe Pb-Zn deposits and Pb-Zn occurrences in the geotectonic framework of central Africa (modified from Kampunzu et al., 2009). I. External fold and thrust belt, II. Domes region, III. Synclinal belt, IV. Katanga high, and V. Kundelungu aulacogen or palaeograben. MDZ (Mwembeshi Dislocation Zone).

The Kipushi (Democratic Republic of the Congo) and Gayna River (Canada) deposits are examples of large deposits of this type, each with 50 Mt of ore. The Zn-Cu dominant Kipushi deposit is characterised by zones of Cu, Zn+Cu and Zn+Pb along its length (Kampunzu et al. 2009). The 80 Mt Pine Point district, which contains 100 individual orebodies (Paradis et al., 2007) is included for comparison (Fig. 7). The data of Leach et al. (2005, 2010) and Paradis et al. (2007) indicate that MVT districts with carbonate-hosted orebodies in the USA and Canada contain an average of 233 Mt with grades of 3.3 wt. % Zn and 2.2 wt. % Pb with a Zn/(Zn+Pb) ratio of 0.72 (n=10).

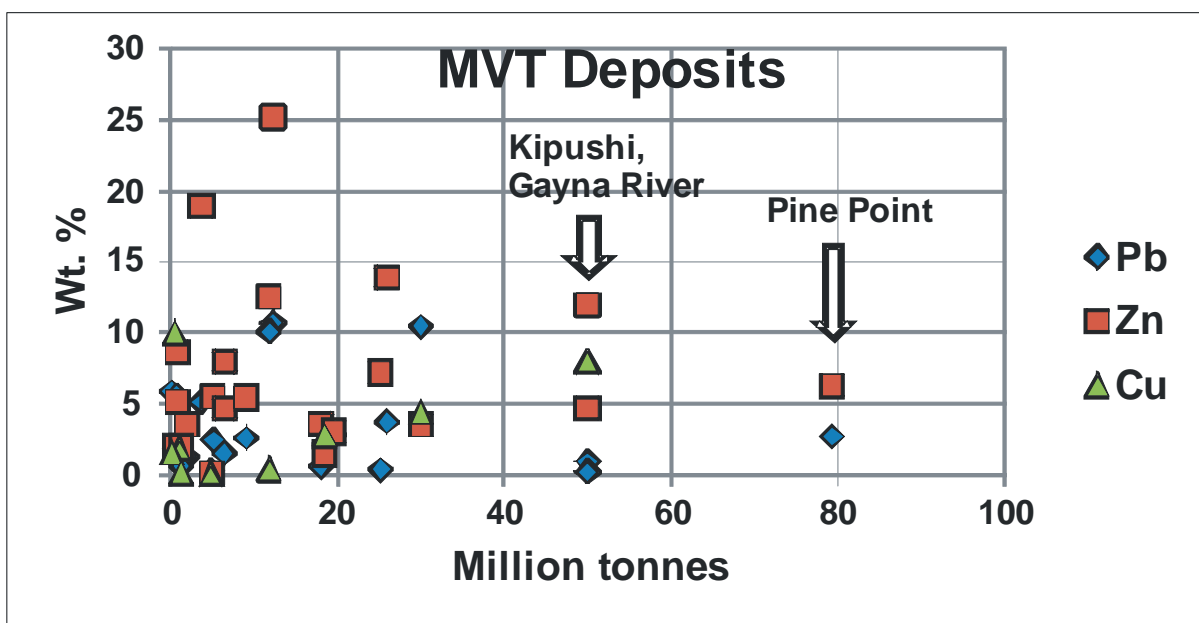


Fig. 7. Grade and tonnage plot for carbonate-hosted MVT deposits in Canada and Africa based on data from Kamona & Günzel (2007), Kamona & Friedrich (2007), Kampunzu et al. (2009) and Paradis et al. (2007).

### 3. Mineralogical and geochemical features

#### 3.1 LTM deposits

The principal sulphides are galena and sphalerite with variable amounts of pyrite, pyrrhotite, marcasite, chalcopyrite and arsenopyrite (Einaudi et al., 1981; Megaw et al., 1988; Thompson & Arehart, 1990). The massive sulphide orebodies commonly exhibit banding due to textural, size or mineralogical differences between bands and they are composed of more than 65 wt. % sulphides. The sulphides usually exhibit a zonal distribution with galena being more abundant than sphalerite in mantos, but the latter is more abundant in chimneys. The chalcopyrite content may increase with depth, and districts that contain both pyrite and pyrrhotite show an increase of pyrrhotite with depth or an increase of pyrite with time.

Tetrahedrite-tennantite, chalcopyrite and arsenopyrite commonly occur near skarns at deep levels, and near mineralization-related intrusions. Acanthite, cinnabar, stibnite, realgar and silver sulfosalts are most common in the peripheral parts of districts. In addition, some skarns also contain bornite, covellite, molybdenite, scheelite, powellite, cassiterite, magnetite, and hematite. Silver occurs in solid solution in galena in most Mexican deposits (Megaw et al., 1988), whereas galena from the Leadville district is devoid of Ag, Sb and Bi, and the source of silver is tetrahedrite and electrum with the former occurring partly as disseminations within galena (Thompson & Arehart, 1990).

The gangue is dominated by carbonates, fluorite, or quartz with or without minor barite and anhydrite. Calc-silicates may be locally present and make up less than 5 % of the mineral content (Megaw et al., 1988). The main minerals of the skarns are pyroxene and garnet with associated wollastonite, bustamite, rhodonite, dannemorite, idocrase, olivine, ilvaite, chlorite, Mn-actinolite, epidote, fluorite and cummingtonite. Skarns are typically zoned from andraditic garnet to hedenbergitic-johannsenitic pyroxene to wollastonite-bustamite to marble (Einaudi et al., 1981; Shimizu & Iyama, 1982).



