

Presidential Address to the Geological Association of Canada, Toronto, Ontario: Base Metal Deposits in Sedimentary Rocks: Some Approaches

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Article abstract

To consider both the deposits and their setting within a sedimentary basin is an instructive and rewarding approach in studying Mississippi Valley-type lead-zinc deposits hosted by sedimentary carbonate rocks. There are now numerous constraints on origin of these deposits, and the sedimentary-diagenetic hypothesis of origin still appears to answer more questions than it poses. Oil in basins seems clearly related to the thermal and structural evolution of sedimentary basins. Ore, in comparison, appears to require coincidence of a specific set of precipitation as sulphides. Recognition of the importance of heat in the maturation of organic matter has led to the development of indices of thermal and organic maturity. It should be possible to apply these indices at least to relatively undeformed Mississippi Valley-type deposits and their host rocks as a means of discovering burial and thermal history. Organic matter commonly is spatially associated with these deposits: a close look at such organic matter in the light of modern petroleum geochemistry should help to determine whether such association is casual, or genetic in terms of affecting source, transport and precipitation

**Presidential Address to the
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Base Metal Deposits in Sedimentary Rocks: Some Approaches

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Abstract

To consider both the deposits and their setting within a sedimentary basin is an instructive and rewarding approach in studying Mississippi Valley-type lead-zinc deposits hosted by sedimentary carbonate rocks. There are now numerous constraints on origin of these deposits, and the sedimentary-diagenetic hypothesis of origin still appears to answer more questions than it poses. Oil in basins seems clearly related to the thermal and structural evolution of sedimentary basins. Ore, in comparison, appears to require coincidence of a specific set of precipitation as sulphides. Recognition of the importance of heat in the maturation of organic matter has led to the development of indices of thermal and organic maturity. It should be possible to apply these indices at least to relatively undeformed Mississippi Valley-type deposits and their host rocks as a means of discovering burial and thermal history. Organic matter commonly is spatially associated with these deposits: a close look at such organic matter in the light of modern petroleum geochemistry should help to determine whether such association is casual, or genetic in terms of affecting source, transport and precipitation.

Introduction

This address deals with one specific but widespread type of base metal deposits, namely carbonate-hosted lead-zinc deposits of Mississippi Valley-type. Characteristics of these deposits have been summarized by

many workers (e.g., Sangster, 1976b), and include the following: sphalerite and galena are the main sulphides; ore minerals are typically open-space fillings with the spaces developed in rocks, not sediments; deposits typically are stratabound (i.e., occur at specific stratigraphic levels); deposits are most common in thick sequences of sedimentary carbonate rocks; dolomite is the most common host rock; host carbonate rocks are unmetamorphosed; igneous rocks are lacking in most settings; organic matter is a common associate; and the age of host carbonates ranges from Proterozoic to Cretaceous, with many deposits developed in Paleozoic carbonates. Heyl *et al.* (1974) list additional characteristics of the classic Mississippi Valley deposits of the United States. Puzzling problems associated with these deposits centre around why they are located in sedimentary carbonates in the first place, and include means of metal transport in the sedimentary setting, localization of the deposits, agent(s) of precipitation, and especially timing of the sulphide mineralization with respect to age of host carbonates. Here we consider firstly the origin of these deposits, a subject of much research and speculation, and secondly some approaches which may be useful in increasing our understanding of their origin. The work of Anderson (1978) and Sangster (1976a, b) on Mississippi Valley-type deposits and that of Powell (1978) on organic geochemistry of sedimentary basins has been particularly useful in preparing this address. The useful disclaimer is appropriate: errors here are mine, and not theirs!

Origin of Mississippi Valley-Type Lead-Zinc Deposits

Characteristics noted above provide important constraints on origin. Additional important constraints are provided by fluid inclusion and isotope data (e.g. Heyl *et al.*, 1974). Study of fluid inclusions indicates temperatures of formation for sulphides in the range about 80°C – 150°C, and that the ore fluid, as trapped in inclusions, is 5-10X as saline as seawater, and commonly is of Na-Ca-Cl composition, locally with droplets of oil. Isotopic data for sulphide sulphur from deposits of Paleozoic and Mesozoic age tend to

parallel isotopic values for seawater sulphate sulphur of the same age as the host rocks (e.g., Sangster, 1976a, fig. 4, p. 228), suggesting 'coeval' sulphate as a sulphide source. Lead isotopes are either anomalous (too much radiogenic lead, e.g. Missouri district, U.S.A.), suggesting shallow crustal sources where radiogenic isotopes have formed, or ordinary, suggesting deep crustal sources.

