

## Sediment-hosted Stratiform Copper Deposits

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*"Every mine manager, mine geologist, and every prospector in the field who appraises the future of mining properties does so on the basis of a theory of ore deposition whether he recognizes this fact or not." (Reno H. Sales, Mining Engineering, Transactions AIME, May 1954, p. 499-505.)*

### INTRODUCTION

A number of features are characteristic of sediment-hosted stratiform copper deposits (SCDs) (endnote 1):

- 1) the presence of a *prominent cupriferous zone*; exceptionally, lead and zinc are abundant, and other metals such as silver and cobalt can also be very significant economically;
- 2) their occurrence in *sedimentary rocks*, without apparent need of coeval igneous activity or metamorphism;
- 3) the *peneconformable, stratiform configuration* of the cupriferous zone (including both ore grade and sub-economic zones) (endnote 2);
- 4) the remarkably *uniform lateral continuity of mineralization along bedding*, suggesting (erroneously) a sedimentary origin;
- 5) the predominance of *fined-grained, disseminated sulphide ore minerals*, typically distributed in well-layered concentrations along the stratification of the host rock;
- 6) the *zoned distribution of metals* and their corresponding ore minerals;
- 7) host sediments that have typically been prepared *syndiagenetically with reducing agents and abundant sulphur*;
- 8) a major thickness of *permeable, coarse-grained, red bed clastic sediments in the immediate footwall of the cupriferous zone*;
- 9) a *temporal and spatial association* of host rocks with strata formed in warm arid climates (evaporitic units, red beds);
- 10) a *post-sedimentary, diagenetic timing* for copper;

11) the deposition of copper from aqueous, chloride-rich solutions upon crossing the *redoxcline* between footwall red beds and reduced, sulphide-bearing grey beds of the host strata; and

12) their common location *in or associated with rift basins* filled with continental red beds  $\pm$  bimodal volcanic strata.

The first 11 features are well-established in an *overprint* depositional model conceived and refined by a number of researchers, mainly during the last three decades. The common (but not invariable) affiliation with rift basins has only become widely recognized in recent years, and still requires confirmation as an fundamental feature in the genesis of all SCDs. The spatial association of many SCDs with continental rifts and the early emplacement of copper in rift-filling sediments, however, suggest that the overprinting mechanism is fundamentally related to the normal development and evolution of continental rift basins. This observation now allows us to describe a unified genetic model for this deposit type based largely on the normal evolution of a continental rift zone within hot arid climates. The many differences in such things as host rock lithologies and associated metals among the various examples of SCDs may eventually be attributed to normal variations among specific rift environments.

The general genetic model described here encompasses a well-established *depositional model*, a reasonably certain *transport model*, and useful speculations on plausible *sources of metals*. The descriptions of these three classic genetic aspects are preceded by a summary of the worldwide distribution of SCDs (Fig. 1) and their economic importance, and by a review of their genetically pertinent features among a representative list of SCDs. The discussion closes with a

recommendation that SCDs be considered a normal, albeit rare, consequence of rift basin evolution at low terrestrial latitudes.

### EXAMPLES AND ECONOMIC SIGNIFICANCE

Although few in number, economic occurrences of SCDs (Table 1) form one of our most important (and most sought after) sources of copper. Their consistent grades and lateral continuity along bedding make SCDs highly attractive exploration targets for copper and related metals. In addition to copper, SCDs provide very significant amounts of cobalt (in Central Africa), lead (in Poland) and silver (in the United States and Poland). Some deposits may contain largely untouched resources of by-product gold, uranium, platinum-group elements and rare-earth elements. SCDs have recently accounted for 20-25% of the western world's production of copper, 80% of its cobalt, and increasingly greater amounts of its silver.

Probably the earliest exploited SCD-related deposits were the native copper lodes in the Lake Superior district of North America and the oxidized copper deposits at Timna in southern Israel, both of which have workings dating back to approximately 4000 B.C. Mining of disseminated sulphide ores began at the end of the 12th century in the famous German Kupferschiefer, and large discoveries were made in the equivalent Permian beds of Poland after World War II. In 1986, Polish production was about 380,000 tonnes of copper metal, and additional deposits are under development.

The Central Africa Copperbelt of Zaire and Zambia has produced both copper and cobalt since the early decades of this century. The total tonnage of ore produced and in reserves and resources is estimated at more than 4.9 billion tonnes, grading 3.37% Cu

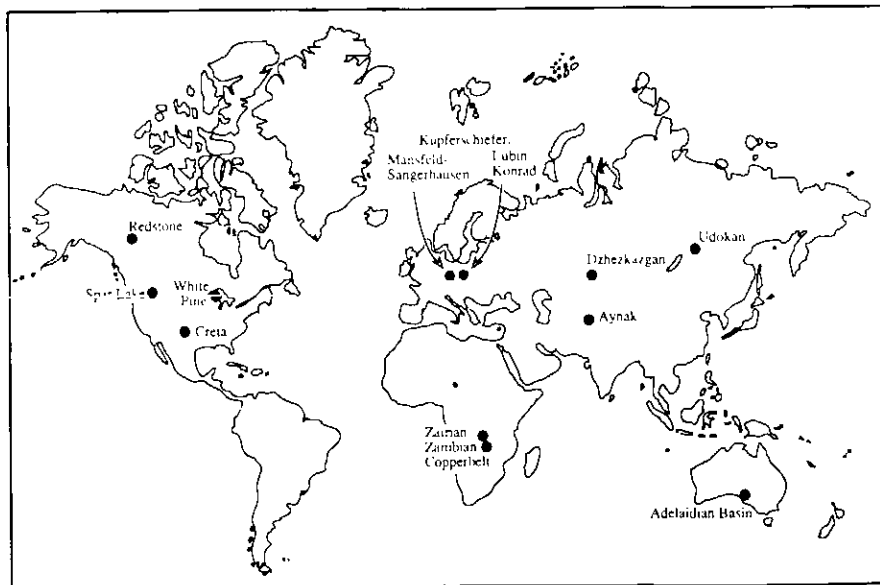


Figure 1 Location of major and other selected sediment-hosted stratiform copper deposits. For a more complete listing, see Kirkham (1989).

(165 mt Cu metal and 4.4 mt Co metal) (Freeman, 1986).

The White Pine mine of northern Michigan was developed as a strategic resource in 1952, with production reaching 23,000 tons per day in 1975. In 1986, it still had reserves of 184 million tons, grading 1.1% Cu and 6.77 g/t Ag (Seasor and Brown, 1986). Highly attractive Ag-Cu deposits have also been developed recently in the Belt Supergroup in Idaho and Montana: the Troy (Spar Lake) mine in Montana produces approximately 7200 tonnes per day from initial reserves of 64 mt grading 54 g/t Ag and 0.76% Cu (Hayes and Balla, 1986).

Other economic SCDs include the large Udokan ( $\geq 10^9$  mt of ore) and Dzhezkazgan ( $\sim 10^9$  mt grading 1.5% Cu) districts of the former USSR (Gustafson and Williams, 1981), and, at the other end of the scale, the thin ( $\sim 15$  cm) Creta deposit in Kansas-Oklahoma-Texas (Johnson, 1974; Smith, 1976), which operated for about ten years in the 1960s and 1970s. Explored, largely uneconomic deposits include the Redstone copperbelt in Canada's Northwest Territories (Ruelle, 1978, 1982), the Adelaiddian Supergroup of South Australia (Rowlands, 1974; Rowlands *et al.*, 1978), and the Witvlei district in Namibia (Anhaeusser and Button, 1976).

#### A PREVIEW OF THE GENERAL MODEL

Briefly stated, the deposition of metals in SCDs involves a diagenetic (two-fold) process (Lovering, 1963): 1) a chemically reducing, commonly carbonaceous and pyritic, grey bed sediment is initially enriched in sulphur (iron sulphide and/or gypsum/anhydrite) by primary, syndiagenetic processes; and then 2) copper  $\pm$  associated metals are zonally *overprinted* on the S-rich host during a post-sedimentary influx of dissolved base metals from adjacent, coarse-grained, highly porous and permeable, continental red bed sediments (Fig. 2). The de-

position of metals is essentially a low temperature chemical reaction between abundant reduced sulphur (e.g., sulphide in pyrite) in the host and base metals added to these sediments. The reduced sediment is an excellent *chemical trap* for the introduced metals. The visually distinctive contact between the red beds and the grey beds, known as a fossil *redoxcline*, is an obvious metallotect for those exploring for SCDs.

The immediate source of copper is soluble *metal chloride complexes* dissolved in the oxidized, saline pore fluids of the red beds. Metal influx can occur by *infiltration* and/or *diffusion*. Infiltration requires an adequate host permeability, and would be expected to become less important as the fine-grained grey beds are compacted and cemented. Where infiltration is seriously restricted, the remaining interconnected pore spaces of the grey beds may still permit diffusion of metals along chemical potential gradients toward

the chemical sink represented by the pyritic grey beds. Metal transport by diffusion over long distances, however, would be unreasonable (Brown, 1971).

A well-defined, *zoned array* of disseminated, fine-grained sulphides results during deposition of common copper-bearing sulphides (e.g., chalcocite, digenite, bornite and chalcopyrite) and other base metal sulphides (e.g., galena and sphalerite) *downstream* from the redoxcline. Chalcocite and digenite (the least soluble cupriferous sulphides) are precipitated close to the redoxcline, whereas bornite and chalcopyrite are deposited progressively further downstream, toward the originally pyritic zone. If a *hematitic zone* results from the influx of oxidizing ore solutions, this reddish alteration zone is immediately upstream of the cupriferous grey beds.

