

## Ore Deposit Models - 6. Mississippi Valley-Type Lead-Zinc Deposits

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### Introduction

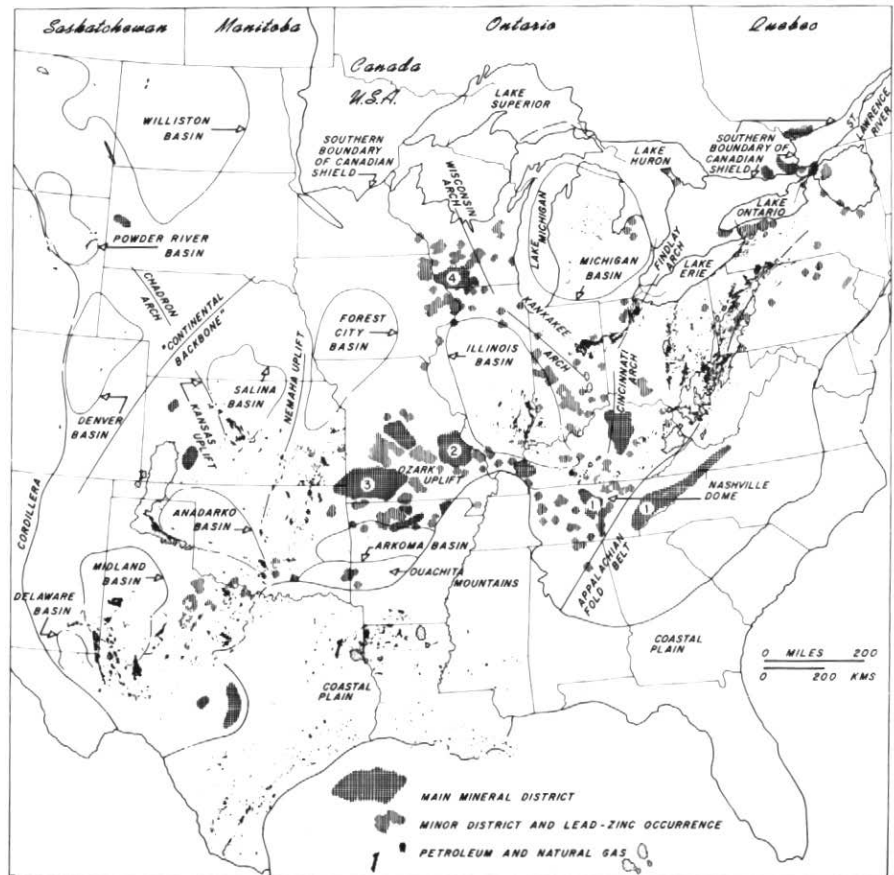
Carbonate-hosted lead-zinc deposits of the Mississippi Valley-type (MVT) appear to be at one end of a spectrum of base-metal ore deposit types which form in sediments some time during the lifetime of a sedimentary basin. The spectrum of deposits includes red-bed copper, shale-hosted lead-zinc, and sandstone-hosted lead, as well as MVT deposits. As in the case of petroleum and natural gas, these ore deposits are now generally viewed as being a normal part of the evolution of a sedimentary basin. Fluids move in sedimentary basins, both during basin formation and long afterwards, in response to hydrostatic gradients established by compaction, thermal gradients, topographic relief, deformation and other factors, and they are capable of transporting and depositing metals. This much is easy to say; elucidating the details is a little more difficult.

Two recent review articles discuss the broader relations between the various types of sediment-hosted deposits mentioned above (Gustafson and Williams, 1981; Bjørlykke and Sangster, 1981). They demonstrate that hypotheses involving syn-sedimentary, diagenetic and epigenetic processes are all alive and well for one or another of these deposit types, and that although certain genetic factors are reasonably clear for each type, the place of each in relation to the others and to the overall process of basin evolution is still not clear in many respects, as considered below.

MVT deposits form the principal source of lead and zinc in the United States, where there are four main districts (Fig. 1): central and east Tennessee, southeast Missouri, the Tri-state area (Missouri, Oklahoma and Kansas), and the Wisconsin area of the Upper Mississippi River valley. All of these districts except east Tennessee are located in essentially undeformed platform carbonates. Important Canadian deposits (Fig. 2) include Pine Point of the Interior Platform, N.W.T. (Skall, 1975); Polaris (Kerr, 1977) and Nanisivik (Olson, 1977) of the northern platform, N.W.T.; Gays River of the Appalachian platform; and Daniel's Harbour of the western Newfoundland platform (Collins and Smith, 1975; Coron, 1982). Promising Cordilleran Orogen deposits in the Rocky Mountain Belt and possibly of future ore grade include Robb Lake in northeastern British Columbia (Macqueen and Thompson, 1978; Manns,



**Figure 2** Location of some major Canadian MVT lead-zinc deposits. Solid circles are existing mines, although only Pine Point, Nanisivik and Daniel's Harbour are currently producing; solid triangles represent possible future mines. 1 - Pine Point, 2 - Polaris, 3 - Nanisivik, 4 - Daniel's Harbour, 5 - Gays River, 6 - Gayna River, 7 - Robb Lake. Also see Macqueen (1976), and Sangster and Lancaster (1976) for the location of many new carbonate-hosted lead-zinc showings in the Rocky Mountain Belt.



**Figure 1** Map of U.S.A. showing major lead-zinc districts, petroleum and natural gas areas, and major basins. Lead-zinc districts: 1 - Tennessee, 2 - Southeast Missouri, 3 - Tri-state, 4 - Upper Mississippi or Wisconsin. Note

concentration of metal areas between basins, and almost complete lack of overlap between metal and petroleum areas. From Anderson, 1978.

1981) and Gayna River in the Mackenzie Mountains, N.W.T. (Hardy, 1979).

Broadly, these deposits are stratabound - confined to individual stratigraphic units. Not included here are those carbonate-hosted deposits which are stratiform or bed-like, and appear to be of syngenetic or early diagenetic origin (e.g., Alpine Triassic deposits of Austria and Poland).

Recent summary articles on aspects of MVT deposits in general, besides those mentioned above, include Anderson (1978), Macqueen (1979), Heyl *et al.* (1974), Ohle (1959, 1980), Sangster and Lancaster (1976), and Wolf (1976, 1981). Mention must also be made of Economic Geology Monograph No. 3 (Brown, 1967), which contains a wealth of useful information on MVT deposits.

Tonnage and grade of a number of MVT districts and deposits are given by Gustafson and Williams (1981) and Barnes *et al.* (1981). It is important to realize that MVT ore deposits are simply unusually large representatives of a ubiquitous phenomenon: occurrences of sphalerite and galena are commonplace in carbonate successions.