Taken together, many of these features provide support for a popular current working hypothesis which sees Mississippi Valley-type lead-zinc deposits as a product of normal sedimentary basin evolution, during the late stages of diagenesis. An analogy is made between the origins of two economically valuable sedimentary rock-hosted commodities – oil, and lead-zinc ores. Indeed, conferences have been convened to examine oil-ore relationships (Garrard, 1977). Each commodity requires a source, undergoes migration of some sort, and is ultimately trapped or precipitated, if we are fortunate, in economic concentrations within geologic settings. In Canada, this working hypothesis has been advanced by Frank Beales and his students (e.g., Jackson and Beales, 1967, also see Macqueen, 1976, and Anderson, 1978). Such a hypothesis finds considerable support in the fact that the salinities and constituent proportions of ions within fluid inclusions in sphalerite closely resemble those of oil-field brines, as noted by White (1974) and others. Basinal brines containing metal-chloride complexes are known from a number of areas (e.g., Anderson, 1978), and some of these are thought to resemble probable ore fluids. Isotopic data from many Mississippi Valley-type deposits support a basinal brine origin for ore fluids, but suggest some admixture of meteoric water in some settings (Heyl *et al.*, 1974).

The settings and origins of oil and lead-zinc ore are compared in Table I. Perhaps the most important differences between these, notwithstanding that both are located in sedimentary basins, lies in the major control. Oil seems clearly related to the thermal and structural evolution of a sedimentary basin, including the development of a suitable trap for this always potentially fugitive constituent. Ore, on the

other hand, appears to require coincidence of a specific set of circumstances – a metal-transporting fluid, a cause or causes of precipitation, and most importantly a cavity system, of karst or other origin, within which precipitation of metallic sulphides can occur in sizeable volumes. Once precipitated as a sulphide, ore appears to remain in place.

It is commonly noted that oil and ore do not occur together. Is this a fact, or a function of our present knowledge of the distribution of these commodities? We exploit oil from the subsurface from a widely spaced system of boreholes; in contrast, we exploit lead-zinc ore from or close to the surface, using open pits, shafts and rooms, and closely spaced grid systems of diamond drill holes. Nevertheless it seems a fact that oil-field brines commonly contain less than one ppm of zinc and lead (e.g. Rittenhouse *et al.*, 1969).

Table 1

Comparison of aspects of oil and lead-zinc ore, Mississippi Valley-type deposits

ASPECT	OIL	ORE
Source	Organic-rich shales or carbonates	Shales, carbonates sandstones, evaporites or basement rocks, igneous rocks
Release	Thermal maturation	Leaching by brines
Migration or Transport	Dewatering of shales Transport as separate phase? in matured state	As chloride complexes ?As organic complexes
Distance of Migration	Local to ?basin-wide	Local?
Time of Migration	Depends on geothermal gradient	Post-lithification
Trapping Deposition	porous, permeable reservoir rocks	Precipitation as sulphides
Temperature of Formation	about 66°C - 150°C	about 80°C - 150°C
Heat	Geothermal liquid window	Geothermal or anomalous?
Role of Organic Matter	Fundamental	Genetic or casual?
Major Control	Evolution of sedimentary basin	Coincidence of specific circumstances
Rock-Water Interaction	Unimportant?	Fundamental
Fluid Volumes	Large	Very large?

Some uncertainties with respect to origin were noted above. Others include the question of one fluid (metals plus sulphur) or two (see Anderson, 1978), fluid volumes, depth of origin below the surface, role of organic matter, and again, timing. We look now at means of refining the current working hypothesis, and perhaps reducing some of these uncertainties.