This mode of emplacement of metals at the deposit scale is reasonably well estab-

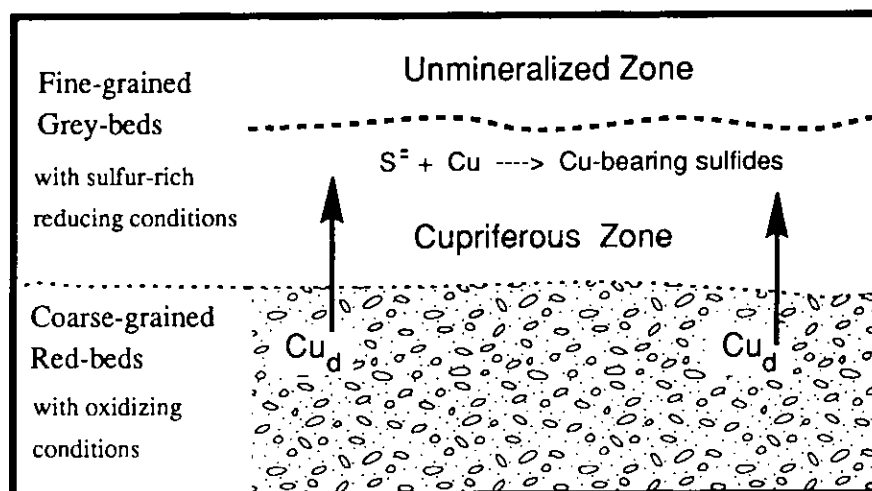


Figure 2 General deposit-scale model for sediment-hosted stratiform copper deposits. The heavy dotted line indicates the furthest advance of copper into the basal grey bed unit.

Table 1 Principal characteristics of representative sediment-hosted stratiform copper deposits.

Deposit	Mineralization Ore Minerals	Host Rocks	Associated Footwall Sediments	Paleoenvironmental Setting
White Pine, Michigan	Cu-(Ag) Cc-Cu	Carbonaceous shale, siltstone, sandstone	Hematitic conglomerate	Rift basin, lacustrine (?) with fan delta
Kupferschiefer, Poland	Cu-Pb-Zn-Ag Cc-Bn-Cp-Ga-Sl	Carbonaceous shale, carbonate, sandstone	Hematitic sandstone	Rift basins; evaporitic basin; hot arid climate
Zairian Copperbelt (Kamoto)	Cu-Co Cc-Bn-Cp-Car	Dolomite, dolomitic carbonaceous shale	Hematitic conglomerate	Coastal sabkha; tectonically detached from basement
Zambian Copperbelt (Nchanga)	Cu-Co Cc-Bn-Cp-Car	Sandstone, argillite, dolomite	Arenaceous sandstone-conglomerate	Rift basin; marginal marine (?)
Redstone, NWT, Canada	Cu-Ag Cc-Bn-Cp	Dolomitic carbonate	Hematitic mudstone/siltstone	Rift basins; marginal-marine sabkhas
Troy (Spar Lake) Montana	Ag-Cu Cc-Bn-Cp-Ga-Sl-Ag	Argillaceous quartzite	Quartzites, siltites	Epicratonic trough

Abbreviations: Cc=chalcocite, Bn=bornite, Cp=chalcopyrite, Ga=galena, Sl=sphalerite, Car=carrollite ( $\text{CuCo}_2\text{S}_4$ ), Cu=native copper, Ag=native silver.

lished from a multitude of detailed studies conducted on many major SCDs since approximately 1960 (e.g., Bartholomé, 1958, 1962; White, 1960). Still, this model has been opposed by vigorous arguments for a syngenetic origin (e.g., Schneiderhöhn, 1932; Garlick, 1940, 1961, 1989). Between the 1940s and the 1960s, the syngenetic school did succeed admirably well in refuting the classic magmatic hydrothermal (epigenetic) concepts of Lindgren (1933), Sales (1959) and others. The syngenetic school did not, however, readily accept (and, in rare cases,

still has not accepted) that its hypotheses could also be erroneous, and that a post-sedimentary addition of metals derived from non-magmatic sources could better explain the genesis of SCDs. In fact, the *diagenetic overprint model* described here offers a timing and mode of mineralization that are commonly more closely related to hydraulic solution flow along aquifers during normal basin diagenesis (endnote 3) than to flow along major epigenetic structures as portrayed in classic magmatic-hydrothermal concepts. In many cases, overprinted mineralization may

have occurred immediately after sedimentation, in still poorly consolidated sediments. In others, there is evidence of initial focussing of ore-forming solutions along large, cross-cutting structures, with local metal influx still controlled at the deposit scale by bedding permeabilities. Fortunately, many SCDs are hosted by essentially unmetamorphosed sediments, and diagenetically early features of the host strata may still be seen. Valuable comparisons may also be made with equivalent sediments in modern basin environments.

In all cases, the SCD mineralization commonly retains certain "sedimentary" characteristics (e.g., a bedded appearance) because the base metal sulphides are deposited as replacements of constituents in initially bedded host rocks. However, this "bedded" replacement mineralization differs importantly from strictly synsedimentary mineralization in many economic and conceptual aspects, including the peneconformable attitude of the entire mineralized zone, the zoning of metals and their ore minerals relative to interpreted paleobasin environments, the timing of metal deposition, and plausible ultimate sources of ore metals.

**TYPE DEPOSITS**

Now let us examine several type examples of SCDs, emphasizing features pertinent to their genesis. Only essential details are given here; more complete descriptions may be found in the references cited.

**White Pine, Michigan**

The Nonesuch Shale host rock at White Pine, Michigan is composed of essentially unmetamorphosed Late Proterozoic sediments which have been only moderately tilted, fractured and faulted by *post-ore* deformation. Ore zones are well exposed in many tens of km<sup>2</sup> of underground mine workings, and in more than 500 continuous-section drill cores distributed over many hundreds of km<sup>2</sup> of the lower Keweenaw peninsula (Ensign *et al.*, 1968). Economic mineralization occurs mainly within the basal 20 m of the ~200 m thick Nonesuch Shale, within two similar stratigraphic sections (the Lower Sandstone-Parting Shale unit and the Upper Sandstone-Upper Shale unit, each 2-3 m thick and grading 1-3% Cu; see Fig. 3). Incised stream channels and oxidation at the top of the Parting Shale indicate minor erosion before subsequent transgression and deposition of the Upper Sandstone.

Copper occurs predominantly as very fine-grained chalcocite (accompanied in lower stratigraphic levels by native copper and trace amounts of silver) in dark, thinly laminated to massive, carbonaceous, clastic sediments. Sulphide grains are typically concentrated along bedding (especially in coarser grained fractions of thin bedding laminae). The distribution of cupriferous sulphides imitates that of syndiagenetic pyrite

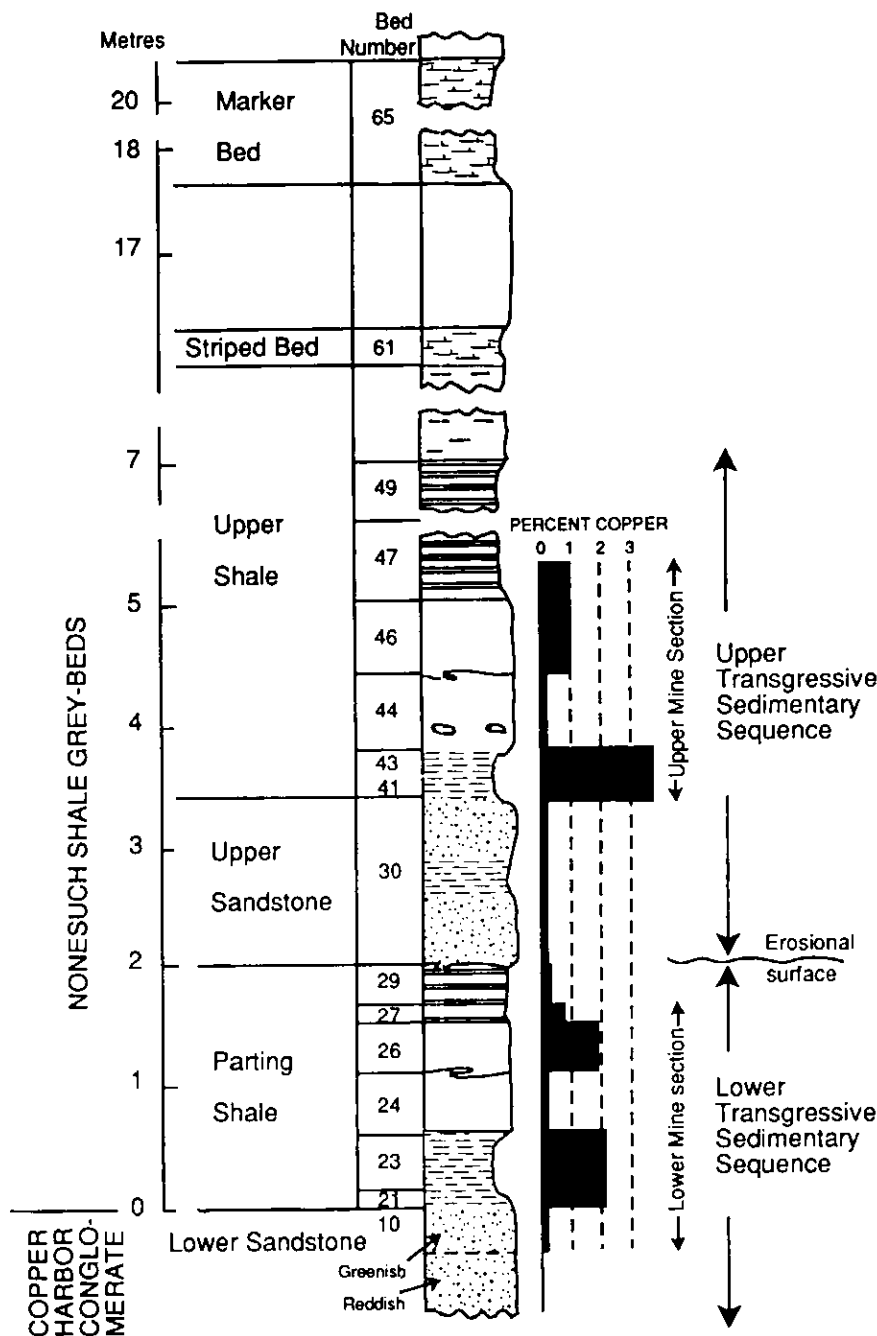


Figure 3 Stratigraphic units and copper mineralization in the basal Nonesuch Shale at White Pine, Michigan. Modified from Ensign *et al.* (1968).

in unmineralized beds and suggests (erroneously) a sedimentary origin for all sulphide minerals, as initially described by White and Wright (1954).