The contacts between mineralization and unaltered carbonate wall rocks are sharp, and where alteration exists it is variable in extent and may appear as zones of disseminated Mn-oxide mineralization, hydrothermal dolomitization and/or recrystallized carbonates (Megaw et al., 1988). Silicification or jasperoid formation varies from poorly to strongly developed peripheral to mineralization in some ore districts, but it may be totally lacking in other districts. Isotopic depletion halos of C and O surround orebodies at La Encantada and Santa Eulalia (Megaw et al., 1988). C and O isotopes in calcite veinlet stockworks above mineralization, and limestone wallrocks adjacent to mineralization show shifts to lighter values.

### 3.2 SEDEX deposits

Sphalerite is the major sulphide with lesser galena, pyrite and marcasite (S. Taylor & Andrew, 1978; Boast et al., 1981a; Andrew & Ashton, 1985; Andrew, 1986a; Ashton et al., 1986). In addition, tennantite is of economic importance at Tynagh (Boast et al., 1981a). Common accessories include chalcopyrite, bornite, pyrrhotite, arsenopyrite, freibergite, pyrargyrite, boulangerite, bournonite, semseyite, jordanite and cylindrite. Principal gangue minerals are barite (except at the Magcobar barite orebodies of Silvermines), calcite, dolomite, siderite, and quartz with fluorite as an accessory. In the upper stratiform ores at Silvermines Ag is directly proportional to Pb due to inclusions of boulangerite and jordanite in galena (S. Taylor & Andrew, 1978). In addition, an isolated lens of rich silver mineralization in barite contains prominent patches of discrete silver minerals such as proustite, xanthoconite, smithite, miargyrite, argentite-acanthite, and argyrodite as well as gersdorffite (S. Taylor, 1984).

The lateral zonation at Silvermines and Tynagh is Cu-Pb-Zn-Mn with Mn forming an extensive aureole of up to 7 km in the carbonates at Tynagh (Russell, 1978). The Magcobar barite body and associated pyrite-rich zones occur on the fringes of the stratiform sulphide ores, whereas the iron-oxide facies of the Iron Formation is lateral to the sulphide mineralization (Andrew, 1986a; Caulfield et al., 1986). Vertical zoning in feeder zones is characterized by increasing Pb/Zn ratios which decrease slightly in the upper parts of the ores as in the feeder zones at Silvermines (S. Taylor, 1984). Zoning patterns at Navan are complex due to variations in the metal content of deposited sulphides with time, resulting in superposition of differing zoning trends (Andrew & Ashton, 1985). Mn, As, Zn and Pb values are irregular, but they form an intensive halo over the mineralization at Navan.

Dolomitization and silicification of Waulsortian micrites is associated with the mineralization at Silvermines, Tynagh and Navan. At Silvermines, dolomitization occurred before silicification of the host rock and precipitation of laminated cherts which in turn preceded sulphide deposition (Andrew, 1986a). Dolomitization at Tynagh occurred before and during mineralization (Boast et al., 1981a; Clifford et al., 1986). In addition, alteration aureoles containing Na and K feldspars surround epigenetic Cu-Pb-Ba veins which represent the final stage of sulphide mineralization (Boast et al., 1981a). According to Clifford et al. (1986), silicification related to dolomitization post-dates the Cu-Pb-Ba veins. In rocks of the Navan Group, zones of complex dolomitization involving both ferroan and non-ferroan dolomite, as well as more coarsely crystalline dolomite, occur only in mineralized areas (Hitzman & Large, 1986).

Depletion in the heavier  $^{13}\text{C}$  and  $^{18}\text{O}$  isotopes was observed in mineralized limestones, ore-stage carbonates and post-ore carbonates with respect to unmineralized Waulsortian limestone at Tynagh (Boast et al., 1981a). The depletion in  $^{13}\text{C}$  and  $^{18}\text{O}$  is a result of isotopic



exchange between host rock and mineralizing fluids. In general, the unmineralized micrites and diagenetic calcites define a heavy isotope end-member, whereas the post-ore carbonates tend to be most depleted in  $^{13}\text{C}$  and  $^{18}\text{O}$ . Carbonates coeval with sulphide mineralization have intermediate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values.

### 3.3 MVT deposits

Sphalerite is the main ore mineral of most MVT districts except Southeast Missouri where galena is more dominant. The gangue generally consists of dolomite, calcite, quartz, marcasite and pyrite (Hagni, 1976, 1983; Hoagland, 1976; Hagni & Trancynger, 1977; McLimans et al., 1980). Chalcopyrite and several Co-Ni sulphides such as siegenite, fletcherite, bravoite, vaesite and polydymite are abundant in Southeast Missouri (Jessey, 1983). Barite and/or fluorite are associated with the mineralization in the Appalachian, Tri-State and Upper Mississippi Valley districts. Sphalerite in the upper Mississippi Valley is characterized by colour banding which can be correlated stratigraphically over several kilometers (MacLimans et al., 1980). Sphalerite in Appalachian deposits also shows fine laminar to single crystal banding with colour variations of light and dark zones (Craig et al., 1983). The dark zones contain numerous inclusions of fluid, vapour and solids, and the darkest bands are rich in hydrocarbons and Cd.

The paragenesis of the ores are complex and variable from deposit to deposit and usually consist of several generations due to repetitive sulphide formation over a long period of time (Hagni & Trancynger, 1977; McLimans et al., 1980; Sverjensky, 1981; Hagni, 1983). Pyrite and marcasite are generally early, followed by chalcopyrite, sphalerite and galena, in that order. According to Jessey (1983), the Ni-Co-Cu minerals in Southeast Missouri preceded Pb-Zn mineralization.

Dolomitization, silicification, recrystallization and associated isotopic changes in the host carbonates are the most significant alteration effects in MVT deposits. In the Southeast Missouri district, an early porosity network was enlarged through the corrosive action of the ore fluids with pre-ore dolomite (Type I) to produce Type II and Type III end-member dolomite compositions (Frank & Lohmann, 1986). The isotopic composition of the host dolomite exhibits trends from Type I dolomite to Type II (depletion of both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic ratios) and Type III (depletion of  $\delta^{13}\text{C}$  and enrichment of  $\delta^{18}\text{O}$ ) dolomites. The isotopic trends suggest a fluid dominated system in which the host rock was pervasively altered in areas of fluid flow to compositions in equilibrium with mineralizing fluids.