Some Approaches to Mississippi Valley-Type Deposits

The sedimentary-diagenetic hypothesis of origin is useful because it provides a rational explanation for the origin of deposits, and a framework and guide for observations. But how can we sharpen this hypothesis, or perhaps help it evolve toward a theory?

Several approaches are possible, including study of the geological setting, burial history of the host rocks, thermal history of the host rocks and deposits, and the possible role of

organic matter in transporting metals or localizing mineral deposits (e.g., Macqueen, 1976). Here I intend to deal with approaches involving the burial and thermal history of the host rocks and deposits, and the role of organic matter.

Occurrence of oil. Figure 1 illustrates the 'liquid window' concept of oil occurrence, as presented by Pusey (1973). This concept describes the occurrence of oil in a wide variety of sedimentary basins, and illustrates the importance of heat in the maturation of organic matter. The genesis of oil in significant volumes depends on suitable starting materials. Kerogen – insoluble organic matter from which oil and natural gas evolve – is of three main types in sediments as shown by Tissot *et al.* (1974). These types are well described by their atomic hydrogen/carbon and atomic oxygen/carbon ratios, as seen in Figure 2. Large volumes of oil are only to be expected from type I kerogen, which appears to be of algal or microbial origin. Type III kerogen probably

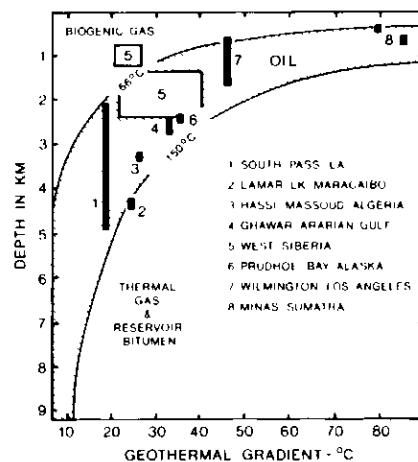


Figure 1.

Liquid window concept of oil occurrence, from Pusey (1973) (redrawn from Macqueen, 1976). Plot of geothermal gradient against depth in km, with liquid window and selected oil fields included. Vertical bars indicate stratigraphic span of significant oil production in each field shown. "Hot" geothermal gradient indicates shallow production. Oil reservoirs found at temperatures of less than about 66°C are believed to be associated with significant uplift after heating or, less commonly, with long distance migration (up). Time is not shown; longer cooking times may compensate for lower temperatures.

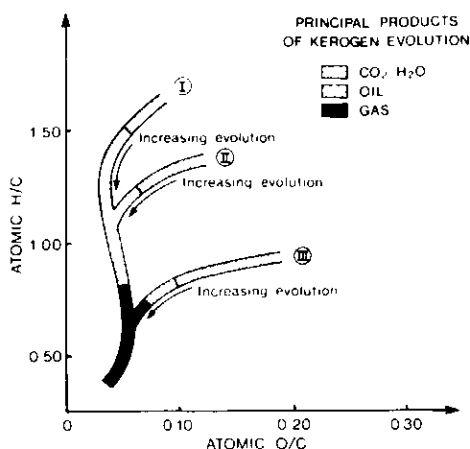


Figure 2. Principal steps of kerogen evolution and hydrocarbon formation, from three main types of kerogen: Type I represents amorphous organic matter of algal or microbial origin, type II, herbaceous material (leaves, pollen, etc); and type III, woody organic matter. Flat parts of curves indicate mostly oxygen loss as CO₂ and H₂O. Steep parts of curves show loss of hydrogen and hydrocarbon generation. Evolution paths I and II correspond to kerogens able to generate abundant oil (particularly I), whereas path III represents hydrogen-poor kerogens which produce mostly methane at depth. From Tissot *et al.* (1974, p. 505).

yields little oil. The evolution of kerogen and the liquid window of oil occurrence describe what is known as the thermal model of oil genesis. Although the model appears generally correct (at least with respect to clastic sequences), Powell and Snowdon (1978) noted that there are exceptions such as the extensive occurrence of dry gas in undermature zones, and the occurrence of oil with an apparent terrestrial organic matter source. No doubt refinements of the thermal model will be made. Here the important point about the thermal model of organic maturation is that much research has been conducted with the goal of evaluating the oil potential of sedimentary basins. This involves discovering the thermal history of sedimentary basins, and the nature of kerogen starting materials. Particular stress has been placed on thermal history through study of organic diagenetic indicators - the response of organic matter in various forms to heat.