The underlying, reddish Copper Harbor Conglomerate (in places 100-200 m thick) may also contain native copper where it is locally bleached, especially directly beneath the Nonesuch Shale. Patchy bleached zones, extending downward from the Nonesuch Shale as much as 6 m, are attributed to reduction of iron ( $\text{Fe}^{3+}$  of hematite  $\rightarrow$   $\text{Fe}^{2+}$  of chlorite), when and where pore fluids were forced out of the basal Nonesuch Shale during compaction (Hamilton, 1967).

The White Pine mineralization is confined to a narrow stratigraphic zone on the reduced (upper) side of the redoxcline that closely follows the contact between the red beds of the Copper Harbor Conglomerate and the overlying grey beds of the Nonesuch Shale. Disseminated chalcocite extends continuously upward through all basal Nonesuch Shale beds to a single, blanket-like, "fringe" surface which separates the cupriferous zone from unmineralized pyritic sediments occupying the remaining 180 m or more of overlying Nonesuch Shale. The abrupt transition (fringe zone) from the cupriferous to pyritic zones has been interpreted as the final position of a post-sedimentary mineralization front which invaded initially iron sulphide-rich beds at the base of essentially unconsolidated Nonesuch Shale sediments (White, 1960; Brown, 1965, 1971; White and Wright, 1966).

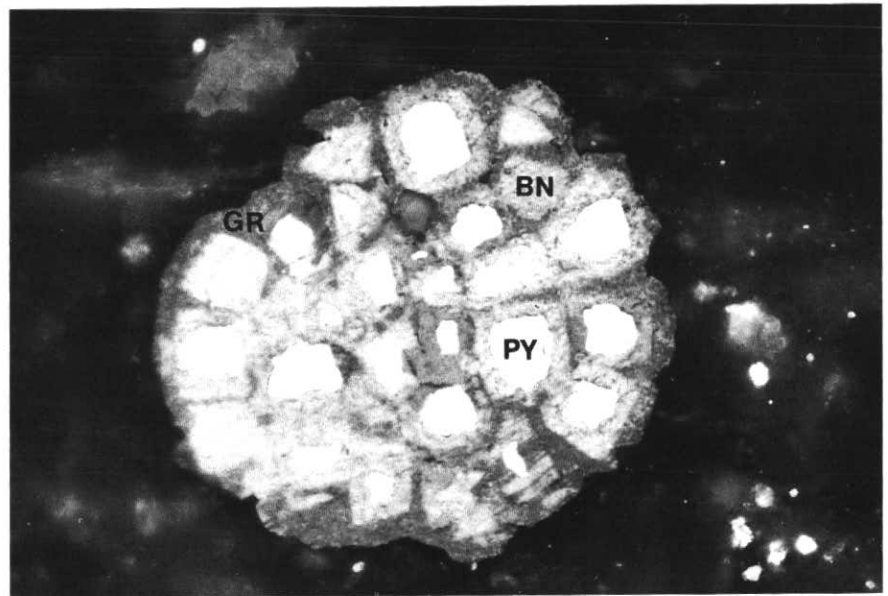
Features supporting this concept of post-sedimentary/pre-deformation overprinted mineralization include: 1) a single, basal cupriferous zone where, in fact, the stratigraphy includes two transgressive sedimentary sequences (Fig. 3); 2) the gentle, but significant, transgression of bedding by the fringe surface; 3) textures along the fringe surface indicating a step-by-step replacement of initial syndiagenetic pyrite by Cu-bearing sulphides (Fig. 4); 4) an inverse correlation between the height of the fringe surface in the basal Nonesuch Shale and the amount of copper in the basal-most Nonesuch beds (interpreted as a chemical filtering of copper from the basal beds, and raising the question as to how there could be a correlation between the amount of copper in the basal beds (Fig. 5, beds 21 and 23) and the position of the fringe surface many metres above, unless the copper did, in fact, pass through those basal beds); and 5) trace but abnormal concentrations of Cd, Pb and Zn (metals which are less sulphophile than copper and more sulphophile than iron) immediately above the fringe surface; anomalous amounts of mercury are also found at a fairly uniform distance above the fringe (Luppens, 1970). Zoned ore mineral patterns analogous to this distribution of accessory metals have been reproduced in the laboratory using diffusion and infiltration processes (Brown,

1974), and by thermodynamic modelling of red bed-derived fluids reacting with reduced host rocks (Reed and Haynes, 1990).

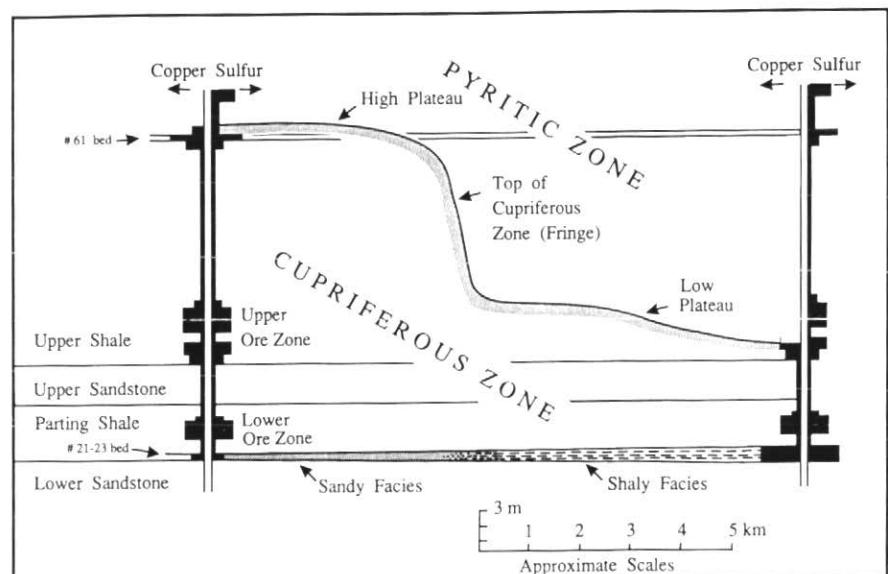
#### Kupferschiefer

The SCDs of this historic copper district are now well known, especially from modern studies in the Fore-Sudetic area of Poland (see Jowett, 1986a, 1986b; Jowett *et al.*, 1987; and many Polish contributions cited in those references). In general, the stratigraphy in the Fore-Sudetic area consists of Lower Permian Rotliegende red beds (250-900 m thick) and Upper Permian Zechstein grey beds (>250 m) which unconformably overlie

a Precambrian/Lower Paleozoic basement. The Rotliegende is composed of basal volcanic and coarse-grained clastic rocks deposited in a fluvial-eolian desert environment. The lower Zechstein grey beds (Fig. 6) include the Zechstein Conglomerate and Zechstein Sandstone, derived from Rotliegende clastic rocks which were reworked by the transgressing Zechstein sea. This initial marine clastic unit is succeeded by a thin (0-20 cm) limestone (Basal Dolomite, also known as the Border Dolomite or Boundary Dolomite), which is, in turn, overlain by the famous Kupferschiefer shale (typically dark grey, carbonaceous, thinly laminated, and



**Figure 4** Partial replacement of a framboidal group of pyrite (PY) grains by bornite (BN). Greenockite (GR, CdS) rims the entire structure. Reflected light, in oil. From Brown (1971).



**Figure 5** Schematic diagram showing the inverse correlation between the thickness of the cupriferous zone and the amount of mineralization in the combined No. 21 and No. 23 beds at White Pine, Michigan. Vertical exaggeration approximately 300x. See text for interpretation. From Brown (1970).

30-90 cm thick), the Zechstein Limestone (5-60 m), and the thick Werra Anhydrite and/or Saltstone.

The mineralized zone (generally 4-5 m thick) of the Fore-Sudetic Monocline includes the "Weissliegende" portions of the pre-Kupferschiefer clastic sediments, the Basal Limestone, the Kupferschiefer, and lower portions of the Zechstein Limestone. Ore grade mineralization (up to 15% Cu and minor amounts of Ag) occurs mostly as intergranular cement in the uppermost Weissliegende (0-15% Cu) and as fine-grained disseminations in the Kupferschiefer (average ~11% Cu).