The C and O isotopes of host rock limestones and dolomite as well as of gangue calcite in the Upper Mississippi Valley define a trend extending from the isotope ratios of unaltered dolomite, through those of limestone and dolomite with decreased  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, to the significantly lower values for calcite deposited late in the ore paragenesis (Sverjensky, 1981b). The significant decrease of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values toward the orebodies is attributed to recrystallization under conditions of progressively higher water to rock ratios near the orebodies.

In the Tri-State district the close association of ore with areas of coarsely crystalline dolomite constitutes the single most important guide to ore (Hagni, 1976). Most orebodies are located along one or both margins of dolomitic zones that are probably dolomitized bioherms (Hagni, 1982). Jasperoid with disseminated sulphides forms a zone around many dolomite zones and its lateral and vertical extent essentially coincides with sulphide mineralization. Recrystallization of limestone occurs for distances of 13 to 27 m beyond the margin of silicification.

Although minor local variations may exist, the following set of minerals is typical of massive Zn-Pb sulphide ores in the low grade metamorphic zone of the Copperbelt of Central Africa: sphalerite+pyrite+galena+chalcopryrite, with subsidiary  $\pm$ arsenopyrite,  $\pm$ gallite,  $\pm$ tennantite,  $\pm$ briartite,  $\pm$ reni rite. Variations in the relative proportions of the three important sulphides (pyrite, galena and sphalerite) result in the identification of massive pyrite ore, galena-rich and sphalerite-rich ores, respectively (Kampunzu et al., 2009). In the Otavi Mountainland mineralogically simple Zn-Pb-dominated ores comprising sphalerite, galena, pyrite, minor chalcopryrite, bornite, colusite, reni rite (such as the Berg Aukas deposit) are distinguished from polymetallic ores of the Tsumeb-type which contain Cu, Pb, Zn and As, as well as trace elements such as Ag, Cd, Ga, Ge, Mo, and Sb. The sulphide assemblages in the latter ores are composed of variable amounts of galena, tennantite, chalcopryrite, sphalerite, chalcocite, enargite, bornite, pyrite, minor germanite, reni rite, briartite, Ge-bearing colusite, and Mo-W sulphides (e.g. Melcher et al., 2006; Kamona & G nz l, 2007).

## 4. Ore fluids

### 4.1 LTM deposits

These deposits are characterized by formation temperatures from 200  to 500  C (Megaw et al., 1988) as well as high chlorine concentrations of up to 21.2 wt. % Cl in fluid inclusions at Providencia (Rye & Haffty, 1969). In addition, Rye & O'Neil (1968) measured  $\delta D$  values in the range -68 and -83 ‰ and  $\delta^{18}O$  from 5.8 to 6.2 ‰. At Leadville the ranges are from -45 to -70 ‰  $\delta D$  and 5 to 8 ‰  $\delta^{18}O$ , respectively (Thompson & Beaty, 1990). Similar values of  $\delta D = -45$  to -60 ‰ and  $\delta^{18}O = 4$  to 9 ‰ have been reported for the Gilman deposit (Beaty, ed. 1990). These values are comparable to those for waters which have equilibrated with magmas (Sheppard, 1986).

In general, the metasomatic fluid of skarn and massive sulphide ores has a low  $CO_2$  content ( $X_{CO_2} < 0.1$ ) and moderate to high salinities (10 to 45 wt. % NaCl equivalent) (Einaudi et al., 1981). Fluid inclusion data from host minerals coeval with sulphide deposition or skarn formation (fluorite, sphalerite, quartz, pyroxene and garnet) indicate homogenization temperatures in the range 200  to 550  C and salinities with a total range from 1 to 60 wt. % NaCl equivalent (Einaudi et al., 1981; Megaw et al., 1988). The extreme variation in salinity may result from various mixtures of highly saline magmatic fluids and later circulating groundwaters (Roedder, 1984). Hotter (400  - 650  C), more saline (>26 wt. % NaCl equivalent) solutions are typical of the skarn zones, whereas the massive sulphide ores were deposited at temperatures between 200  and 450  C and variable salinities. Boiling appears to be characteristic of shallower environments (0.3 to 1 kb).

### 4.2 SEDEX deposits

Detailed fluid inclusion studies have been carried out at the Silvermines deposit (Samson & Russell, 1983, 1987). The mineralizing fluids have high Na concentrations with lesser, more variable K and Ca, and uniformly low Mg concentrations. Fluid inclusion waters in quartz, dolomite, sphalerite, galena and barite have  $\delta D$  values in the range of -23 to -58 ‰. The calculated  $\delta^{18}O$  values of the mineralizing fluid, based on mineral values for quartz and dolomite, range from 1.1 to 7.7 ‰. The data represent aqueous fluids that equilibrated with the geosynclinal sequence and granites underlying the deposit (Samson & Russell, 1987).

The  $\delta D$  and  $\delta^{18}O$  values of the ore fluid at Silvermines partly overlap that of both MVT and LTM ore fluids.

Homogenization temperatures and salinities in SEDEX deposits range from 100 to 260 °C and from 8 to 28 wt. % NaCl equivalent, respectively with deposition temperatures of Pb-Zn mineralization varying from 100° to 185° C at Navan, 150° to 195° C at Tynagh and 180° to 240° C at Silvermines (Andrew, 1986b). Ore stage fluids at Silvermines were more saline (12 to 22 wt. % NaCl equivalent) than those at Tynagh and Navan which had salinities ranging from 8 to 12 wt. % NaCl equivalent. According to Samson & Russell (1987), at Silvermines a negative correlation between the homogenization temperature and salinity of quartz-hosted fluid inclusions indicates mixing of high temperature, low salinity (8 to 12 wt. % NaCl equivalent) fluids with lower temperature, high salinity (18 to 22 wt. % NaCl equivalent) fluids.