**Characteristics**

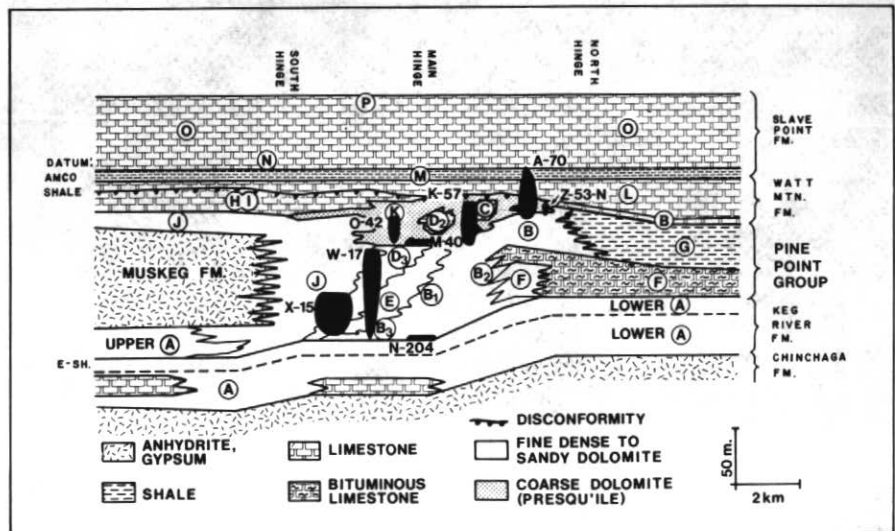
Recognizing general characteristics minimizes differences, some of which may be highly important. MVT deposits are diverse! The following generalizations (some of them tentative) are based on Ohle's (1959) pioneer work, updated over the past two decades. In sum, these generalizations describe the MVT ore deposit class.

*Setting.* 1) Most deposits occur in carbonate rocks, with a strong bias toward dolomites. 2) Deposits occur in most sedimentary basins in all parts of the world. Host rocks range in age from Proterozoic to Cretaceous, although many fewer deposits are known in the Proterozoic, Jurassic, and Cretaceous than in the Cambro-Ordovician and Carboniferous, which to 1962 contained about 80% of MVT deposits in the coterminous United States (Beales and Onasick, 1970). Deposits in Cenozoic rocks are curiously lacking. 3) Deposits tend to be found at or near the edges of basins as presently preserved, or on arches between basins (Fig. 1). 4) They may occur in relatively undisturbed platform carbonates, or within foreland fold and thrust belts. 5) Individual deposits, similar to one another in their occurrence, tend to occur in districts which may be distributed over hundreds of square kilometres (Fig. 1). This argues against strictly local sources for metals and sulphur. 6) In most districts, local igneous rocks are unknown. 7) Host carbonate rocks are

unmetamorphosed. 8) For settings located in relatively undisturbed platform settings, stratigraphic evidence suggests that mineralization took place at relatively shallow depths, perhaps a few hundred to  $\approx 1000$  metres, thus involving pressures not exceeding several hundred atmospheres. Geothermal gradients of 25 - 30° C/Km are typical in these environments, yielding average host rock temperatures that are significantly less than 100 - 150° C: thus either a heat source at shallow depths is a requisite, or heated fluids must have migrated from a deeper source (see White, 1974; Macqueen and Powell, in press). 9) Some deposits appear to be strongly controlled by unconformity-associated features such as paleokarst terrane (e.g., East Tennessee; Daniel's Harbour; Nanisivik; Pine Point, Figs. 3 and 4). 10) Some deposits tend to be localized along facies fronts between platform carbonates and basinal shales (e.g., Robb Lake). 11) Although early workers commonly suggested that deposits were located within carbonate reef masses, subsequent work

on many deposits demonstrates that actual reef-hosted deposits are minor. Deposits are closely controlled by the prior development of porosity, and thus may be located in platform carbonates of biostromal character, or back-reef or fore-reef settings (e.g., Pine Point, Fig. 3; Skall, 1975).

*Deposits.* 1) Most deposits have relatively simple mineralogy, with galena and/or sphalerite as the main ore minerals (Fig. 4), nearly always accompanied by pyrite and/or marcasite. Barite and fluorite are common in some districts. Chalcopyrite is a minor to very minor associate of some deposits. Commonly, galena is low in silver, and sphalerite is low in iron. 2) Deposits clearly are epigenetic: sulphides were emplaced in pre-existing pore spaces commonly developed within breccias or paleokarst topography which in turn developed within lithified carbonates (Fig. 4, 5). 3) Studies of fluid inclusions within coarsely crystalline sphalerite, barite and carbonates have established two important facts: a) mineralization



**Figure 3** Schematic south-to-north cross-section through Middle Devonian Pine Point property, N.W.T., Canada, showing: division into lithologic facies A - P; main rock types; E - shale marker (Keg River Fm) and Amco Shale marker (Watt Mountain Fm) which indicate influence of hinge zones identified across top of diagram; Muskeg evaporites of Elk Point Basin to south, and G facies shales of shale basin to north; barrier complex of Facies A-L; unconformity between facies H/I and L, suggested to control karsting in underlying units; and projected stratigraphic locations of some of the major orebodies (A-70, K-57, X-15, etc.). Two facies (B, F) are rich in indigenous organic matter. Organic geochemical studies of indigenous organic matter, heavy oil and bitumen demonstrate that the carbonate barrier on the property has a low temperature history

( $\approx 60^\circ$  C maximum), and that the orebodies, with fluid inclusion filling temperatures to  $\approx 100^\circ$  C, represent thermal anomalies. An attractive explanation for the origin of the orebodies and the pyrobitumen which is associated with them is abiogenic reduction of sulphate, a mechanism with which the sulphur isotope data are compatible. This is the "mixing" model described herein, with a local source for H<sub>2</sub>S. Considering carbonate-hosted lead-zinc deposits as a whole, Pine Point is perhaps atypical in that it is situated between an evaporite basin to the south and a shale basin to the north, and the barrier has acted and acts today as a conduit localizing fluid flow over a large area (Hitchon, 1969). From Macqueen and Powell (in press; original diagram and lithologic facies after Skall, 1975; and Kyle, 1981).