Two important zones of diagenesis have been overprinted on the upper Rotliegende/lower Zechstein strata: 1) the "Weissliegende", a greyish white zone of variable thickness directly underlying the Kupferschiefer, which apparently formed by bleaching (reduction) of Rotliegende and basal Zechstein clastic units when anoxic pore fluids were forced out of the carbonaceous Zechstein beds by compaction; and 2) the "Rote Fäule", an irregular zone of reddish oxidation which extends continuously upward from the Rotliegende into basal Zechstein beds (Fig. 6). The Rote Fäule alteration seems to have followed the formation of the Weissliegende zone. Both zones have economic significance: the Weissliegende commonly hosts ore, whereas the Rote Fäule is hematitic and contains no mineralization.

The Weissliegende is especially prominent where potential aquicludes are thin or absent in basal Zechstein strata (fine-grained, compact beds of the Basal Limestone, Kupferschiefer, Zechstein Limestone), i.e., where pore fluids from the marine beds could more easily penetrate downward into the Rotliegende aquifer (Kucha and Pawlikowski, 1986). Where well-developed, the Weissliegende zone is commonly cemented by anhydrite, presumably derived from the overlying Werra Anhydrite. Anhydrite-cemented Weissliegende is typically poorly

mineralized, apparently due to its low porosity.

The Rote Fäule attains its highest stratigraphic levels where the Rotliegende basin pinches out next to the Alpine-age regional fault along the southern edge of the Fore-Sudetic Monocline, and over Rotliegende sand dunes which were reworked and beveled offshore by the transgressive Zechstein sea. It is typically overlain by rich, base metal sulphide mineralization in the adjacent Zechstein grey beds, and was probably produced during late diagenesis by a generally upward penetration of oxidizing ore solutions. In eastern Germany, the peneconformable zoning of the Rote Fäule and its associated base metal sulphides around offshore sandbars is not related to nearby paleocoastlines, as would be expected with a synsedimentary origin (Rentzsch, 1974). Also, the upward and laterally outward zoning of metals from the Fore-Sudetic horst block into the adjacent Zechstein sediments suggests a syn- or post-fault control of mineralization at the basin scale.

On the Fore-Sudetic Monocline, ore minerals consist dominantly of chalcocite, bornite and chalcopyrite, grading upward and northeastward toward galena-sphalerite-rich zones where pyrite predominates. Most mineralization is disseminated and intergranular, relative to grains of the host rock. Pyrite is replaced and commonly superseded by base metal sulphide minerals. Ore sulphides occur in replacement nodules and in veinlets parallel to and crosscutting bedding. Traces of disseminated pyrite and chalcopyrite have also been noted along the base of the Weissliegende, suggesting a late, inverse, vertical zoning of Cu-Fe sulphides toward the underlying Rote Fäule, in addition to the prominent upward Cu → Fe-Pb-Zn sulphide zoning in the Zechstein beds (Kucha and Pawlikowski, 1986).

The Kupferschiefer mineralization differs from that at White Pine in several aspects, but the essential elements of the overprint

model proposed for the Michigan deposit are repeated. The Rotliegende ore solutions, however, apparently carried abundant Pb and Zn as well as Cu and Ag. In fact, copper mineralization is restricted to approximately 2% of the Zechstein basin, whereas lead and zinc exceed copper in total mass, and surpass copper in areal distribution. Kucha (1982, 1985) and Unrug (1985) remind us of the noble metal potential of the Kupferschiefer.

**Central African Copperbelt**

This belt, the giant of those containing SCDs, is notable for its cobalt content, in addition to immense amounts of copper. The Shaban (formerly Katangan) copperbelt of Zaire, and the politically separate Zambian (formerly Northern Rhodesian) copperbelt, together form a single, ~500 km long and 30-50 km wide, Central African Copperbelt (1300-650 Ma) along the late Proterozoic Lufilian Arc (Fig. 7) (Cahen, 1974, 1982; Cailteux, 1977; Lefebvre, 1989).

In Zaire, the unmetamorphosed Shaban Supergroup host rocks consist largely of extensive dolomites and dolomitic shales (in part stromatolitic) which were probably deposited along a broad coastal marine platform. At Kamoto, they are tectonically detached from a basement presumed to lie some tens to hundreds of kilometres to the south; large rotated "écailles" (megabreccia blocks of mine dimensions; Fig. 8) float in tilted, overturned, folded and diapiric attitudes within the younger Kundelungu strata. Mineralized grey beds (lower Mines Group) overlie a sterile, reddish, alluvial, footwall clastic unit (RAT Group) and underlie unmineralized, dark grey, pyritic, dolomitic shales and siltstones (upper Mines Group).

Disseminated chalcocite, bornite and carrollite (CuCo<sub>2</sub>S<sub>4</sub>) of the Lower Orebody (~15 m thick) grade into a bornite-chalcopyrite-carrollite assemblage in the Upper Orebody (~12 m thick) and then into disseminated pyrite and minor chalcopyrite in the hanging-wall strata. Core from regionally distributed drill holes indicates that the Cu → Fe zoning is peneconformable, as seen in the Kupferschiefer and at White Pine.

Paragenetic textures among the well-preserved sulphides indicate repeatedly that disseminated, fine-grained, syndiagenetic pyrite was the first sulphide to form. Besides the progressive replacement of pyrite to form a zoned array of Cu-Co-Fe-bearing sulphides, studies by Bartholomé (1962) and Bartholomé *et al.* (1973) show that syndiagenetic pyrite is encased in authigenic quartz, in rims of early diagenetic magnesite nodules, and in carrollite porphyroblasts, and was thus protected from replacement when Cu-bearing sulphides were subsequently deposited in the interstices of the immediately surrounding host sediment. More precisely, it seems that pyrite formed in the absence of cobalt in the initial pore solu-

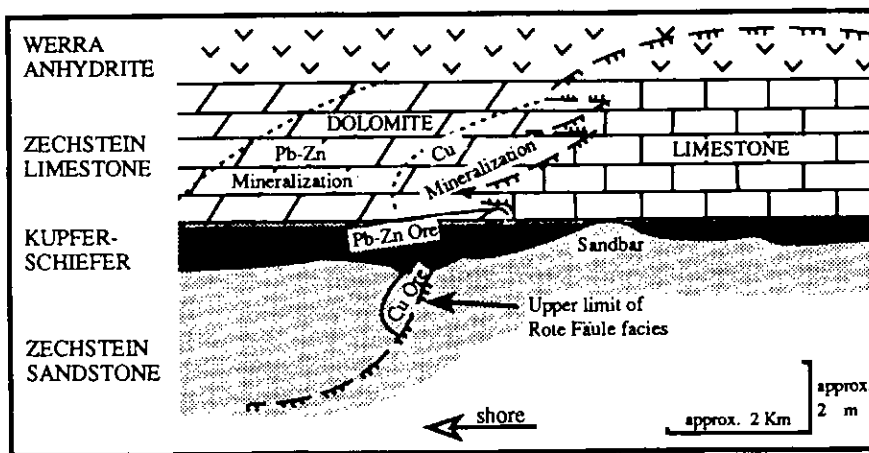


Figure 6 Stratigraphy of the Kupferschiefer host sediments, showing the transgressive zoning of copper- and lead-zinc-sulphide mineralization above the Rote Fäule hematitic alteration facies.



tion because the cores of pyrite grains are Co-free. Cobalt was introduced later, to form carrollite and Co-rich rims on pyrite grains. Carrollite, signaling the earliest arrival of copper, is followed paragenetically by cupiferous sulphides, which represent the main stage of copper mineralization.

In Zambia, the Roan Supergroup host rocks are moderately to strongly deformed and metamorphosed, are well exposed in large open pits and underground mines, and can also be studied in core from extensive drilling programs. Mineralization generally occurs in a basal clastic unit (Footwall Arenite orebodies) and in overlying argillaceous and dolomitic units (Ore Shale orebodies). In vertically stacked argillites, mineralization commonly occurs directly beneath compact, argillaceous carbonate beds. Individual ore zones may measure several kilometres in strike length and tens of metres in thickness (Mendelsohn, 1961, 1989; Fleischer *et al.*, 1976).

Ore minerals are typically disseminated and consist mainly of chalcocite, bornite and chalcopyrite (as well as carrollite in most, but not all, deposits). In contrast to the Kamoto deposits, however, sulphides are both laterally and vertically, and in some case inversely, zoned within individual orebodies; chalcocite and bornite are generally proximal to paleotopographically high granitic basement, whereas pyrite predominates in surrounding distal areas. Barren pyritic zones are also common over offshore basement highs and where bioherms have grown on and around basement highs (Annels, 1974). Zinc has been found in significant amounts (up to 3%) in the distal pyritic zones.

The Cu-Fe zoning has been attributed, in a syngenetic hypothesis, to transport of copper to marine basins in fresh water streams and to simultaneous deposition of copper (less soluble than iron) sulphides in near-shore locations while pyrite formed in deeper offshore environments (Garlick, 1961, 1989). According to this hypothesis, the zoned sequence of Cu-rich to Fe-rich sulphides reflects the direction of transport toward deeper, more anoxic water and follows the corresponding sequence of sulphide mineral stabilities across low-temperature Eh-pH diagrams. The same sequence of sulphide stabilities, however, may be generated as an overprint of copper on sulphide-rich sediments in an epigenetic process. Thus, the redox argument is permissive to both hypotheses, and not diagnostic of either.

The syngenetic concept encounters serious difficulties in explaining numerous crucial aspects of the Zambian deposits, including:

- 1) the efficient transport of large quantities of ore metals in fresh water (resort is typically made to the formation of metal colloids and anomalous amounts of metals that can be attached to transported clay particles);
- 2) the absence of excessive amounts of clas-

tic debris, which would result from rivers emptying into the sedimentary basin and which would severely dilute sedimentary concentrations of ore metals;

3) adequate hinterland sources of copper (the suggested erosion of older orebodies of adequate size in the basement requires confirmation); and

4) the provenance of cobalt from the hinterland that is largely granitic and Co-poor.