#### 4.3 MVT deposits

The ore fluids of MVT deposits have low temperatures (100° to 150° C), uniform salinity, density and composition (Roedder, 1967, 1984). The gross salinity of the fluid inclusions is usually >15 wt. % NaCl equivalent and frequently >20 % wt. % NaCl equivalent, but no daughter crystals are found, indicating the presence of cations other than Na (Roedder, 1984). Fluid inclusion investigations have shown that MVT deposits form from highly concentrated Na-Ca-Cl brines (Newhouse, 1932; Hall & Friedman, 1963; Roedder, 1967). Apart from Na and Ca chlorides, the solutions contain minor K and Mg with total sulphur (expressed as  $SO_4^{2-}$ ) seldom exceeding a few thousand ppm. The density is always >1.0 g/cm<sup>3</sup> and frequently >1.1 g/cm<sup>3</sup> and the solute composition is uniform among various MVT districts. In addition, organic matter is frequently but not always observed as gases such as methane, as immiscible oil-like droplets, and as organic compounds in solution in the brines (Roedder, 1984).

Other regional fluid inclusion studies by Leach (1979), Leach & Rowan (1986) and Rowan & Leach (1989) have shown that sphalerite and associated sparry dolomite in the Ozark region have homogenization temperatures in the range 77° to 140° C with salinities from 14 to >23 wt. % NaCl equivalent. The narrow temperature range for sphalerite suggests that the ore fluid was near thermal equilibrium with rocks over a rather large geographic distribution. Even higher fluid inclusion temperatures have been found in sparry dolomite from the Reelfoot Rift Complex where values in the range of 150° to 280° C have been recorded (Leach et al., 1997). According to Leach et al. (1997), these high homogenization temperatures may be related to widespread igneous activity in the Reelfoot Rift Complex in Late Pennsylvanian to Permian times.

As discussed by Kampunzu et al. (2009), fluid inclusions studies in the Pb-Zn-Cu deposits of central Africa indicate at least two stages of mineralization: an earlier high temperature (220° to 390° C) and moderate to high salinity (15 to 43 wt. % NaCl equivalent) stage and a later stage associated with lower fluid temperature ( $\leq 80^\circ$  to 180° C) and variable salinities (<12 to 31 wt. % NaCl equivalent).

The ore fluids have  $\delta D$  values ranging from 0 to -45 ‰ and  $\delta^{18}O$  values from -3 to +4.7 ‰ (Hall & Friedman, 1963; Pinkney & Rye, 1972). Hall & Friedman (1963) established that the concentrations of deuterium in ore-stage fluids were relatively high in comparison to that in late gangue calcite which had low deuterium concentrations similar to the local groundwaters. In general MVT ore fluids are similar to SEDEX ore fluids in terms of salinity and homogenization temperatures as indicated above.

## 5. Sulphur and lead isotopes

### 5.1 LTM deposits

The isotope ratios of sulphides (including sphalerite, galena, pyrite, chalcopyrite and pyrrhotite) are homogeneous and cluster around  $0 \pm 4$  ‰  $\delta^{34}\text{S}$  in most LTM deposits (Sawkins, 1964; Rye, 1974; Gilmer et al., 1988; Thompson & Beaty, 1990; Beaty, 1990). Deposits with homogeneous isotope ratios clustering around  $0 \pm 4$  ‰ include Providencia, Velardeña, Leadville and Gilman. Other deposits have positive homogeneous values in the range +5.9 to +9.6 ‰ as at Temperino in Italy (Corsini et al., 1980) or from +18.9 to +24.1 ‰ as at Los Lamentos (Megaw et al., 1988). Isotopic equilibrium between sulphide species may or may not have been maintained during mineral deposition.

At Santa Eulalia, a wide spread is observed at the East Camp deposit with  $\delta^{34}\text{S}$  ratios ranging from +4 to -11 ‰, whereas a much narrower spread occurs in the West Camp deposit where negative values from -8 to -15 ‰ are characteristic (Megaw et al., 1988).

The lead isotope ratios of galena from Mexico are relatively homogeneous within individual mineral districts, and deposits of similar type exhibit similar isotope ratios (Cumming et al., 1979). Lead isotope data for Cenozoic limestone replacement and vein deposits define a linear array which is regarded as a secondary isochron resulting from a two-stage process. The linear array partly coincides with the field of mature arc volcanics of Doe & Zartman (1979), but extends to more radiogenic compositions characterized by pelagic sediments and/or upper crustal material. Isotopic data for these carbonate replacement deposits are characterized by intermediate values between the less radiogenic SEDEX deposits and the more radiogenic MVT Appalachian subdistrict of Ivanhoe-Austinville.

### 5.2 SEDEX deposits

The  $\delta^{34}\text{S}$  ratios of sulphide minerals from the epigenetic feeder zones at Silvermines and Keel cluster around  $0 \pm 10$  ‰ (Coomer & Robinson, 1976; Caulfield et al., 1986). Other sulphides, particularly from the stratiform zones at Silvermines and most of the sulphides from Tynagh, are characterized by isotopically light sulphur generally ranging from -42.5 to -4 ‰. Sulphides with relatively narrower spreads occur within this wide range of  $\delta^{34}\text{S}$  values, such as most of the stage one pyrite (-3.1 to -7.4 ‰) at Tynagh, stratiform ore sphalerite and galena (-20 and -18 ‰) at Silvermines, and sedimentary sphalerite (-15 and -22 ‰) from Navan (Coomer & Robinson, 1976; Boast et al., 1981a; I.K. Anderson et al., 1986). Pyrite from hydrothermal vents at Silvermines also exhibits relatively homogeneous  $\delta^{34}\text{S}$  values in the range -42.5 to -31.3 ‰ (Type I pyrite vents) and -23.7 to -18.4 ‰ (Type II pyrite vents) (Boyce et al., 1983).