temperatures on average ranged from 80° C to 200° C, and b) ore-bearing fluids were highly saline Na-Ca-Cl brines, 5 to 10x the salinity of seawater (Roedder, 1976, 1979). 4) Organic materials in the form of kerogen or bitumen in the host rocks and/or petroleum in fluid inclusions is very commonly observed in MVT districts (Fig. 4E, 5B). 5) Isotope studies show that sulphur is generally heavy and with fairly wide-ranging values. This establishes a crustal, ultimately sea-water origin involving sulphate-reduction at some time in the genetic story. Bacterial action is no longer believed to be the only viable mechanism of sulphate reduction below 100° C, but is still a distinct possibility in many districts as long as the site of reduction is at some distance from the

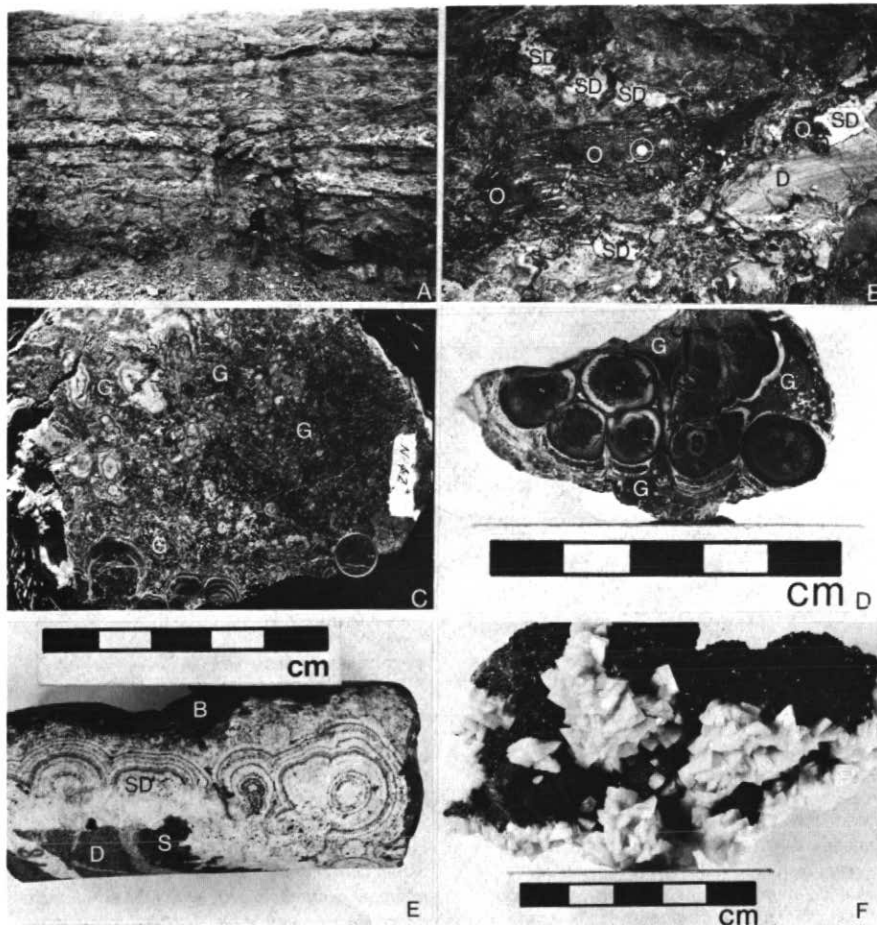
site of sulphide deposition, since deposition temperatures are usually too high for the bacteria (Ohmoto and Rye, 1979).

Lead isotopes can also show a considerable range in any one district, and are commonly highly radiogenic, yielding future ages (negative model ages). Data are generally consistent with a basement or reworked sediment (crustal) source for the lead, but do not point to specific sources (Doe and Zartman, 1979). Both the sulphur and lead isotope data furnish important constraints on models for individual areas, but cannot be expected to supply unique answers independent of other observations, anymore than can fluid inclusions or alteration studies. 6) Open space, developed by a variety of mechanisms in carbonate rocks (Choquette and Pray, 1970), seems to be a

prime requisite for the development of an economic deposit (Callahan, 1967) (also see Figs. 3, 4 and 5). How much carbonate dissolution accompanies ore deposition is a matter of controversy (Heyl *et al.*, 1959; Beales, 1975).

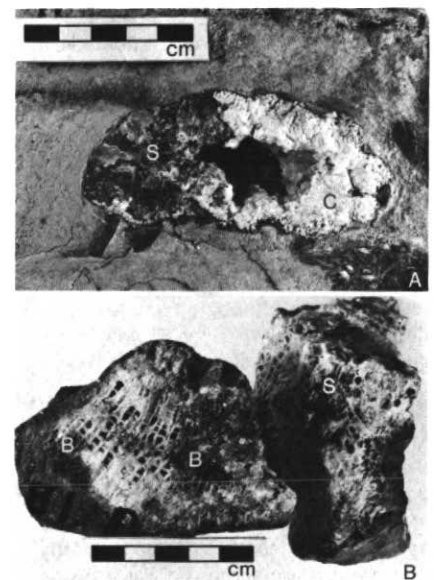
#### Model of Origin

Collectively, the above characteristics support the sedimentary-diagenetic model of origin. The now-classic statement of this model is that of Jackson and Beales (1967; also see Beales and Jackson, 1966), who used the Pine Point deposits as an example. In this model, basin-derived fluids which acquire heat, metals and other solutes during their travels, deposit sulphides in the carbonates they encounter as they emerge from deeper parts of the basin. Fluids driven by sediment compaction derive their metals through brine leaching, carry them as chloride or organic complexes, and precipitate them as sulphides where H<sub>2</sub>S is encountered. Jackson and Beales (1967) viewed H<sub>2</sub>S as filtering into the migration route from nearby evaporites, where it was produced by sulphate-reducing bacteria possibly in the presence of petroleum. This model has survived remarkably well for the Pine Point deposits, and has been applied in many other areas with various modifications. In fact, most



**Figure 4** All views from Pine Point property, N.W.T. (A) - sagged solution breccia in Presqu'île dolomite (facies K; Skall, 1975), orebody N-38A; note abundant white sparry dolomite. (B) - close view of breccia in main ore zone, orebody N-38A; D, host dolomite; SD, white sparry dolomite; O, high-grade banded and colloform lead-zinc ore; 25¢ piece (circled) gives scale. (C) - high-grade ore showing colloform sphaerite (light to medium grey), infilled with massive galena (G, dark grey), orebody N-42;

10¢ piece gives scale. (D) - close view of colloform sphaerite infilled with massive galena, G, orebody N-42. (E) - colloform white sparry dolomite, SD, alternating with black pyrobitumen, overlain by soft bitumen, B; also shows host dolomite, D; and sphaerite mineralization, S; drillcore. (F) - euhedral black sphaerite crystals intergrown with and overgrown by white sparry dolomite ("saddle dolomite" of Radke and Mathis, 1980); orebody M-40.