In addition, if the syngenetic model is to be considered tenable for the Zambian deposits, it should explain the formation of comparable Cu-Co deposits in the sabkha environments of the Kamoto deposits.

Such difficulties, reviewed along with several other aspects by Sweeney *et al.* (1991), are avoided in a genetic model which includes the subsurface circulation of chloride brines transporting metals as soluble metal-chloride complexes. The sulphide zoning may be explained by a prominent flow of ore solutions both across and along bedding. Annels (1974, 1989) proposed that ore solutions rose, at basin scale, along permeable clastic rocks overlying the basement/Roan contact and then, at mine scale, migrated laterally along bedding, particularly beneath compact carbonate units in the mine section (Fig. 9).

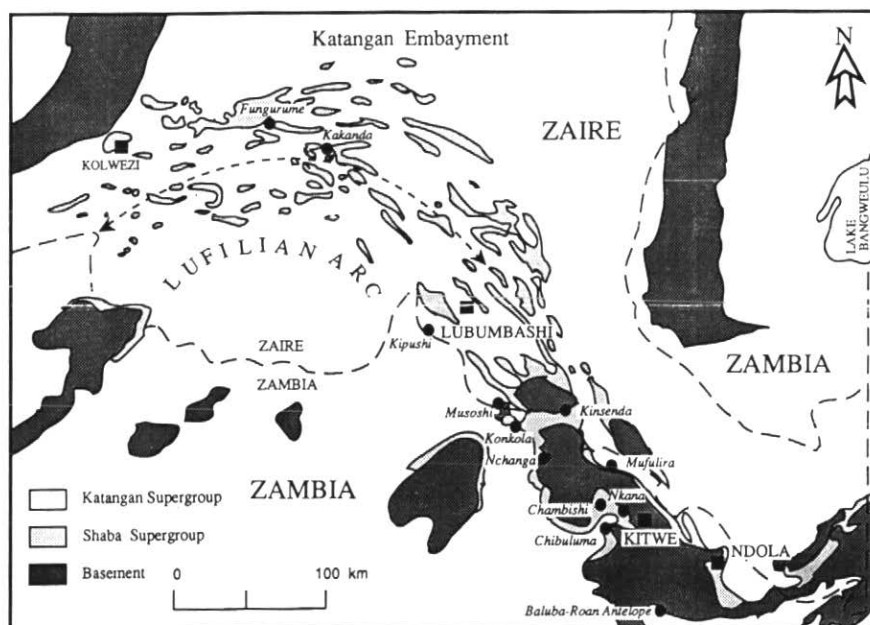
Unfortunately, this concept of partial bedding/parallel flow has not been fully appreciated until recent years, perhaps due largely to the predominance of vertical zoning in early overprint models developed for White Pine and Kamoto. The following case demonstrates, once more, the need to consider all available channels, at all scales, in order to understand the particular circulation of ore solutions in any given deposit.

### Troy (Spar Lake), Montana

This deposit is a textbook example of post-sedimentary mineralization that appears to have been guided initially across bedding by post-lithification faults and then laterally along the more permeable lithologies within a thick sequence of clastic sediments cut by the faults. Once more, the ore mineralogy consists of common base metal sulphides (including important co-product silver), and again, the sulphides are zoned according to their relative low-temperature solubilities (Cu-rich sulphides near the site of influx, and Fe-rich sulphides and galena farther downstream) (Hayes and Balla, 1986; Hayes and Einaudi, 1986).

In this case, however, the configurations of mineralized zones resemble the familiar hydraulic front of C-shaped (roll-type) sandstone-hosted uranium deposits. At Troy, ascending ore solutions were apparently initially guided across stratigraphy by a subvertical fault, and then migrated laterally along orthoquartzitic aquifer beds enclosed by chloritic quartzite aquicludes (Fig. 10b). Mineralization extends laterally along bedding as far as the quartzites remain permeable; where the orthoquartzites grade by facies changes into less permeable chloritic quartzites, copper mineralization grades into unreplaced pyrite. The pyrite is accompanied by galena, which was swept ahead of the cupiferous sulphides, as in White Pine, the Kupferschiefer, and other SCDs. Similar C-shaped hydraulic configurations, indicative of along-bedding flow of ore solutions, are observed in the Kona Dolomite mineralization in northern Michigan (Taylor, 1972) and in Zambia (Annels and Simmonds, 1984).

Sulphide textures at Troy (and in the Kona



**Figure 7** Location of major ore deposits in the Lufilian Arc of Zaire and the continuation of this copperbelt into Zambia. For location, see Figure 1.

Dolomite) indicate that the introduced metals were precipitated by reaction with an initial interstitial pyrite in the aquifers. The coincidence of mineralized zones with major sub-vertical faults at the mine scale (Fig. 10a) indicates that mineralization took place *after lithification*, and hence was not early diagenetic in timing, as has been proposed for White Pine and Kamoto.

**Redstone (Coates Lake), Northwest Territories**

Recent detailed studies of this Late Proterozoic SCD mineralization indicate a *very early diagenetic* emplacement of copper in well-preserved peritidal sediments. The Transi-

tion Zone host rocks (~110 m thick) represent repeated transgressive/regressive red bed/grey bed sedimentation between the underlying, alluvial red beds of the Redstone River Formation (0-1000 m thick) and overlying, euxinic, marine carbonates of the Coppercap Formation (~250 m thick).

The sulphide assemblage (principally chalcocite, digenite, bornite, chalcopyrite and pyrite, together with minor to trace amounts of sphalerite, galena and molybdenite) occurs as fine-grained disseminations and laminae within several, thin, blanket-like units formed of evaporitic dolosiltite, dololutite and microbial-laminated limestone and dolostone. Mineralization at

Coates Lake occurs in the lower three carbonate units, with iron sulphide and minor amounts of sphalerite and galena in the overlying carbonate units.

The petrology, stratigraphy and sedimentology of the Redstone deposit suggest that the host strata were deposited along arid shorelines in environments comparable to those of modern sabkhas (Ruelle, 1978, 1982; Jefferson, 1978, 1983; Chartrand, 1981, 1986; Jefferson and Ruelle, 1986; Chartrand and Brown, 1985). Copper deposition, involving syndiagenetic to very early diagenetic concentrations of sulphates and sulphides, occurred where cupriferous fluids infiltrated porous, permeable sediments during very early diagenesis. Ore-stage sulphides filled fenestral pores and cemented framework grains in the host sediments, before burial, to an estimated 100 m, at which depth these pores would have collapsed. On the other hand, the occurrence of a single copper zone and overlying lead-zinc mineralization suggests a single overprinting mineralization event continuing through deposition of the majority of the Transition Zone.

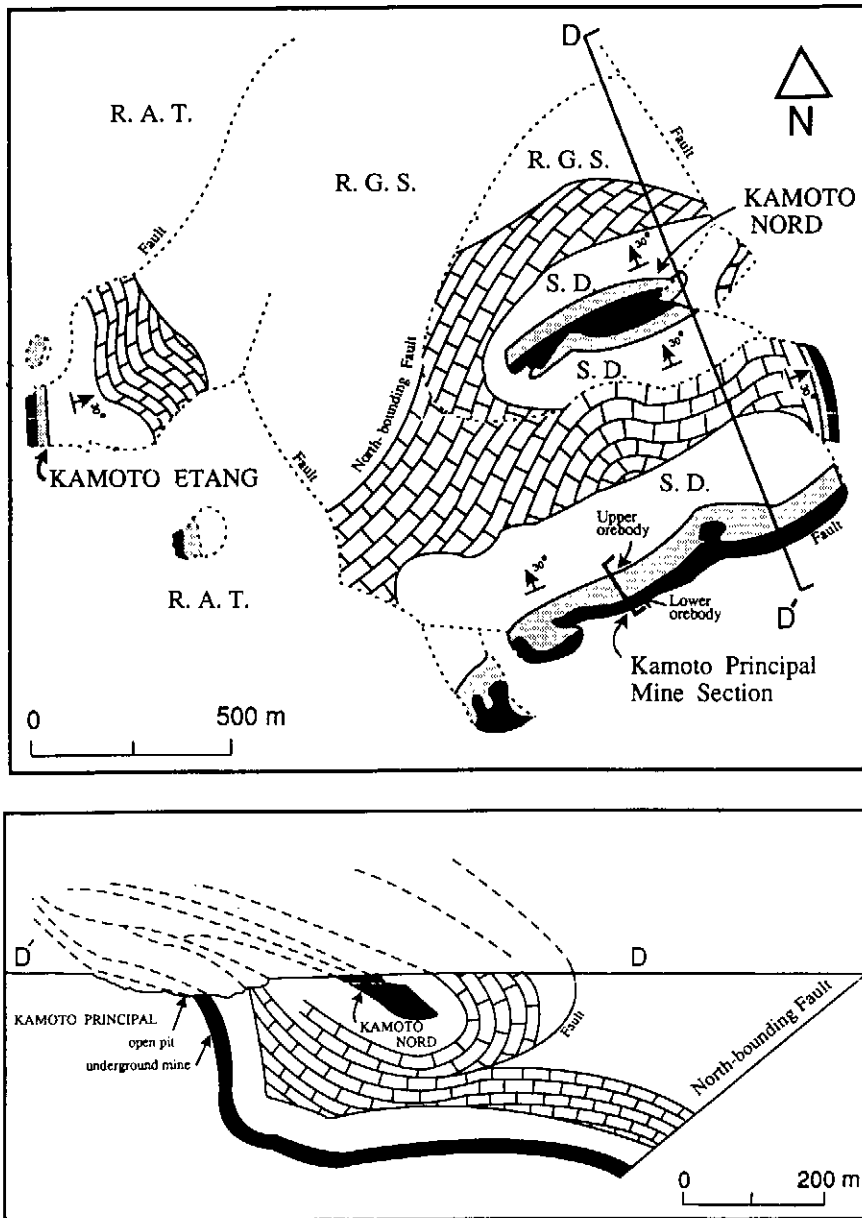
**A DIPLOGENETIC DEPOSITIONAL MODEL**

The above descriptions demonstrate that stratiform copper deposits are distinctly variable in many aspects, such as their host lithologies, metal ratios, and the timing of metal influx relative to sedimentation and diagenesis. Some basic features of genetic importance are, however, shared by all members of this deposit type.