Organic diagenetic indicators. Table II summarizes main indices of organic maturity. The term 'organic maturity' refers to the progressive thermal evolu-

tion of organic matter: specifically, to the oil generating potential of a sedimentary sequence as described by the liquid window of oil occurrence. The response of organic matter to heat provides a maximum-reading geothermometer, for the changes are not reversible. Pollen, spores and conodonts are examined visually: vitrinite, a coal maceral, is examined in terms of its ability to reflect light under controlled conditions, which is related to both maximum temperature attained and the time over which this temperature prevailed. Use of kerogen (insoluble organic matter) and bitumen (soluble organic matter) as indices of organic maturity involves determining their compositional properties, which are known to change systematically upon exposure to heat.

Powell's (1978) work in assessing the hydrocarbon potential of the Canadian Arctic Islands provides an example. In the Sverdrup Basin, the facies of organic metamorphism are as follows: undermature to 1500m below surface; marginally mature to about 3000m; mature to about 4500m, and overmature below 4500m below surface. Boundaries of these zones depend largely on geothermal gradient; volumes of oil to be expected depend on geothermal gradient and a sizable quantity of suitable starting material, namely algal or microbial amorphous organic matter with high atomic hydrogen/carbon ratio.

Thus by studying in situ organic diagenetic indicators, we may arrive at an estimate of the degree of organic maturity of a particular stratigraphic

level within a sedimentary sequence, and accordingly the thermal history of that level. The approach is partly empirical because of the complexity of starting materials and thermocatalytic transformations: nevertheless, it works.

Organic matter in rocks. The term 'bitumen' is now in common usage to describe organic matter which is soluble in benzene and methanol or other organic solvents. Bitumen can be further divided into: a) resins, asphaltenes, and nitrogen, sulphur, oxygen compounds; and b) hydrocarbons. The hydrocarbons in bitumen are in turn divisible into a saturated fraction (single carbon bonds), consisting of paraffins and naphthenes, and an unsaturated fraction (double carbon bonds) or aromatic hydrocarbons. Like other indices of organic maturity, bitumen shows systematic changes with depth. At immature stratigraphic levels, generally thought to be those where temperatures above about 66°C have not prevailed for any length of time, in situ soluble organic matter typically has a low percentage of hydrocarbons, and a low saturated hydrocarbon to aromatic hydrocarbon ratio. In situ bitumen within organic mature zones typically shows a higher percentage of hydrocarbons, and a higher saturate/aromatic ratio. Other progressive changes are also observed from immature to increasingly mature stratigraphic levels, including the gas chromatographic character of the saturated hydrocarbon fraction, and atomic hydrogen/carbon and oxygen/carbon ratios within the associated insoluble

Table II
Indices of organic maturity

	Immature < about 66°C	Mature about 66°C about 150°C	Metamorphosed > about 150°C
Pollen; Spores	Yellow	Yellow-orange to brown to black	Black
Conodonts	Pale Yellow	Brown	Brown to black
Vitrinite Reflectance (Ro)	<0.5	0.5 - about 1.2	> about 1.2
Kerogen	> 1.5	1.5 - about 0.75	< about 0.75
Bitumen	- Low extract volumes - No (or minor) oil	- High extract volumes - Major oil	- Dry gas + pyrobitumen

material or kerogen (e.g., Powell, 1978). It is important to stress that we are considering here changes that occur within organic matter in typical source rocks, not necessarily changes that occur during or after petroleum migration from a source rock to a reservoir.

Much of our present level of understanding of these processes has been gained over the past decade owing to strong stimulus from the petroleum industry. How can we apply this new knowledge to Mississippi Valley-type lead-zinc deposits?