**Figure 5** (A) - vug in dolomite of Middle Silurian Eramosa Member, Lockport-Amabel Formation, Guelph, Ontario, partly filled with sphaerite, S, and calcite, C. (B) - Location as (A); favositid corals showing local infill with sphaerite, S, right specimen; and bitumen, B, left specimen. Eramosa rocks are rich in organic matter, which appears to have provided the H<sub>2</sub>S for sphaerite and local galena precipitation (McIntyre, 1980).

subsequent discussions of MVT deposit origins accept the sedimentary-diagenetic or "basin evolution" approach, and can be seen as variations of the Jackson-Beales model but with differences as to source of metals, fluid drive mechanism, solution chemistry, and mechanism of precipitation.

Brines found in fluid inclusions of the minerals of MVT deposits are so similar to those encountered in petroleum exploration boreholes in sedimentary basins, and deposits and basinal fluids are commonly so far removed from known igneous rocks, that the formerly popular magmatic-hydrothermal hypothesis of origin is no longer widely held.

**Fluid Origins and Movement**

Since sediment porosity decreases from 70 to 80% at the sediment-water interface to 0 to 20% at a depth of 3000 m or so, there is clearly an upward movement of large volumes of fluid caused by compaction. Basinal fluids invariably become more saline and warmer with depth either through shale filtration or evaporite dissolution (another area of controversy), and the upward movement of warm brines is generally believed to be responsible for the primary migration of petroleum from source beds to physical traps (Burst, 1976; Roberts and Cordell, 1980). It is natural to think along similar lines for the analogous movement of metals from source beds to chemical traps (Garrard, 1977). This analogy is made even more appealing for those cases (e.g., Pine Point) where abundant bitumen is present and is called upon as a reducing agent for sulphate. No commercial metallic deposits are associated with petroleum reservoirs, however, and the geographic distributions of each are antipathetic, at least in the U.S.A. (Fig. 1).

Seawater has a normal salinity of 35 parts per thousand, whereas brines from the deeper parts of sedimentary basins may reach salinities of 150 to 300 parts per thousand, a dramatic increase. Brines with the highest salinities involve such a large increase as compared with seawater, that derivation of salts from evaporites seems essential. This could be either by dissolution of salt beds, perhaps by surface-derived groundwaters, or by expulsion of interstitial fluids from evaporite beds.

Isotopic studies of oxygen and hydrogen show that the water in basinal brines is neither concentrated seawater nor meteoric water with added salts (Taylor, 1974; White, 1974). In each of five major sedimentary basins in North America, brine compositions appear to be best explained by the brines being complex

mixtures of seawater and meteoric water, modified by rock-water interactions within the basin and possibly by other, unknown factors (White, 1974). Clearly, brines do not have a simple origin.

The mechanism and timing of primary migration of petroleum remains one of the most enigmatic features in basin evolution, and much the same can be said of metal migration. In fact, the metal migration puzzle is probably worse: although petroleum is known to come from organic-rich shales, practically every rock in the stratigraphic column has been proposed at one time or another as a source rock for metals! In addition, although compaction probably does produce large volumes of the right kind of fluids, it restricts deposit origins to an early stage of the history of the basin, and it is not at all clear how compaction at depths of 2 to 3 km, required to give the requisite temperatures and salinities, would result in the flow of that fluid through the shallower carbonate horizons at the basin edge.

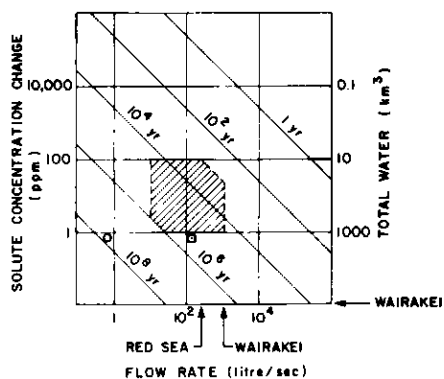
As shown in Figure 6, large deposits probably require on the order of thousands of cubic km of fluid. For example, the Viburnum trend in S.E. Missouri contains about  $3 \times 10^{12}$  g Pb (Gustafson and Williams, 1981, Fig. 3). Precipitated at the rate of 10 ppm, this requires  $3 \times 10^{18}$  g or 3000 Km<sup>3</sup> of water (saline fluid). Rickard *et al.* (1979) calculated that  $2.4 \times 10^{18}$  g water was needed to produce the Laisvall deposit, using 1 ppm Pb. Hitchon (1968) estimated that pore water in the Western Canada sedimentary basin now occupies 265,000 Km<sup>3</sup>, a truly impressive figure, especially since at least some of it contains considerable zinc (Table I; Billings *et al.*, 1969).

If we assume that compaction at depths of 2 to 3 km results in an average of 0.1 litres of fluid per metre of burial (Hanor, 1979, based on Johns and Shimoyama, 1972), the  $2.242 \times 10^6$  Km<sup>3</sup> of sediments in the Western Canada basin (Hitchon, 1968) would produce approximately 200,000 Km<sup>3</sup> of fluid, probably with a minimum temperature between 50 to 100° C and a salinity of at least 15 wt% (Hanor, 1979). Even allowing for the fact that the Western Canada basin is bigger than most, and that not all the fluids produced will be funneled through an ore-depositing environment, it seems clear that we are dealing with a viable source of fluids. (For comparison, the oceans of the world contain  $1.4 \times 10^9$  Km<sup>3</sup> water).

As for the hydraulic drive required to flush these brines up to higher levels, Toth (1980) suggests that topography-driven cross-formational flow can penetrate to deep levels, and over long periods of time can be involved in both petroleum

and metal migration. This would free the timing of ore formation from the early basin formation stage apparently required if compaction alone is called upon to drive fluids. Another suggestion is that of Hanor (1979) who calculated that at deeper levels in sedimentary basins the observed increase in the density of brines due to increasing salt content is almost exactly counterbalanced by the decrease in density due to rising temperatures. Any slight increase in temperature at depth could produce gravitationally buoyant brines having a tendency to move upwards.