**Syndiagenetic Ground Preparation**

One of the most consistent features of SCDs is their occurrence in chemically anoxic, sulphur-rich grey beds lying immediately "downstream" of oxic continental red beds (endnote 4). Any base metals that cross the abrupt chemical transition from oxidized reddish beds to reduced greyish beds should precipitate as sulphides in the grey beds by reaction with the abundant sulphide available there. Thus, mineralized grey beds generally represent a basal cupriferous zone immediately overlying a fossil redoxcline, and the remaining unmineralized grey beds (commonly pyritic) represent remnants of the original S-rich sediment further downstream from the redoxcline.

In contrast to the oxidized footwall strata, the mineralized and pyritic sediments may be greyish and/or greenish (even buff if essentially devoid of organic matter; endnote 5), but never reddish. An anoxic environment generally results from the presence of carbonaceous matter, and an abundance of sulphur is normally assured by the presence of pyrite or more primitive iron sulphides. Primary and very early diagenetic sulphates such as gypsum or anhydrite can also provide early diagenetic sulphide through biogenic reduction. From S isotope analyses, Hoy and Ohmoto (1989) also proposed that a



**Figure 8** (a) (upper) Plan view of a portion of the Kolwezi mining district, showing the deformed and tilted megabreccia blocks hosting the Kamoto Principal, Kamoto Nord and Kamoto Etang mines. Economic mineralization is hosted by the basal portions of the Kamoto Dolostone (dotted patterns) and S.D. Formation (white). Section D-D' is illustrated in Figure 8b. From Demesmaeker (1963). (b) (lower) Profiles through the stratigraphy of the Kamoto Principal and Kamoto Nord mines (for location, see line D-D' of Figure 8a).

significant portion of the sulphur in the Kamoto deposits was introduced as sulphate with the oxidized ore solution.

Variations in the lithologic composition of the host grey beds (generally ranging from fine-grained clastic beds to carbonates) suggest that the bulk composition of the host does not play a vital role in the formation of SCDs. The only essential features of the host seem to be the presence of reactive organic matter and sulphur, to assure the formation and stability of disseminated sulphide mineralization, and an adequate permeability, to allow entry of ore-forming solutions. Because accumulations of organic matter and sulphides indicate rather specific sedimentary environments (e.g., anoxic), however, there is an indirect link between host lithologies and their eventual mineralization. For example, all favourable host sediments for the type deposits described above were formed and diagenetically modified in subaqueous environments (marine, or saline lacustrine; endnote 6), as opposed to subaerial continental red bed environments (Lombard, 1956).

The favourable, anoxic, S-rich character of the sediment is initiated by stagnant subaqueous conditions, in which anaerobic, sulphate-reducing bacteria (e.g., *Desulphovibrio*) proliferate. Within a newly deposited sediment rich in organic matter and depleted in oxygen, anaerobic bacteria feed on the organic debris, obtain their required oxygen from sulphate, and produce HS<sup>-</sup> and H<sub>2</sub>S as part of their normal metabolic activity. Typically, these soluble sulphides then react immediately with the abundant iron available in most sediments (e.g., in mafic clasts) to form primitive syndiagenetic iron sulphides (e.g., hydrotroilite, mackinawite and greigite), which soon evolve to pyrite during early diagenesis (Berner, 1971; Trudinger, 1976; Trudinger and Williams, 1982, Trudinger *et al.*, 1985).

The initial stock of sulphate for biogenic reduction is generally provided from the basin water, by diffusion downward into the basin sediment, by a prior syndiagenetic accumulation of evaporitic sulphate minerals (typically gypsum/anhydrite), and/or by addition of dissolved sulphate within the ore-forming solution itself. The sulphur isotope compositions of the resulting sulphides are generally light and highly variable ( $\delta^{34}\text{S} = -25 \pm 20$  per mil; Ohmoto *et al.*, 1990) and indicate marine or saline lacustrine sources for the original sulphate, followed by biogenic sulphate reduction.

End member environments which readily provide these fetid syndiagenetic conditions include: 1) sabkha-type evaporitic sediments, 2) deep water "Black Sea-type" basin muds, 3) black deltaic muds, and 4) shallow "coal basin" waters. Sabkha environments, which typically produce thin layers of microbial-laminated carbonate (e.g., algal laminae alternating with thin layers of fine carbonate sand), are especially anoxic because of the

high activity of anaerobic microbes immediately beneath the subaerial sabkha sur-

face (Kendall, 1984).

Deep anoxic muds of large meromictic

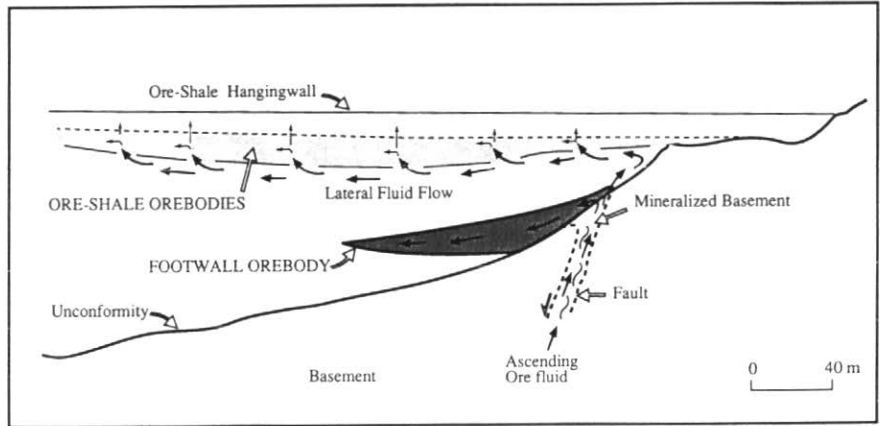


Figure 9 Interpretative diagram depicting the mineralization process for Footwall and Ore-shale orebodies in the Zambian copperbelt. Modified after Annelis (1989).

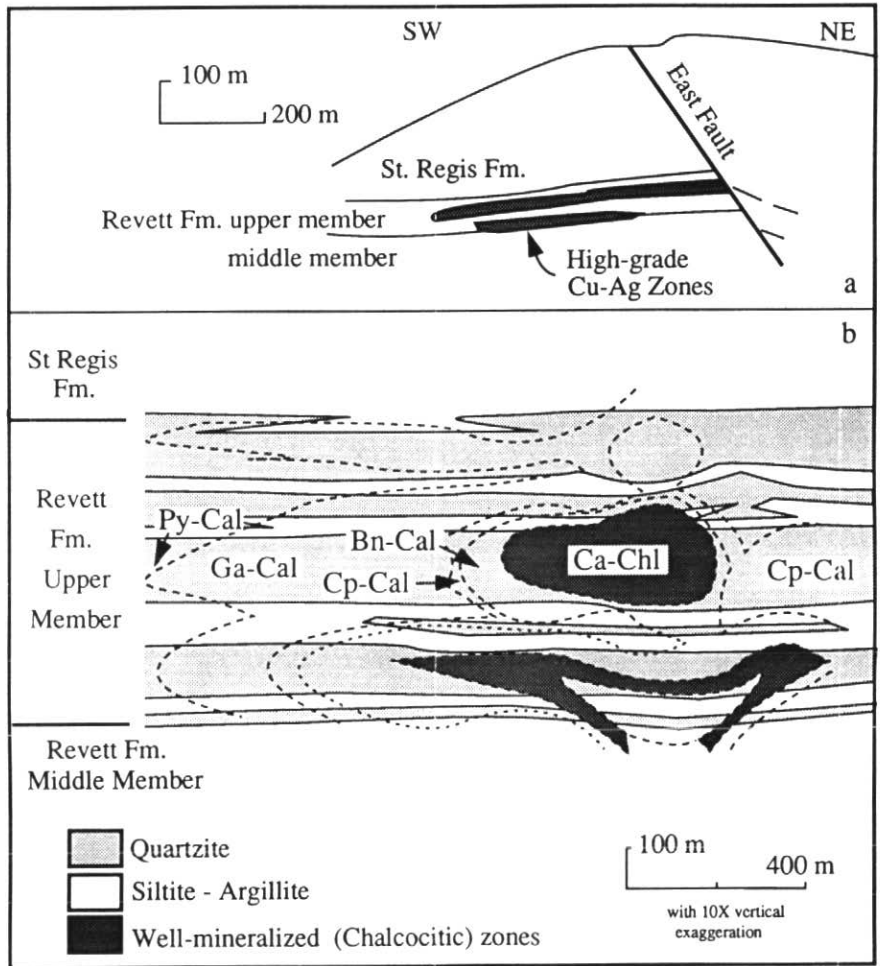


Figure 10 Stratiform copper-silver mineralization preferentially located in relatively permeable quartzitic strata of the upper Revett Formation at Spar Lake (Troy), Montana. (a) Ore-forming fluids may have risen along cross-cutting faults and spread laterally along the originally more permeable strata. (b) Mineralized zones have hydraulic configurations zoned laterally outward, passing from copper-rich (Cc-Chl = chalcocite-chlorite; Bn-Cal = bornite-calcite; Cp-Cal = chalcopyrite-calcite) to lead-rich (Ga-Cal = galena-calcite) toward originally pyritic zones (Py-Cal = pyrite-calcite). Mineralization is restricted in the less permeable silty units. Modified after Hayes and Balla (1986).



water bodies (e.g., the Black Sea) form as a result of "permanently" stagnant, deep-basin water (endnote 7) (Degens and Stoffers, 1980). Organic debris, constantly settling from the biologically active, near-surface, photic zone of the basin water, assures depletion of oxygen in deep waters and bottom muds, and provides food for sulphate-reducing bacteria at these deep levels. Similarly, deltaic muds may retain anoxic conditions if they contain an abundance of organic debris to nourish bacteria. Initially, aerobic bacteria would consume any available oxygen in the sediment, and then give way to their anaerobic cousins, which thrive in the subsequent anoxic conditions.