Sulphides with heavy  $\delta^{34}\text{S}$  values of up to +14 ‰ include post-sedimentary galena at Navan (0 to +14 ‰), and sphalerite and galena from Tatestown (-3 to +14 ‰) (I.K. Anderson et al., 1986; Caulfield et al., 1986). Barite from the Irish deposits forms a fourth distinct isotopic group characterized by positive  $\delta^{34}\text{S}$  values in the range 14.2 to 22.6 ‰ (Boyce et al., 1983; Andrew & Ashton, 1985; Caulfield et al., 1986).

Caulfield et al. (1986) observed that the lead isotope ratios of the Irish deposits depend on geographic location rather than on the mode of occurrence or age of host rocks, indicating direct involvement of local basement rocks. The  $^{206}/^{204}\text{Pb}$  isotope ratios are parallel to basement trends of Caledonide inheritance and closely follow geophysically identified basement structures. The isotope data defines a linear array of both Lower Paleozoic and Carboniferous-hosted mineralization on the lead-lead plot which reflects mixing between a



less radiogenic source with a mantle type lead signature and a more radiogenic source with upper crustal type characteristics (O'Keefe, 1986).

With the exception of the Navan deposit, the lead isotope ratios of galena from Tynagh and Silvermines (Boast et al., 1981b; Boast, 1983), as well as minor deposits such as Keel, Tatestown, Ballinalack and Moyvoughly (Caulfield et al., 1986), are characterized by uniform values within a given deposit. All the lenses except the stratigraphically highest number 1 lens at Navan have uniform isotope ratios on a lens scale (Mills et al., 1987). In general, the average  $^{206}/^{204}\text{Pb}$  ratio decreases from the stratigraphically lowest number 5 lens to the number 1 lens. The number 1 lens contains a less radiogenic component in addition to the more radiogenic lead characteristic of the other lenses.

### 5.3 MVT deposits

The isotope ratios of sulphur in MVT deposits are generally positive and uniform as in the Upper Mississippi Valley (Pinckney & Rafter, 1972; MacLimagans, 1975), or positive with wide ranges as in Southeast Missouri (Sverjensky, 1981). Sulphur with negative isotope ratios has been reported from the Tri-State district (Ault & Kulp, 1960; Deloule et al., 1986).

The data of Pinckney & Rafter (1972) for the stratigraphically correlated bands in ores from four deposits in the Upper Mississippi Valley indicate that the total  $\delta^{34}\text{S}$  range of the main stage sulphides is from 6.3 to 15.9 ‰, but individual sulphides have narrower spreads. The bands include early (bands 1 to 7), intermediate (bands 8 to 10), and late (bands 11 to 18) paragenetic stages. The latest stage is represented by post-sphalerite deposition of galena. The isotopic variations as deposition proceeded are small and largely due to equilibrium isotopic fractionation between sphalerite and galena with decreasing temperature from an ore fluid with essentially constant  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  (Pinckney & Rafter, 1972; MacLimagans, 1975).

An example of isotopic disequilibrium during sulphide precipitation is provided by sulphides from the Buick mine, Southeast Missouri (Sverjensky, 1981) where the successive stages include early (dark sphalerite), intermediate (cuboctahedral galena), late (cubic galena) and latest (pale sphalerite). Early sphalerite ( $\delta^{34}\text{S} = 17.54$  ‰) and intermediate galena ( $\delta^{34}\text{S} = 16.53$  ‰) have similar average values, but galena has a wider spread ranging from 13.0 to 21.1 ‰. Cubic galena of the late stage is isotopically distinct from the earlier phases as indicated by a spread from 0.2 to 9.9 ‰. The latest stage of sphalerite is a minor phase with isotope ratios overlapping those for cuboctahedral and cubic galena.

In the Tri-State district Deloule et al. (1986) found a total range of -6 to -12 ‰  $\delta^{34}\text{S}$  in a single galena crystal from the Pitcher orebody. The inner part of the crystal had a constant  $\delta^{34}\text{S}$  ratio of -9 ‰  $\delta^{34}\text{S}$ , whereas the outer part had a value of -12 ‰  $\delta^{34}\text{S}$  with local variations. The main variation is spatially related to a major change in the lead isotope ratio of the crystal, indicating a common source for the lead and sulphur.

In southern and central Africa, the sulphur isotopes of MVT deposits fall into three categories: (1) heavy and homogeneous  $\delta^{34}\text{S}$  values (e.g. Tsumeb  $\delta^{34}\text{S} = 20.5$  ‰,  $n = 35$ ; Kamona & Günzel (2007)), (2) highly variable with a wide range of values (e.g. Kombat  $\delta^{34}\text{S} = -11.3$  ‰ to  $+26.2$  ‰ with an average value of  $+5.2$  ‰,  $n = 19$ ; Hughes (1987)) and (3) negative and homogeneous  $\delta^{34}\text{S}$  values (e.g. Kabwe  $\delta^{34}\text{S} = -15.8$  ‰,  $n = 43$ ; Kamona & Friedrich (2007)). The negative and homogeneous sulphur isotope ratios of ore sulphides (-18 to -12 ‰  $\delta^{34}\text{S}$ ) from Kabwe are typical of sedimentary sulphides produced through bacterial reduction of seawater sulphate and suggest a sedimentary source for the sulphur, whereas the heavy  $\delta^{34}\text{S}$  isotopes at Tsumeb and other deposits (Berg Aukas, Khusib Springs) indicate

seawater as the ultimate source of the sulphur (Kamona & Günzel, 2007). A seawater sulphate source is also suggested for the Kipushi deposit (Kampunzu et al., 2009).

The seawater sulphate may have been initially concentrated in basinal brines and evaporite beds that later provided heavy sulphur to ore-forming hydrothermal solutions that eventually deposited the base metals in the carbonate host rocks. The large variation in the sulphur isotope ratios at Kombat is more enigmatic and could be due to thermochemical sulphate reduction (Innes & Chaplin, 1986), mixing of seawater with a fluid containing isotopically light sulphur derived by bacteriogenic reduction of seawater sulphate, variations in oxygen fugacity and/or pH with decreasing temperature (Hughes, 1987) or the involvement of a magmatic ore fluid (Innes & Chaplin, 1986).