Clearly, modelling of time-temperature-salinity-fluid flow history of sedimentary basins is a vital area for research (Jarvis and McKenzie, 1980). With respect to MVT deposits, Sharp (1978) pioneered numerical simulation of a compacting sedimentary basin, obtaining predicted one-dimensional fluid flow rates along a fault zone within the basin modelled. As noted by Cathles (1981), in a general review of fluid flow and the genesis of hydrothermal ore deposits, Sharp's (1978) data support the stratific, Jackson-Beales hypothesis for the genesis of MVT deposits. Garven and Freeze (1982) applied two-dimensional numerical modelling to the problem by simultaneous solution of equations of fluid flow, heat transport,



**Figure 6** Relationship between flow-rate, fluid volumes, concentration change and time for deposition of 20 million tons of 5% ore. Also shown are flow rates of the Red Sea, and Wairakei geothermal system (New Zealand). Geologically more reasonable conditions are shown in the shaded area, and are based on flow rates within an open cross-sectional area of 12,250 m<sup>2</sup> (Roedder, 1960). As noted in the text, the specific discharge of 1.8 m<sup>3</sup>/yr per square metre and 0.72 ppm metal modelled by Garven and Freeze (1982) results in conditions plotted at the small square using their cross-sectional area of  $2 \times 10^6$  m<sup>2</sup>, or at the small circled point using Roedder's (1960) cross-sectional area value of 12,250 m<sup>2</sup>. Original concept and diagram from Roedder (1960); used by Anderson (1978).

mass transport and chemical reactions, based on modern groundwater and contaminant migration concepts. Figure 7 (from Garven and Freeze, 1982) shows the general configuration of the basin and fluid flow regime they considered. The modelling allows one to follow the spreading of aqueous metal from a source bed in the shale unit throughout the rest of the basin. Their gravity-driven circulation model is capable of enormous variations, but the particular results cited in their paper give a specific discharge of 1.8 m<sup>3</sup>/yr m<sup>2</sup> at the deposition site. Using a sub-1 ppm level of metal precipitation (0.72 ppm), the volumes and times required for precipitation of 10<sup>6</sup> tons of metal (or 20 x 10<sup>6</sup> tons of 5% ore) are shown in Figure 6 for two different cross-sectional areas. These lie outside Roedder's (1960) chosen "reasonable" conditions primarily due to the low metal concentration used, (shaded in Fig. 6), but obviously the method shows great promise in constraining models of ore genesis.

#### Ore Fluids

Fluid inclusion evidence from MVT deposits provides some of the best constraints on the origin of these deposits. There are more data on fluid inclusions from MVT deposits than any other ore deposits (Roedder, 1979). Inclusions studied reside in sphalerite, carbonates, fluorite, and barite (this latter mineral commonly gives rather different results). The similarity of the fluid inclusion data from deposit to deposit is remarkable, regardless of whether the deposit consists largely of galena, or sphalerite, or fluorite (Roedder, 1979). The fluid inclusion data reveal the following characteristics (Roedder, 1976, 1979): a) density is always greater than 1, and commonly greater than 1.1; b) salinity is usually greater than 15 weight per cent salts (150 parts per thousand, implying a four-fold or greater increase over seawater), but NaCl "daughter" crystals are almost unknown, indicating the presence of appreciable amounts of ions in the inclusions other than Na and Cl; c) the inclusions contain concentrated solutions of Na and Ca chlorides, with minor amounts of K, Mg, and Br, locally heavy metals such as Cu, Zn; d) organic matter is common, as methane or similar gases, or immiscible oil-like droplets, or in solution within the brines; e) fluid inclusion filling temperatures cover the range from about 80° C to 200° C, but are most commonly in the range of 100° C to 150° C.

K/Na ratios have been determined on a number of fluids from MVT deposit inclusions, and they are all higher than the highest values in oilfield waters (Roedder,

1979). This could mean that the fluids are at least partly composed of interstitial fluids from evaporite beds, enriched in residual K. An alternative explanation, that the temperatures were generally higher for MVT fluids than for oilfield brines (resulting in a different exchange ratio with the sediments), does not seem to be borne out by comparing the temperature ranges involved: they are very similar.

There is scope for further work on the organic components of these inclusions, given the great progress made in our understanding of organic geochemistry (e.g., Tissot and Welte, 1978; Macqueen, 1979). Meanwhile the fluid inclusion data are important components of any theory of origin of these deposits. For example, the high temperatures and salinities that characterize MVT deposits rule out postulated origins which feature cold surface waters alone as ore-forming fluids, including seawater or groundwater.

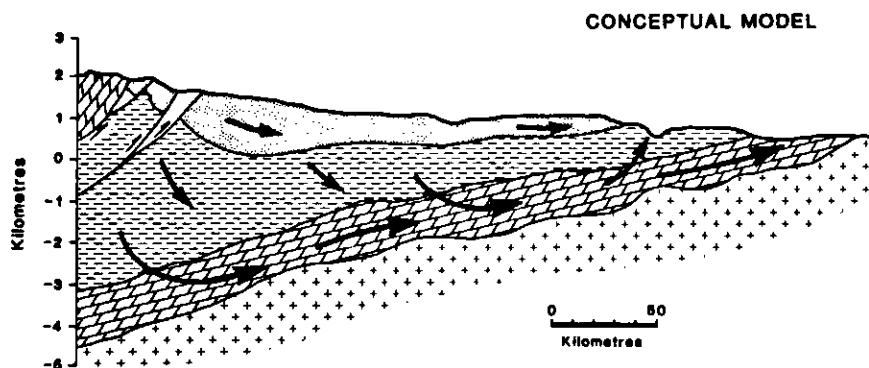
*Metals.* Experimental work and direct observation of natural brines demonstrate that chloride-rich brines have the ability

to leach trace quantities of metals from rocks through which they flow (e.g., Ellis, 1968; Carpenter *et al.*, 1974). This may involve either desorption of loosely bound metals, or release of metals on recrystallization of certain mineral species (Helgeson, 1967). A third possibility is the release of metals from metal-organic complexes through thermal alteration or destruction of such complexes.