Application to Mississippi Valley-Type Deposits

As noted above, organic matter commonly is associated with these deposits. Whether such association is casual or genetic, the nature of the associated organic matter, and the nature of dispersed organic matter present in host carbonates, can serve as a useful guide to the thermal history of both host rocks and at least potentially, mineral deposits. If the association should prove to be genetic, i.e., organic matter in some fashion brings about precipitation of metallic sulphides, all aspects of organic matter attain much importance.

The most fruitful settings for careful study of dispersed organic matter and bitumen are those such as the classic Tri-state or Upper Mississippi Valley areas, where rocks are essentially undisturbed tectonically. Within deformed settings (e.g., Rocky Mountain Belt, Macqueen and Thompson, 1978), organic matter has been thermally metamorphosed, probably by deep burial, rendering it of limited value other than as a means of estimating maximum temperature.

We consider two general cases: a) lead-zinc deposit and host rocks were exposed to the same maximum paleotemperatures, and b) lead-zinc deposit formed at temperatures in excess of the maximum host rock paleotemperatures

Deposit same temperature as host rocks. Here we would not expect gradients in either organic or inorganic paleotemperature indicators. Because 'normal' geothermal heat is involved, thermal potential for fluid flow of a convective nature should be absent or

limited. The implication for this case is that mineralization may be 'late', and 'deep', i.e., to have taken place under an appreciable sedimentary load during the time that host rocks reached temperatures typical of Mississippi Valley-type lead-zinc deposits. This reasoning underlies the data of Figure 3, for the Robb Lake lead-zinc deposit of northeastern British Columbia. Figure 3 combines burial history, indicated maximum paleotemperatures, and reasonable gradients. Although the host rocks are Devonian in age, in this model mineralization is indicated as occurring at depths of 2-3½ km, and during late Triassic to early Cretaceous time. Note also that matured petroleum would not be expected before late Pennsylvanian time, and could have been produced until Cretaceous time, thus overlapping the inferred time of lead-zinc mineralization. Kerr (1977) has applied this reasoning to the Cornwallis carbonate-hosted lead-zinc deposits of the Arctic Islands. The best single test of this model would be

discovery of the time of mineralization. In classical Mississippi Valley districts as White (1978) and others have pointed out, however, there is little evidence that the formerly overlying sedimentary section was ever thick enough, assuming reasonable geothermal gradients, for the host rocks to have reached temperatures of about 80° - 150°C. Perhaps, then, the second case is a more common situation.

Deposit hotter than host rocks. In this situation, the deposits represent former thermal anomalies with respect to their enclosing host rocks. Here we might expect that fluids would move through thermal potential; we also have the possibility of convective flow, which might help get around the question of the large fluid volumes which appear necessary to form an ore deposit (e.g., Anderson, 1978). The further implication of this alternative model is that mineralization may be 'early' and 'shallow', with heat and fluids being derived from some depth. Additionally, we

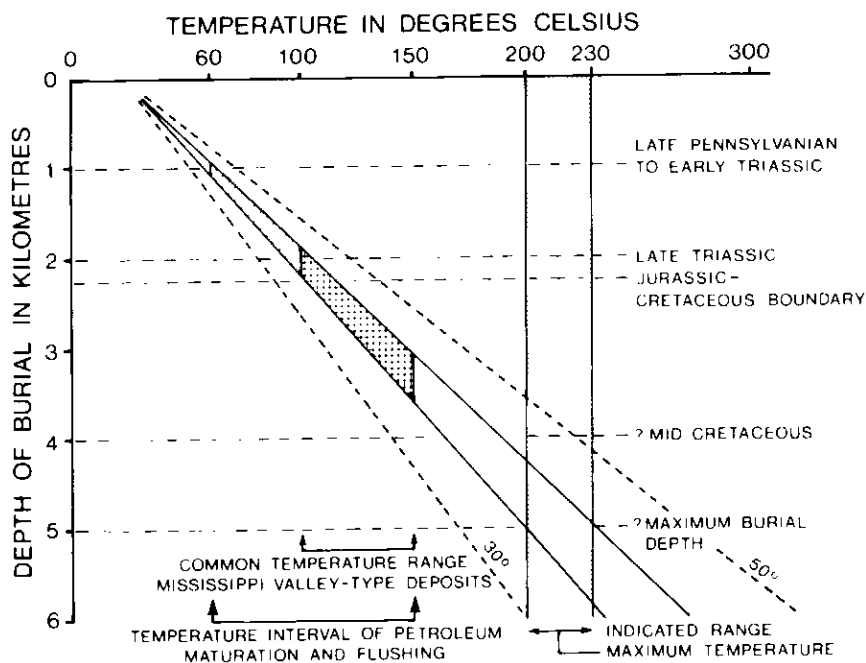


Figure 3.