Mississippi Valley type deposits of the United States are characterized by anomalous radiogenic linear trends that do not fit standard lead evolution models (Heyl et al., 1966). This anomalously radiogenic lead is traditionally termed "J-type" after the Joplin galena in the Tri-state district. Galena from the Appalachian district is the least radiogenic of all the MVT Pb-Zn districts (Heyl et al., 1966).

In contrast, the lead isotopes of galena from the Austinville-Ivanhoe subdistrict of the Appalachians (Foley et al., 1981) have a relatively narrow spread. According to Foley et al. (1981), galenas of different generations have distinctive lead isotope ratios, with galena becoming increasingly more radiogenic as ore deposition proceeded. In addition, smaller orebodies have a wider range in lead ratios and are more radiogenic than larger orebodies due to contamination by more radiogenic crustal lead.

Lead isotopic variations have also been observed in single galena crystals from MVT deposits (e.g. Sverjensky, 1981; Deloule et al., 1986; Crocetti et al., 1988). The data indicate frequent and rapid isotopic changes that show increasing radiogenic lead with time. In addition, the data shows several isotopic domains that suggest mixing between at least three end members with distinct isotope ratios such as different sedimentary layers and basement rocks (Deloule et al., 1986).

Sulphides from the Zn-Pb orebodies in southern and central Africa show small variations in their Pb isotopic compositions with values typical of the upper continental crust (Hughes et al., 1984; Kamona et al., 1999).

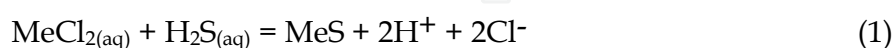
## 6. Discussion

### 6.1 LTM deposits

The  $\delta D$  and  $\delta^{18}O$  ratios for waters in fluid inclusions at Providencia and Leadville (Rye & O'Neil, 1968; Thompson & Beaty, 1990), as well as the close spatial and temporal relationship between ores and intrusives, suggest a magmatic origin for the ore fluids and metals (Shimazaki, 1980; Einaudi et al., 1981). The deposits may be associated with subduction-related, magnetite-series granitoids (Einaudi et al., 1981) or with magnetite- and ilmenite-series granitoids as in Japan (Shimazaki, 1980).

The lead isotope data of Cumming et al. (1979) indicates that in the case of the Mexican deposits, the lead was derived from the Cenozoic mantle as well as from the Precambrian crust by magma contamination. The sulphur isotope values do not indicate a unique magmatic source for all the deposits since the  $\delta^{34}S$  values of granitoid source-magmas are controlled by geographic location and may therefore reflect sulphur isotope ratios of local country rocks (Ohmoto, 1986). Nevertheless, a predominantly magmatic sulphur source is indicated in deposits such as Providencia (Rye, 1974; Sawkins, 1964), Velardeña (Gilmer et al., 1988), and Leadville (Thompson & Beaty, 1990).

The high concentrations of chlorine in fluid inclusions at Providencia (Rye & Haffty, 1969) indicate that the major metals are transported as chloride complexes to the deposition site. The general lack of sulphates suggests that  $\text{H}_2\text{S}$  is the dominant sulphur species (Ohmoto, 1986). The solutions were moving up fast enough to maintain uniformly heated wall rocks adjacent to the fluid conduits as indicated by the low vertical temperature gradient of less than  $50^\circ \text{C/km}$  at Providencia (Sawkins, 1964). Initial skarn formation by infiltrational metasomatism and diffusion in limestones occurs between  $400^\circ$  and  $650^\circ \text{C}$  and precedes sulphide deposition (Einaudi et al., 1981; Einaudi & Burt, 1982). Sulphide deposition takes place as a consequence of declining temperature, local oxidation-reduction reactions, or neutralization of the ore fluid at the marble contact. A generalized reaction between metal chlorides and hydrogen sulphide leading to sulphide deposition is (Barnes, 1979):



where Me is metal (e.g. Zn or Pb). From reaction (1) deposition of sulphides could be caused by an increase in reduced sulphur (due to sulphate reduction or leaching of previously formed sulphide minerals), an increase in pH (e.g. acid neutralization by carbonate dissolution), and a decrease in chloride concentration (by removal of  $\text{Cl}^-$  ions through pairing by ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). A decrease in temperature of the chloride-sulphide bearing fluid stabilizes  $\text{H}_2\text{S}$  relative to  $\text{SO}_2$  and thus promotes deposition of metal sulphides (Rubin & Kyle, 1988).

## 6.2 SEDEX deposits

In the case of SEDEX deposits there is no general consensus about fluid and metal sources (White, 1986). The problem is caused by the fact that although the lead isotope data indicates the involvement of basement rocks, it does not distinguish between lead derived directly from the basement and lead from disaggregated basement rocks. O'Keefe (1986) established that epigenetic lead veins hosted in Lower Paleozoic rocks in Ireland are of the same age and have been derived from the same lead sources as the surrounding Carboniferous-hosted deposits, suggesting a pre-Carboniferous source for the mineralization. The relative abundance of Pb over Cu indicates silicic continental-derived rocks and sediments which are relatively rich in Pb rather than deep ocean rifts and basaltic rocks with high Cu and Zn but low Pb contents (White, 1986).

A basement source for the metals in the Irish SEDEX deposits is postulated by the deep convection cell model of Russell (1978) and Russell et al. (1981) in which fluid convection within deep fault structures in upper crustal rocks leads to ore fluid generation. In the model, the ore solution evolves from seawater into a brine capable of leaching metals from underlying rocks during fluid-rock interaction with increasing depth down to the base of the brittle zone in the upper crust where temperatures approach  $250^\circ \text{C}$ .