There is no agreement on which kinds of rocks may act as metal sources. Many workers have postulated shale sources because shales normally are (relatively) enriched in trace metals, and because changes in clay mineralogy and structure with increasing burial and temperature could release such metals (e.g., Macqueen, 1976). Some have advocated a carbonate source for metals, with metals being released to aqueous solutions during the replacement of initial metastable forms aragonite and high-magnesium calcite by the stable forms, low Mg-calcite and dolomite (Dunsmore and Shearman, 1977). These carbonate mineralogical changes appear to occur too early in the diagenesis of sediments to be of much

**Table 1** Naturally occurring metal-bearing brines.

Location	Depth	Temperature	Metal content (ppm)		Reference
			Zn	Pb	
Gulf Coast	8000 - 13000 ft.	100° - 150° C	360	100	Carpenter <i>et al.</i> , 1974
Northern Alberta	to ≈ 1000 m	≈ 76° C	19	—	Billings <i>et al.</i> , 1969
Cheleken Peninsula USSR	to 1000 m	74° - 97.5° C	2.7	5.4	Lebedev, 1973; White, 1981
Red Sea	sea floor	≈ 56° C	5.4	0.63	White, 1981
Salton Sea, California	≈ 1100 m	≈ 340° C	540	102	Helgeson, 1967; White, 1981
East Pacific Rise (21° N)	sea floor	350° - 410° C	not known	not known	Hekinian <i>et al.</i> , 1980



**Figure 7** Conceptual model of fluid flow in a carbonate unit which could be the locus of a stratabound orebody, as given by Garven and Freeze (1982). Precambrian basement (+ pattern) is overlain by a carbonate unit which localizes fluid flow from overlying shale units; compactional fluid flow through carbonate unit is enhanced by topographic cross-formational flow (Toth, 1980) from elevated thrust-faulted landmass to the left. Garven and Freeze's

(1982) approach to quantify this conceptual model is to use finite element computer programs to solve the coupled equations of fluid flow, heat transport and mass transport for a series of two-dimensional crosssections (normal to the figure) representative of sedimentary basins. Metals, leached from a source unit or units in the shales, spread throughout the basin as a function of time and flow parameters, and concentrate at the discharge end.

use as major metal sources for MVT deposits. A third possibility as a metal source is evaporite beds, as advocated by Davidson (1966) and recently revived by Thiede and Cameron (1978) from their study of metal concentrations in the Middle Devonian Elk Point evaporite sequence of the Western Canada basin. Their work suggests a possible explanation for one of the intriguing problems associated with MVT deposits - why they are so scarce in copper and iron compared with zinc and lead. The Elk Point data suggest that copper remains in the brine during the evaporation process, whereas lead and zinc enter solid phases such as gypsum and anhydrite. Copper-rich residual brines could lead to the formation of red-bed copper deposits on a local scale, whereas lead and zinc would be mobilized much later by circulating connate fluids which dissolved evaporites, becoming highly saline in the process.

Chloride brines with geologically significant metal contents are known in a number of areas (Table I). Gulf Coast, northern Alberta and Cheleken Peninsula brines occur in normal sedimentary basins: others shown in Table I are related to near-surface volcanic rocks or abnormal heat sources unknown in Mississippi Valley-type deposit settings. Nevertheless, these occurrences verify that metal transport in chloride-rich brines occurs widely in nature, something hardly suspected a couple of decades ago (White, 1981). Hitchon (1977, 1980) has shown that the content of effectively all components of geothermal brines of the type shown in Table I falls within the concentration limits of sedimentary basin formation waters. The high salinity and high metal content of the geothermal brines are matched by the deeper, hotter more saline formation waters (Hitchon, 1977, 1980). Hitchon (1977) could find no systematic differences in the composition of these brines that could not be reasonably attributed to differences in temperature and host rocks. Nevertheless, lead and zinc are not common in oilfield waters: minor element compositions of 832 oilfield waters showed none with Pb or Zn in excess of 1 ppm (Rittenhouse *et al.*, 1969).

**Sulphur.** Most subsurface brines contain low amounts of sulphur, in the range of a few tens to a few thousands of parts per million. This is nearly always present as sulphate, rather than the reduced sulphide which is required to precipitate a sulphide ore deposit. Brines which contain even a small amount of H<sub>2</sub>S are invariably very low in metal content, at least over the temperature ranges which appear to characterize MVT deposits (<= 200°C).

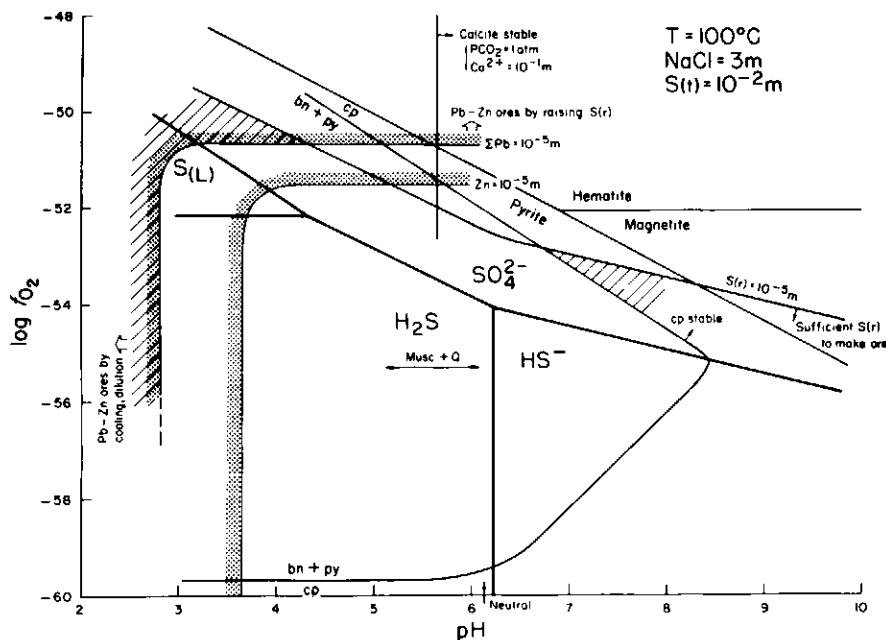
**Transport**

**Brine Chemistry.** A major geochemical problem in MVT deposits is whether the metals and reduced sulphur (H<sub>2</sub>S and perhaps HS<sup>-</sup>) were transported together to the site of deposition, or whether the metals were carried in an essentially H<sub>2</sub>S-free solution and were precipitated by the addition of H<sub>2</sub>S as the solution passed through the carbonate host rocks. Both experimental and geological observations bear on this point.

The parameters controlling the solubility of ZnS and PbS in NaCl-rich brines at 100-150°C are reasonably well understood (Barrett and Anderson, in press), because there is a satisfying level of agreement between experimentally measured and theoretically calculated metal values under controlled conditions. This allows calculation of metal values of brines under various proposed geological conditions, and the general conclusion is that ZnS and especially PbS solubilities in the presence of significant H<sub>2</sub>S concentrations are too low to allow transport

**Table II Reasons For Deposition**

1) pH change	} ore solution must bring both metal and sulphide
2) Cooling	
3) Dilution	
4) Increase in reduced sulphur	} ore solution brings only metal; sulphide supplied at site
A) by reducing SO <sub>4</sub> <sup>2-</sup> already in the brine	
a) internally (e.g., dissolved CH <sub>4</sub> )	
b) externally (e.g., petroleum encountered)	
B) by adding H <sub>2</sub> S to brine	
a) bacterial sulphate reduction	
b) thermal degradation of petroleum	
c) non-bacterial sulphate reduction by organic material	
d) from pre-existing sulphate minerals	
- from Anderson (1978).	