Temperature-depth plot for Devonian lead-zinc host rocks, Robb Lake, northeastern British Columbia. Included are geothermal gradients from 30-50°C, interpreted burial history to an estimated maximum of 5 km, and estimated maximum host rock paleotemperatures in the range of

200-230°C. In this model, mineralization took place at burial depths of 2 km or greater, and during late Triassic to Cretaceous time; depth and timing are a consequence of 'normal' geothermal heat and burial history. From Macqueen and Thompson (1978, p. 1757, see for derivation and details)

might expect to discover gradients in paleotemperature indicators, especially organic indicators, at least those which were present in host rocks upon arrival of metal-bearing fluids (unless such gradients are destroyed by later deep burial). Gradients ought to depend on the thermal contrast between metal-bearing solutions and host carbonates, and on the duration of heating. Arbitrarily we may consider that a thermal contrast in the range of 10°–20°C between metal-bearing solutions and host carbonate rocks is likely to be too low to provide measurable effects, although this requires study. A higher contrast (perhaps 40°–50°C?), however, should provide measurable effects in terms of alteration of in situ organic matter. The maximum effects should be seen when unaltered host rock organic matter distant from mineralization is compared with organic indicators in or very close to the ore zone.

Possible alteration effects. What alteration effects might we expect? Pollen and spores are not common in carbonates, but if present should show visually observable colour changes from orange to brown or brown to black. Vitrinite is also not expected in carbonates, but a thermal contrast in the region of 50°C could provide an increase in reflectivity (Ro) from .2 to .5 Ro units. Conodonts are common in Paleozoic carbonates at least, and should show an increase in the conodont alteration index – a darkening in colour (Epstein *et al.*, 1977). Kerogen could be expected to show a decrease of perhaps 0.1 to 0.2 in atomic hydrogen/carbon ratio (Fig. 1). Perhaps the most sensitive index might be given by bitumen, which appears to respond to slight changes in temperature which persist over some length of time, i.e., are not merely ephemeral. What might be expected in bitumen derived from amorphous organic matter, type I kerogen of Figure 2, is local thermal maturation, including a higher percentage of hydrocarbons in organic solvent extracts, higher saturated fraction to aromatic fraction ratios, and saturated fraction gas chromatographic character which indicates increased organic maturity (e.g., lower n-alkanes to naphthenes ratio); or possibly organic metamorphism.

Have these effects been observed in a thermally anomalous situation? Two examples may be mentioned in which amorphous organic matter at least shows increased maturation in such a setting. Rashid and McAlary (1977) have documented early maturation of organic matter (i.e., at an anomalously shallow depth) and genesis of hydrocarbons in Cretaceous clastic rocks of the Scotian shelf above a salt piercement dome. Maturation has occurred there because of the high heat conductivity of salt. Powell (1978) reported increased maturation of organic matter within Triassic clastic sediments of the Sverdrup Basin, where these sediments have been intruded by igneous dykes and sills. Thus the effects of thermal anomalies may be seen in the response of bitumen. Simple calculations suggest these effects may well be observable in Mississippi Valley-type settings, and should be well worth looking for. It must be emphasized that these responses are only to be expected where organic matter occurs in situ, permitting its use as an indicator of paleothermal effects.

The implication of the above reasoning is that organic matter may have only a casual association with lead-zinc deposits. But organic matter may have a genetic role or roles, as seen in Table III.

Genetic roles of organic matter.