Objections raised against the deep fluid convection cell model concern the lack of an intimate water-rock contact (Cathles, 1986) and the absence of suitable rock types such as basalts susceptible to mineral:solution disequilibrium (Lydon, 1986). Lydon (1986) proposed a stratal aquifer model in which the ore fluid is generated from connate waters within an arenaceous aquifer. The metals are derived mostly from clays and iron-oxide pigments in the aquifer itself with minor contributions from faulted basement rocks during reflux convection to depths of 1-3 km and not up to 15 km as in the Russell model. Dense chloride rich brines were produced by evaporitic conditions during the early part of a marine

transgression and collected as connate pore waters in Old Red Sandstone lithologies within a basinal structure. The brines became geopressured and heated to over 200° C due to hydraulic sealing and thermal insulation by about 500 m of semi-compacted Lower Carboniferous shale and argillaceous limestone. Heat to the stratal aquifer is supplied directly by conduction from basement rocks and by reflux convection of brines along dilatant fault zones to depths of 3 km.

The sources of sulphur are less problematic. The sulphur isotope ratios of sulphides from the epigenetic feeder zones of the Irish SEDEX deposits are similar to those of diagenetic and vein sulphides in underlying Lower Paleozoic strata from which the sulphur was presumably leached (I.K. Anderson et al., 1989). An ultimate source for the sulphur may be Caledonian granites in the age range 390 to 435 Ma which have a mean  $\delta^{34}\text{S}$  value of  $+0.7 \pm 2.6$  ‰ (Laouar, et al., 1990). Isotopically light sulphur with ratios from -42.5 to -4 ‰ is considered to have originated through bacteriogenic reduction of Lower Carboniferous seawater sulphate and was the dominant sulphur source in the Pb-Zn deposits (Hitzman & Large, 1986; I.K. Anderson et al., 1989). A third group of sulphides in the Irish SEDEX ores is characterized by  $\delta^{34}\text{S}$  values in the range -3 to +14 ‰. The heavy sulphur component in these sulphides is believed to be of evaporitic origin (Caulfield et al., 1986), but it may represent deep-seated sulphur or low temperature chemical reduction of seawater at the deposition site (I.K. Anderson et al., 1986). Barite formed by reaction of exhaled  $\text{Ba}^{2+}$  with Lower Carboniferous seawater sulphate (Boyce et al., 1983).

It is generally agreed that stratiform sediment-hosted ores are deposited with or soon after the enclosing sediments and are therefore syngenetic or syndiagenetic (White, 1986). In the deep fluid convection model, circulation of seawater is initiated during rifting and is driven by a high geothermal gradient as indicated by local volcanic flows and/or shallow intrusives in the rock successions at Navan, Tynagh and Silvermines (Russell et al., 1981). The modified seawater with metals and  $\text{H}_2\text{S}$  in solution returns to surface along convective updrafts such as intersecting major fractures. Ore deposition takes place as a result of fluid mixing with alkaline groundwaters and seawater brines. In contrast, in the stratal aquifer model, geopressured formation waters are released intermittently to the surface along fault zones during periods of tectonic activity (Lydon, 1983) and ore precipitation takes place from a brine pool in a third-order basin due to cooling and/or bacteriogenic reduction of sulphate to sulphide within the water column.

### 6.3 MVT deposits

The origin of MVT deposits is regarded as a normal part of sedimentary basin evolution (Jackson & Beales, 1967). According to the basinal brine model of Beales & Jackson (1966, 1967), ore-forming brines are produced during burial of sediments. Heat, metals and other solutes are acquired during brine migration along aquifers. The similarity of the fluid inclusion data in minerals from MVT deposits to typical oil-field brines with respect to element compositions, high salinities, and hydrogen and oxygen isotopes has been noted (Hall & Friedman, 1963; Roedder, 1967). The main difference is the much lower Na/K ratio of MVT fluids (Sawkins, 1968; White, 1968). This difference may be due to water-rock interactions in aquifers during fluid migration (Sverjensky, 1984; Roedder, 1984), or to contributions of interstitial fluids from evaporite beds enriched in residual potassium (G.M. Anderson & Macqueen, 1982). According to Crocetti & Holland (1989), the lower Na/K ratio of MVT fluids results from equilibration with K-feldspar-albite assemblages in basement



and/or sedimentary rocks, whereas higher ratios are due to equilibrium reactions with clay minerals.

The much higher salinities of the brines compared to seawater result from dissolution of salt beds by surface-derived groundwaters or by expulsion of interstitial fluids from evaporite beds (G.M. Anderson & Macqueen, 1982). The chloride-rich brines are able to leach metals from rocks during fluid migration by desorption of loosely bound metals, or release of metals from metal-organic complexes through thermal alteration or destruction of such complexes.

The isotope ratios of sulphur are generally positive and may be uniform or have wide ranges, indicating a crustal, ultimately seawater origin involving sulphate reduction (G.M. Anderson & Macqueen, 1982; Sverjensky, 1986). Multiple sources for the lead have been suggested, including a radiogenic lead component from the basement rocks, lead from carbonate cements and feldspars in sandstones, and normal lead from oil-field brines (Brown, 1967; Doe & Delevaux, 1972). The isotopic studies of Deloule et al. (1986) indicate that numerous and discontinuous inputs of Pb and S from isotopically distinct sources such as different sedimentary layers and basement rocks in the same basin are involved.

In the basinal-brine model, fluids are expelled from strata by sediment compaction during early stages of diagenesis. However, Bethke (1986) observes that fluids displaced from deep basins by compaction-driven flow move too slowly to avoid conductive cooling and cannot account for the deposition temperatures of 100° to 150° C. Episodic dewatering from overpressured aquifers (Cathles & Smith, 1983) also appears to be incapable of adequate heat transfer because of the small volumes required and a narrowly defined aquifer (Leach & Rowan, 1986). In addition, significant overpressures did not develop in basins such as the Illinois basin in the Upper Mississippi Valley (Bethke, 1986). A gravity-driven groundwater flow system due to topographic differences across basins with high heat flows and adequate aquifer permeabilities is considered more likely for the mid-continent districts (Bethke, 1986; Leach & Rowan, 1986).