**Figure 8** Sphalerite and galena solubilities and mineral stability fields as a function of oxidation state ( $\log f_{O_2}$ ) and acidity (pH). The diagram indicates how experimentally-derived solubility data can be related to mineral stability fields in attempting to understand conditions of transport and deposition. S(r), S(t), S(L): reduced, total and liquid sulphur, bn = bornite, py = pyrite, cp = chalcocopyrite. Musc + Q: pH stability range of muscovite + quartz. The left-hand hatched area is the range of conditions where more than 2 ppm of Pb can

be transported with sufficient H<sub>2</sub>S to provide ore. This is generally below a pH of 3 except for a little wedge up to pH 4. Alternatively, hundreds of ppm Pb can be transported above  $f_{O_2}$  of  $10^{-5.1}$  with sulphur as sulphate. Sphalerite is more soluble than galena, requiring a less acid pH to achieve the same concentration as shown by the stippled  $10^{-5}$  m Zn contour. The assumed conditions of course may be oversimplified, as in most models. Modified from Anderson (1975).

of ore-forming quantities of both metals and  $H_2S$  in the same solution (Anderson, 1975). A possible exception to this generalization has been provided by Sverjensky *et al.* (1979) who on the basis of lead and sulphur isotope data on galena from the Buick Mine, southeast Missouri, suggested that lead and sulphur were transported together in the same solution. Either the sulphur was present as sulphate, or if as sulphide, unrealistically low pH levels are required as noted.

Experimental work to date has only considered inorganic complexing, principally chloride. It is possible that as yet unknown complexing effects are important, and the most likely candidate at the moment is organic complexing. The concentration of organic ligands is small, but their effects could be large (Barnes *et al.*, 1981).

### Deposition of Sulphides

Depositional mechanisms depend fundamentally on the nature of the metal-transporting solutions, and particularly the source of sulphide as noted above. Generally we can recognize two cases: one in which the metals and reduced sulphur ( $H_2S$ ,  $HS^-$ ) travel together in the ore-forming solution ("non-mixing" model), and a second case in which the sulphide is derived at the site of ore deposition, possibly by reduction of sulphate carried by the ore-forming solution ("mixing" model). Table II provides a summary of possible depositional mechanisms for each case.

*"Non-Mixing" Model.* Metals and reduced sulphur travel together. In this case, we appear to have a transport problem because metal solubilities in solutions containing appreciable amounts of reduced sulphur are so low. If this model is to operate under realistic geological conditions (i.e., at pH values of 4-5 or greater; Fig. 8), some form of metal transport other than chloride complexing is required, such as organic complexing. Bisulphide complexes ( $HS^-$ ) for Pb have been ruled out (Hamann and Anderson, 1978; Giordano and Barnes, 1981). If this model should apply, Anderson (1975) has shown that precipitation of sulphides could occur through cooling, dilution by groundwater, or by pH change. Geological evidence tending to support this model includes such features as the district-wide sphalerite banding recognized by McLimans *et al.* (1980) in the southwestern Wisconsin district (Fig. 1). They argue that individual local sources of sulphur could not produce such a consistent feature. In some areas, e.g., southeast Missouri (Fig. 1), extensive dis-

solution of previously-deposited sulphides has taken place. This is difficult to explain if the sulphides are as insoluble as advocated by the "mixing" model school of thought. Large, well-formed sulphide crystals also have been considered by some workers to indicate the absence of large degrees of supersaturation or large concentration gradients, both more likely features of the "mixing" models.

*"Mixing" Model.* Here, sulphide is supplied at the site of deposition by a number of possible mechanisms, as seen in Table II. Because low pH values are required to transport metals and sulphides together, Anderson (1975), Beales (1975) and others have favoured this model. "Mixing" models which involve adding  $H_2S$  to metal-bearing brines at the site of ore deposition (e.g. by brine-derived or locally derived sulphate being reduced by organic matter) are much more attractive hydrodynamically than the mixing of two transported solutions, one carrying metals and the other carrying reduced sulphur.

The only reasonable source of reduced sulphur is sulphate, either from locally available sulphate minerals or dissolved brine-transported sulphate. Organic matter, common in many MVT settings, is a likely reducing agent at the temperatures involved (Table II). Bacterial sulphate reduction is unlikely at temperatures above about 80° C. Thermal degradation of petroleum to yield sulphide has yet to be evaluated for most settings, but is not a likely factor at Pine Point (Macqueen and Powell, in press).

Bringing metals and  $H_2S$  together at the site of ore deposition would seem to be capable of generating large concentration gradients, high degrees of supersaturation, and relatively rapid precipitation of sulfides. These in turn should result in very fine-grained crystals; dendritic, hopper and other high-energy crystal forms; and isotopic and compositional disequilibrium. The sulphides at Pine Point show evidence of relatively rapid deposition and crystal growth in the form of dendritic and hopper galena, which is consistent with the addition of  $H_2S$  to metal-bearing brines. Unlike many settings, Pine Point has an abundance of locally available sulphate. All of these features have been found in places in some MVT deposits, but they are by no means typical.

On the other hand, the "mixing" process may take place extremely slowly, say by diffusion of  $H_2S$  through wall rocks into the hydrothermal system, resulting in typical well-formed and large

sulphide crystals considered by some workers to be indicative of the operation of the "non-mixing" model! The problem is not solved! If large sulphide crystals are involved, however, slow addition of reduced sulphur is required to prevent widespread nucleation and the deposition of a sludge of extremely fine-grained sulphide crystals ("dumping" of sulphide). This also implies only very slight degrees of supersaturation.

If the  $H_2S$  is produced locally, one should be able to see some evidence of this, such as the presence of gypsum or anhydrite as well as a reducing agent such as organic material. The association of bitumen with MVT deposits is quite characteristic, but association with sulphates is less so. Beales and Hardy (1980) have argued that for MVT deposit sites where sulphates are missing, their former presence ("occult gypsum") can be demonstrated by gypsum inclusions in dolomite. Their interpretation is supported by the work of Radke and Mathis (1980), who suggested that white sparry dolomite (their "saddle dolomite"), so common in many MVT settings, is related to sulphate reduction.