Source, transport and precipitation are all aspects of Mississippi Valley-type orebodies in which organic matter has

Table III

Possible roles of organic matter in genesis of Mississippi Valley-type Pb-zn deposits

A. Source rocks for metals
– initial concentration as metal-organic complexes
– organic (thermal) maturation frees metals
B. Transport
– Metals travel as chloride and organic complexes
C. Sulphide precipitation
– petroleum-sulphate reaction at site, yielding H ₂ S
– H ₂ S supplied directly from sulphur compounds in petroleum
– chloride brines alter organic matter, releasing H ₂ S

been suggested to play a role. Earlier I emphasized possible genetic relationships between petroleum and mineral deposits (Macqueen, 1976). We need to know more about sources and the behaviour of metal-organic complexes during diagenesis before item A of Table III can be evaluated properly: at present, these are only interesting suggestions. Transport of metals as organic complexes might alleviate the low solubility of chloride complexes and hence large volumes of fluids required as noted by Anderson (1978) and others. This is a geochemically messy area in which to conduct research because of the difficulty of duplicating natural systems in terms of organic complexes, and because biological processes (e.g., bacterial) may be significant. This is also true of precipitation of sulphides at suitable sites. Hydrogen sulphide is a widespread component of carbonate rocks; it is also an effective metal sulphide precipitator. We need to know more, however, about its genesis in proximity to sulphide settings. Is a non-bacterial petroleum-sulphate reaction feasible (e.g., Dunsmore and Shearman, 1977)? Or are anaerobic sulphate-reducing bacteria, feeding on petroleum, effective in continuous production of requisite volumes of H₂S? It is well known that shallow groundwaters can carry sulphate for long periods of time in the absence of organic matter. Upon encountering organic matter in a suitable form, sulphate content is drastically reduced, and H₂S produced, through bacterial action. It is also known that such sulphate-reducing bacteria can be active up to temperatures in the vicinity of 80°C (e.g., Dunsmore and Shearman, 1977). Another possibility for producing H₂S is through reduction of sulphur-bearing resins or asphaltenes. It is likely that the character of petroleum or bitumen involved in such reactions or processes has been altered distinctively, for example in the normal or isoprenoid alkane fractions of saturated hydrocarbons. Given the state of the art in petroleum geochemistry in the late 1970s, such alterations should be detectable. Study of the widely reported petroleum associated with, for example, the classic Mississippi Valley deposits may be highly rewarding in helping to evaluate these suggestions.

The third suggestion of part C in Table III implies thermal metamorphism of organic matter, and seems unlikely at least in the non-deformed setting in which many Mississippi Valley-type deposits occur.

Studies of Mineral Deposits and Organic Matter.

Several studies may be mentioned, not all of the deposits are of Mississippi Valley-type, however. Perring (1972) determined that bitumens associated with lead-zinc deposits in North Derbyshire, England are of biological origin but have been biodegraded, probably by bacteria. Bitumens appeared to be of local origin. Saxby (1976) considered the significance of organic matter in ore genesis, and advanced some of the suggestions noted above, especially those regarding the possible importance of metal-organic compounds. Saxby also looked at kerogens from a variety of Australian mineral deposits. On a graph of atomic hydrogen/carbon versus atomic oxygen/carbon metamorphism has been reached (Saxby, 1976, p. 125). Connan (1977) examined relationships between bitumen and a sulphide-bearing barite deposit in France, concluding that the bitumens are more or less affected by bacterial degradation, and that the degree of biodegradation of bitumens is linked to the abundance of sulphides (galena, bornite and others) in the vicinity. In this case, biodegradation by sulphate-reducing bacteria seems to have provided a sulphide source.

Conclusions

In the foregoing I have theorized without much data - a capital mistake according to Sherlock Holmes, because one begins to twist facts to suit theories, instead of the reverse! My aim in this brief review, however, has been to show that there is some very interesting work to be done over the next few years on Mississippi Valley-type deposits. New and powerful tools are at our disposal in the form of methods to unravel the burial and thermal history of host rocks and ore deposits, and the possible importance of organic matter in ore genesis. This in no way disparages all the excellent studies that underlie our present understanding, as mentioned above. The challenge now

is to elevate the present working hypothesis to a theory, or discard or modify that working hypotheses and adopt another. There is no shortage of interesting problems remaining.

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