The fluids are expelled from basins that have undergone deformation or uplift as indicated by the proximity of MVT deposits to tectonically deformed or uplifted basin margins, a coincidence which may be an important unifying factor for MVT deposits in diverse geologic provinces (Leach & Rowan, 1986). Other mechanisms include topography-driven, sediment compaction and overloading, overpressured gas reservoirs, and thermal and density reflux drives (e.g. Leach et al., 2010; Vearncombe et al., 1996)

Due to the low solubilities of sphalerite and galena in the presence of significant H<sub>2</sub>S in solutions at 100° to 150° C, the metals and H<sub>2</sub>S are not transported together (G.M. Anderson, 1983). The sulphide is instead supplied at the deposition site by reduction of sulphate already in the brine or by adding H<sub>2</sub>S to the brine, resulting in sulphide deposition. The source of reduced sulphur is sulphate, either from locally available sulphate minerals or dissolved brine-transported sulphate. This is the so-called "mixing-model" which has been applied with success at the Pine Point deposit where H<sub>2</sub>S was derived locally through thermochemical reactions involving sulphate, bitumen and H<sub>2</sub>S (Macqueen & Powell, 1986). Alternatively, transport of metals and H<sub>2</sub>S in the order of 1 ppm is possible under conditions of acidic pH and high total dissolved CO<sub>2</sub> concentrations (Sverjensky, 1986), as indicated by the correlation of Pb and S isotopes in galena in the Southeast Missouri district and the district wide sphalerite color banding in the Upper Mississippi Valley. This is the "non-mixing" or "reduced-sulphur" model in which deposition of metal sulphides may be caused by pH change, cooling or dilution with groundwater.

The Zn-Pb-(Cu) deposits of southern and central Africa formed from basinal brines during two main mineralizing events that characterize syntectonic deposits (e.g., Kabwe, Tsumeb) and post-tectonic deposits (e.g., Kipushi). These deposits exhibit many of the typical characteristics of Mississippi Valley-type ore-forming systems, including their classical stratabound, epigenetic nature and occurrence in clusters within platform marine carbonates overlying continental crust (e.g. Frimmel et al., 1996; Kampunzu et al., 2009). A sialic crustal origin of the metals from basinal sediments and basement rocks is supported by lead and strontium isotope data, whereas the sulphur isotope compositions are compatible with a sedimentary origin of sulphur from seawater via evaporites and/or diagenetic sulphides. The main ore-forming fluids were saline with moderate to high temperatures and could have been produced by normal geothermal gradients during basin evolution. Ore deposition occurred in carbonate rocks with favourable permeable structures including faults, veins, breccias and hydrothermal karsts as a result of cooling, fluid mixing, pH change or addition of H<sub>2</sub>S.

Although the one universal and fundamental characteristic of MVT deposits is the absence of igneous rocks that are potential sources of the ore solutions (Ohle, 1959), intermittent igneous activity occurred in the Southeast Missouri district from Cambrian to Cretaceous time (Thacker & K.H. Anderson, 1977). In particular, Paleozoic explosive igneous activity and intrusion of dikes occurred during Upper Cambrian and Devonian times in the district (Gerdemann & Myers, 1972). In addition, a volcanic tuff bed of up to 1 m or more in thickness occurs over a limited area near the top of a sandy transition zone at the Lamotte-Bonneterre contact. Although the igneous activity was localized and short-lived to have had much direct bearing on the mineralization, it provides evidence that the region had a high geothermal gradient (Gerdemann & Myers, 1972).

## 7. Conclusions

Carbonate-hosted Pb-Zn deposits range from high temperature, intrusion -related LTM ores through moderate temperature, syngenetic to syndiagenetic SEDEX ores to low and moderate temperature MVT ores characterized by a lack of associated igneous rocks. Metal ratios expressed as Zn/(Zn+Pb) vary from 0.5 in LTM districts to 0.7 in both SEDEX and MVT deposits. Pyrite, sphalerite and galena are the major sulphides, but the mineral paragenesis and relative proportions of these sulphides vary from deposit to deposit, even within the same district. On average Ag grades are relatively high in LTM (>200 ppm) compared to SEDEX (63 ppm) and MVT (96.8 ppm) ore deposits. Copper may be significant in some MVT deposits, especially those in which sulphosalts of tennantite and tetrahedrite form part of the mineral paragenesis as at the Tsumeb and Kipushi deposits.

There are numerous mechanisms that may be responsible for MVT ore fluid migration in sedimentary basins, including topography-driven, sediment compaction, orogenic squeezing, overpressured gas reservoirs, as well as thermal and density reflux mechanisms. However, no single mechanism can be applied to all districts. In the case of the LTM deposits metal and sulphur sources include mantle and crustal rocks, whereas for SEDEX and MVT deposits the metals may have been derived from basement rocks as well as basin sediments during fluid-rock interactions over a prolonged period of time in sedimentary basins with a high heat flow. In all three cases the formation of large deposits requires focusing of ore fluids along conduits that include faults and folds, stratigraphic aquifers, discontinuities and contacts, breccias, pinch-outs and reefs in carbonate host rocks.

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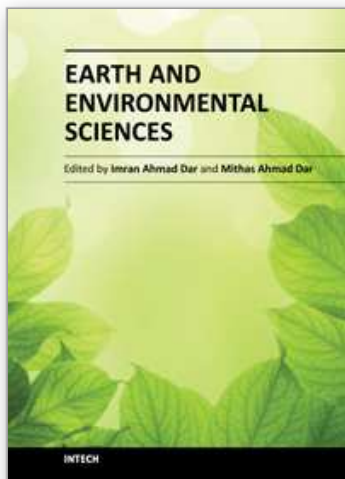
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We are increasingly faced with environmental problems and required to make important decisions. In many cases an understanding of one or more geologic processes is essential to finding the appropriate solution. Earth and Environmental Sciences are by their very nature a dynamic field in which new issues continue to arise and old ones often evolve. The principal aim of this book is to present the reader with a broad overview of Earth and Environmental Sciences. Hopefully, this recent research will provide the reader with a useful foundation for discussing and evaluating specific environmental issues, as well as for developing ideas for problem solving. The book has been divided into nine sections; Geology, Geochemistry, Seismology, Hydrology, Hydrogeology, Mineralogy, Soil, Remote Sensing and Environmental Sciences.

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