Shallow coal basin environments may also retain anoxic bottom conditions beneath a thin layer of brackish water if atmospheric oxygen is effectively excluded, for example, beneath a floating organic mat. Although coal beds do commonly contain important minor quantities of metals (Coveney and Martin, 1983), they are not known to host SCDs, probably because of other deficiencies, such as inadequate supplies of metals.

#### Overprinted Base Metal Mineralization

Once formed, a still porous, sulphide-rich, grey bed is prepared for the second event in the formation of SCDs, i.e., the precipitation of introduced metals. Because most base metal sulphides are less soluble than iron sulphides, introduced metals should replace earlier, syngenetic, iron sulphide minerals. This replacement process is commonly confirmed texturally (e.g., as partial or complete pseudomorphic replacements of pyrite by base metal sulphides, described above).

Also, as predictable from the well-known Schuermann series, copper precipitates closest to the redoxcline because it is the least soluble or most sulphophile of the common base metal sulphides, whereas the more soluble metals, such as Pb, Zn and Cd, are carried downstream along the influx path and precipitate farther from the redoxcline. This zoning of metals is represented by an orderly array of sulphide minerals, with chalcocite (the most insoluble) generally most abundant close to the redoxcline. Bornite and chalcocopyrite are progressively more abundant downstream, toward the unmineralized pyritic host strata. The lead, zinc and cadmium sulphides occur still farther downstream than the cupriferous sulphides. Pseudomorphs of copper-rich sulphides after individual disseminated pyrite grains, after pyritic framboidal structures, and after pyritic nodules, confirm the progressive replacement process.

In addition to the replacement of iron sulphide, base metals may also obtain their reactant sulphur by replacement of sulphate minerals. Pseudomorphs after sulphate nodules and blade-shaped gypsum/anhydrite grains may result. The apparent single-stage replacement of sulphate grains by sulphides

requires an intervening reduction of sulphate, thought to involve sulphate-reducing bacteria in very early diagenetic muds (Chartrand and Brown, 1985). Annels (1974, 1989) described ore-stage replacements of nodular sulphate by a quartz-carbonate assemblage, and suggested that sulphide could also be produced by high-temperature, inorganic reduction of sulphate involving a hydrocarbon reactant (endnote 8).

Another potential source of local sulphide could be an H<sub>2</sub>S-rich hydrocarbon gas accumulating in and below fine-grained, grey bed, cap rocks (Jowett, 1989; Peryt, 1989). The H<sub>2</sub>S could be produced by bacterial reduction of sulphate derived from associated marine beds (Gablina, 1981), or at a more mature stage of diagenesis when organic matter in deep basin sediments would undergo thermal maturation and release organically complexed sulphur to pore solutions. The second scenario may apply where multiple sources of sulphur are suggested (Hoy and Ohmoto, 1989; Branam and Ripley, 1990; Jowett *et al.*, 1991).

Bacterial sulphate reduction in the uppermost levels of bottom muds rich in organic matter could conceivably result in direct precipitation of base metals arriving from an underlying source, without an intermediate stage of iron sulphide deposition (Haynes, 1986). This concept has not been confirmed by textural observations. On closer reflection, it would require a very specific metal influx rate, such that metals reach the host sediment at the same rate as sulphide is produced biogenically. If metals are introduced at a slower rate, precursor iron sulphides should form; if introduced at a faster rate, the metals could be toxic to bacteria in the pore water. Bacteria could undoubtedly survive temporary periods of excess dissolved metal by self-encapsulation in protective membranes (Margulis *et al.*, 1983), but it is questionable whether they could proliferate under these conditions. The preferred model, based largely on observed replacement textures and metal zoning, is one in which the normally abundant iron of labile sediments reacts with biogenic sulphide to precipitate initial iron sulphides, which in turn would cause precipitation of subsequently introduced base metals.

#### SHORT-RANGE TRANSPORT OF METALS INTO HOST ROCKS

The zoned, overprinted character of base metals in SCDs indicates that copper and other ore stage metals (endnote 9) were typically introduced from the footwall red beds, i.e., from a reservoir of oxidized pore fluid on the hematitic side of the redoxcline. Just as conditions in the host rock are particularly favourable for the deposition of cupriferous sulphides, the pore fluids in hematitic red beds are unfavourable for sulphide mineral stabilities. The red bed chemistry and permeability are suited instead for

the solution and transport of base metals (see Eh-pH fields of Fig. 11).

What were the chemical and physical characteristics of the ore solutions, and what is the probable range of metal concentrations in such solutions? The *ambient temperatures were probably low*, in most cases below 100°C. Supporting evidence for a low temperature environment includes: 1) the lack of obvious hydrothermal alteration, 2) the preservation of delicate molecular structures in hydrocarbons (e.g., kerogens which readily break down at moderate temperatures), and 3) the formation and preservation of low-temperature sulphides (e.g., orthorhombic chalcocite, which is unstable at temperatures higher than 103°C; djurleite (Cu<sub>1.96</sub>S), which is unstable at temperatures higher than 93°C; and S-rich bornites, which are unstable at temperatures higher than ~75°C). The lack of significant metamorphism at several deposits (see descriptions above) enables us to observe many of these temperature-sensitive features. The ore solution should be *oxidizing* due to equilibration of the fluid with ferric oxide (hematite and/or goethite) in the red beds. *Neutral to moderately acid pHs* would be dictated by buffering with carbonates and common silicate minerals (e.g., K-feldspar, illite, kaolinite).

Although fresh water is incapable of dissolving appreciable amounts of most metals (except under exceptionally acid conditions), low-temperature brines can have important base metal solubilities due to metal-chloride complexing under the near-neutral oxidizing conditions prevalent in hematitic red beds (Helgeson, 1964; Brown, 1971; Rose, 1976, 1989; Sverjensky, 1987; Reed and Haynes, 1990). Such brines are commonly encountered as evolved pore fluids in deep sedimentary basins (D.E. White, 1968).

Stability diagrams for these predicted conditions (Fig. 11) suggest that dissolved copper may attain 1-100 ppm levels in the pores of red beds, and similar solubilities may be found for related metals such as silver, lead, zinc and cobalt (Rose, 1989). Like copper, high-silver solubilities also require highly oxidizing, acid conditions. Thus, suitable conditions for significant base metal solubilities in red bed equilibrated brines contrast sharply with the much lower solubilities possible in pyritic, carbonaceous grey beds, where copper would precipitate immediately upon encountering iron sulphides.

Dissolved metals in a red bed aquifer may cross the redoxcline into grey beds by *infiltration* (or advection, i.e., bodily transport of dissolved species in an aqueous solution), or *diffusion* (migration of dissolved metals down a chemical potential gradient within a stationary aqueous solution). Infiltration along aquifers and across the redoxcline would probably be the dominant process for metal transport over substantial distances within porous red beds, along possible pre-

ore faults (identified or assumed), and into the adjacent grey beds. Diffusion may be significant for short distances, especially if a steep chemical potential gradient is maintained by continuous precipitation of highly insoluble cupriforous sulphides within the grey beds. Diffusion may be the only recourse where infiltration is seriously impeded across aquicludes (endnote 10). Using best estimates for rates of infiltration and diffusion for the White Pine deposit, Brown (1971) showed that either mechanism alone, or infiltration gradually superceded by diffusion as the sediment became more impermeable under compaction, could deposit the quantities of copper observed in the basal Nonesuch Shale beds within approximately  $10^6$  years.

The physical entry of metals into generally fine-grained host sediment may be perpendicular, oblique or parallel to bedding (or to a subparallel redoxcline). In the case of diffusion, the direction is probably perpendicular or subperpendicular to bedding because the strongest chemical potential gradient would be maintained in that direction by continuous deposition and depletion of ore metals downstream from the footwall source of metals. An essentially perpendicular influx of metals would seem to apply at White Pine and for the Kupferschiefer, where zones of metals are peneconformable to bedding across very broad areas.

Oblique and bedding-parallel flow of ore solutions is also possible, especially within aquifers. At Redstone, a largely horizontal influx of ore solutions is envisaged across intercalated red bed and carbonate units (Ruelle, 1982; Jefferson, 1983; Chartrand, 1986). According to the principle of hydraulic refraction, however, local flow could have been subperpendicular to bedding within the relatively compact and slightly permeable carbonate host beds.