*Depositional Setting.* One of the most striking features of MVT deposits is their association with carbonates, and further, with zones of extensive localized solution and collapse of carbonates. This is often karst-related, but not always, and considerable variation seems to exist in the relative timing of carbonate solution and sulphide precipitation. Where sulphide brecciation is observed, post-sulphide carbonate solution is inferred. Such solution could be simultaneous with sulphide deposition, however, and the common association of ore and solution features leads to the hypothesis that precipitation is caused by the pH change occurring where the metal-bearing solution encounters the carbonate rocks. In this case, however, since reaction with carbonates is very rapid, we should find the deposits strongly associated with facies changes, whereas they are commonly surrounded by carbonate rocks.

Although the ore-solution may be in equilibrium with carbonate during transport, deposition of sulphides from chloride complexes will inevitably release acid, for example  $ZnCl_2(aq) + H_2S = ZnS + 2HCl(aq)$ . This acid could not escape from the system without dissolving carbonate. Thus sulphide deposition itself should help in creating solution collapse and open space, and the association between ores and collapse zones including brecciated ore becomes easier to understand. Slight cooling in the ore

zone would also result in carbonate dissolution, but leaves open the question of why solution and collapse is often so closely related to the sulphide zones.

Either, or both, fluorite and barite are commonly associated with MVT deposits. Holland and Malinin (1979) discussed the solubility of these minerals and mentioned that decrease in temperature is probably a common reason for precipitation of both. Very small temperature changes are likely in the MVT situation, but if sulphide precipitation was accompanied by carbonate dissolution, the increase in calcium would precipitate fluorite if the solution was near saturation with fluorite. Nordstrom and Jenne (1977) have shown that this is the case for geothermal waters in the western U.S.A. Thus  $\text{Ca}^{2+}$  is released by  $\text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$  and then reacts with F ions:  $\text{Ca}^{2+} + 2\text{F}^- = \text{CaF}_2$ .

The presence of barite in MVT ores has been used as an argument against an oxidized ore solution, since the solubility of barite is so small in  $\text{SO}_2$  bearing solutions. Strictly speaking, it is an argument against an  $\text{SO}_2$  bearing brine, not against an oxidized brine. A low  $-\text{SO}_2$ ,  $\text{Ba}^{2+}$ -bearing brine, on encountering a region in its flow path rich in  $\text{H}_2\text{S}$ , would be expected to precipitate barite either on the periphery of the  $\text{H}_2\text{S}$  zone or above it, since an  $\text{H}_2\text{S}$ -rich zone would be surrounded by an oxidized  $\text{SO}_2$  rich zone. This is the case for example in the Peninsines (Sawkins, 1966).

### Exploration Philosophy

The discovery of many carbonate-hosted lead-zinc showings in the Rocky Mountain Belt in the 1970's (Macqueen, 1976; Sangster and Lancaster, 1976) demonstrates that MVT deposit characteristics discussed above are instrumental in exploration. What are the general exploration concepts involved? Favourable ground includes carbonate successions developed on the flanks of large, deep basins (Pine Point, Polaris, Daniel's Harbour, etc.). In these basin margin settings, unconformities and possible karsting are "good signs". Basement control in the form of arching, flexing or faulting may provide fluid escape routes or heat sources or both, also "good signs". Dolomitized sequences, and the presence of evaporites and organic matter are all favourable indicators. Carbonate fronts between basinal shales and platform carbonates are also promising. The major control on the location of MVT ore deposits is not merely a structural or stratigraphic trap, but appears to be the happy coincidence of large volumes of pore space, base metals, and a source of

sulphide or a precipitating agent. Promising platform successions where these requisites may be met include the Lower Paleozoic of the Mackenzie River area, N.W.T., the Silurian of Ontario, and the Ordovician of Manitoba. As we gain increased understanding of existing deposits such as Pine Point, we will undoubtedly be in a better position to prospect such vast areas as the Lower Mackenzie River, and southern Manitoba and Ontario.

### Problems

Of all the problems noted, perhaps *timing* is the most critical. For most MVT deposit settings, we have almost no idea when mineralization occurred. Beales *et al.* (1980), using paleomagnetism, obtained a Late Pennsylvanian date (paleomagnetic pole) for a deposit hosted by Cambrian carbonate rock in the Viburnum trend, southeast Missouri: Radiometric dating of microgram quantities of Rb-Sr or the U series from galenas is an exceptionally painstaking but potentially valuable dating method (R.L. Armstrong, pers. commun., 1980). K/Ar direct dating is a promising approach as begun by York *et al.* (1980). Better knowledge of timing will permit us to make much more conclusive statements about where mineralization fits in the overall scheme of basin evolution. Chemistry remains a problem: why do these deposits contain only lead and zinc in economic quantities? Is it the gathering mechanism or the precipitating mechanism that chooses the lead and zinc? (Meyer, 1981) All evidence at the moment points to source rock control.

What is the local and regional *hydrology* of particular MVT districts and deposits? In particular, what flow paths are involved and over what dimensions and time durations did they operate? Groundwater hydrologists are most comfortable with the dynamic systems encountered in modern groundwater studies, but it is clear that their approach has much to offer. Might the fluids responsible for one type of base metal deposit have also formed another type earlier/deeper in their evolution, due to differing physical and chemical conditions? Can the fluids which move petroleum also be ore-forming fluids?

Are *evaporites* critical to the origin of MVT deposits, either in the fluid migration routes or at the deposition site, as suggested by the high salinities in the fluid inclusions? Why are MVT deposits almost invariably associated with dolomites (dolostones of some authors) rather than limestones? How much *solution of carbonate* is there at any particular property or in any district and what

has caused it? What is the contribution of *organic matter* to the story: do hydrocarbons or hydrocarbon/sulphate reactions govern the location of many or most MVT deposits by supplying  $\text{H}_2\text{S}$  locally? What causes *metal zoning* in districts or at individual properties: Pine Point, for example, tends to have lead-cored orebodies with zinc and iron envelopes (Kyle, 1981) - why? What *ground preparation mechanisms* govern the location of particular deposits? What role do *broad-scale tectonic processes*, for example plate margin interactions or spreading rate sealevel changes, play in the story? Some of these questions have implications for prospecting, whereas others are more academic.

Three areas seem to us to offer outstanding promise in MVT deposit research. These are dating of deposits, either by paleomagnetic means or by direct radiometric dating; further observational and experimental assessment of the role of organic matter in metal-organic complexing reactions or in generating or providing  $\text{H}_2\text{S}$ ; and hydrogeological modelling of MVT deposit basinal systems. There is no shortage of intriguing problems to study!

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