In the case of C-shaped, "roll front" configurations (e.g., Troy), flow should be mainly parallel to bedding, following the best aquifers in the overall ore section. Solutions forming C-shaped configurations could also reach preferred local aquifers along coarse-grained units pinching out from distal stratigraphic sections.

For more complex host-sediment configurations (e.g., rapid facies variations, pinch-outs against basement highs, and sediments wrapped around bioherms, such as found in Zambia), local flow directions should be determined largely by the best available porosities and channelways encountered by solutions generally attempting to migrate under compressive or buoyant forces.

#### METAL SOURCES AND LONG-RANGE TRANSPORT OF METALS TO THE REDOXCLINE

The deposit-scale features of the SCD model require complementary basin-scale sources of metals, and appropriate means of

transporting metals from these sources to the redoxcline at the red bed/grey bed interface. To date, our ideas on plausible metal sources and long-range metal transport are more conceptual than definitive. Nevertheless, many aspects can be reasonably well inferred from our knowledge of strata hosting and underlying SCDs, from the general behaviour of metals and fluid flow in sedimentary basins, and from the post-sedimentary/pre-metamorphic timing of mineralization.

As mentioned above, the concept of a distant magmatic hydrothermal (telethermal) source of metals was rejected for the African Copperbelt deposits when the underlying granites were identified as basement and not intrusive into SCD host rocks. Similarly, in most other examples of SCD mineralization, a direct linkage with magmatic activity has not been substantiated. The most attractive alternative sources appear to be related, instead, to the formation and evolution of the host basins and to the dominant

lithologies within these basins.

#### Basin-Scale Circulation

Whatever the ultimate source of metals, the ore-forming solution must be brought to the base of the redoxcline in large volumes with significant metal contents. In the absence of a magmatic mechanism, or a compressive tectonic event, the only conceivable driving forces behind this long-range circulation of ore solutions are related to the force of gravity and the heat of deep lithospheric or asthenospheric material.

For example, pore fluids may be driven from a sedimentary pile by simple *compaction* under the accumulating load of overlying beds. Water-escape structures formed during early compaction are now recognized in abundance in red beds underlying many SCDs, and in certain cases these structures may have been formed by escaping pore waters that had already become saline and metalliferous (Lustwerk and Wassermann,

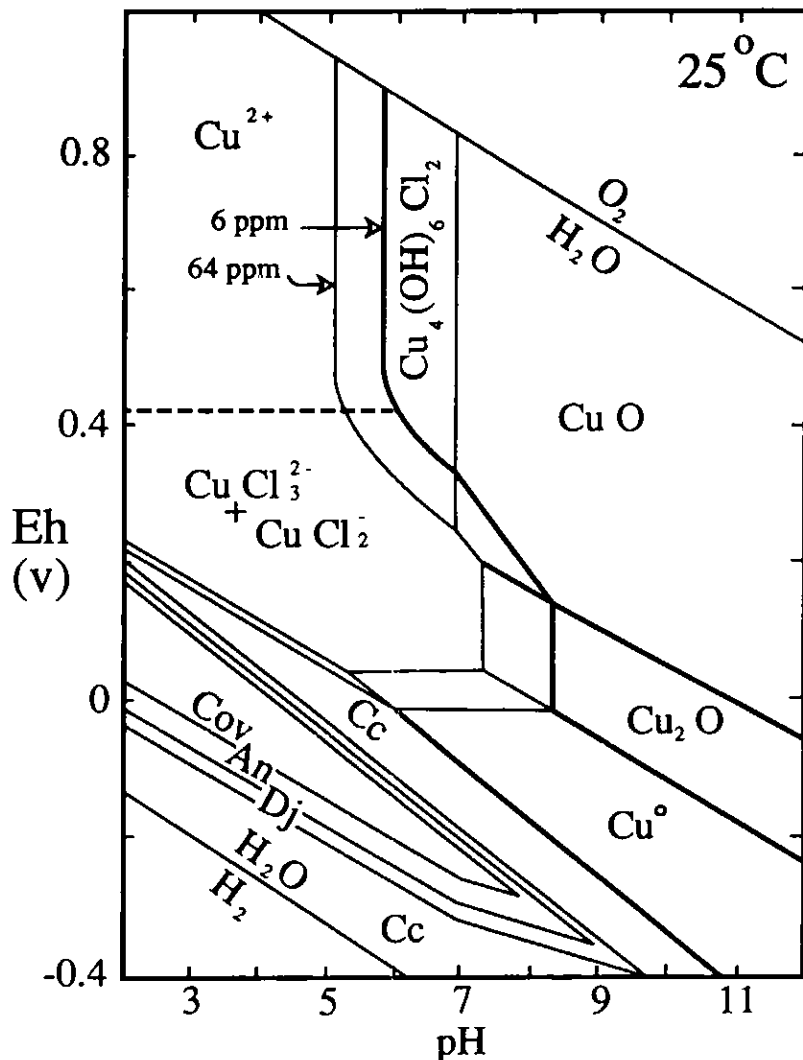


Figure 11 Contoured solubilities of copper chloride complexes for a low-temperature aqueous solution containing 0.5 molar chloride. High copper solubilities (exceeding 64 ppm) may occur in modestly oxidizing, neutral to acidic solutions. From Rose (1989).

1989). In effect, these de-watering structures provide a multitude of channelways that increase across-bedding permeabilities, especially in fine- to medium-grained sediments.

Widespread basin compaction alone is unlikely to have been an adequate transport mechanism, however, because it would generate a single pass of a widely dispersed ore solution beneath the overlying grey beds, and would hence require a large quantity of solution, or a very metal-rich solution, or both, to form major ore deposits. Nevertheless, this difficulty might be circumvented if there were abundant water-escape structures in limited areas so as to focus pore solutions beneath reasonably local portions of the overlying grey beds, *i.e.*, into basin areas corresponding to the lateral dimensions of SCD deposits.

Basin waters may also be driven toward surface by *hydraulic heads* of recharge water in distant highland areas (*cf.* recent models for Mississippi Valley-type deposits; see Garven, 1985; Leach and Rowan, 1986). In this case, the volume of water circulated could be orders of magnitude larger than that generated by compaction alone. White (1971) suggested that, at White Pine, recharge took place along topographically elevated Copper Harbor-equivalent beds on the north limb of the Lake Superior syncline. Alternatively, the hydrologic flow of subsurface fluids in the Keweenaw basin may have been induced by reversals of tectonic movement along basin boundary faults.

The ore solution could also be *thermally recycled*. After depositing metals on the reduced side of the redoxcline, an initially warm pore fluid could cool and descend again within widespread convection cells to be reheated and recharged with metals (Jowett, 1986a). Being dense, the ore-forming brine should not lose its identity by mixing with near-surface waters, according to the density stratification model of D.E. White (1968).

This recycling mechanism requires accumulations or additions of heat deep within the basin, however. Plausible sources of essentially internal heat could include: 1) *accumulated crustal and mantle heat*, including abnormal heat in areas of high heat flow; 2) the *heat of known or assumed footwall intrusive/extrusive bodies*, including latent heat of rapidly buried volcanic rocks; and 3) the *heat of rising hot salt diapirs*. In the last case, the evaporite could play a dual role, in providing heat and in assuring high salinities in pore solutions at depth.

The typically fine-grained host strata of SCDs and their associated evaporite beds could also help to circulate solutions within the underlying permeable red beds by acting both as an aquiclude and as a *thermal insulator*, as in the sedex lead-zinc model (Lydon, 1983). Under these circumstances, the heat accumulating beneath the grey beds and evaporites could eventually overcome the

inherent stability of dense brines typically found at deep stratigraphic levels of large sedimentary basins (Hanor, 1979). A 2 molar (~10 wt.%) NaCl solution becomes buoyant relative to overlying cool fresh water at ~130°C, and a 3 molar solution becomes buoyant at ~180°C. Provided that adequate sources of heat can be postulated, a deep brine could be destabilized thermally and rising plumes of heated ore fluid could result.

Considering the common association of SCDs with zones of intra-cratonic, continental rifting, *upwellings of mantle or deep crustal material* may be likely sources of heat, creating steep geothermal gradients beneath grey bed hosts. During the extensional tectonics associated with rifting, abnormal amounts of heat should reach upper crustal levels due to the broad upward flexure of hot asthenosphere, possibly accompanied by local intrusions and extrusions of magma along the rifting crust. If this heat could be confined beneath aquicludes (such as the fine-grained grey beds and evaporites typically associated with SCDs), it could warm and recirculate brines for extended periods of time within the coarse-grained red beds underlying the redoxcline.

Finally, the occurrence of aquicludes in the stratigraphic section can result in *overpressuring* (geopressuring) of pore solutions in underlying aquifers (Hanor, 1979). During active sediment accumulation in a basin, the escape of pore fluids beneath an aquiclude may be retarded such that the pore pressures in the sediment exceed hydrostatic levels and approach lithostatic pressures. At the same time, the pore waters in sediments immediately above the aquiclude may be able to escape freely toward surface and so have only hydrostatic pressures. If the aquiclude is suddenly fractured (tectonically?), solutions in the previously confined pores beneath the aquiclude may escape rapidly across the aquiclude toward surface. Cathles (1981) postulated that a basin may generate repeated expulsions of warm pore fluids in this manner. The tectonic fracturing of the basin strata could be related to syn-sedimentary fault-block movements in the rift basin.

In this context, the grey beds overlying a red bed aquifer could have one or more roles in the overall SCD-forming environment: in creating a *receptive environment for metal deposition*, in acting as an *effective thermal insulator* to assure heated ore solutions both at the source and during long-range transport of metals to the redoxcline, and in forming *overpressured pore solutions* that may rise rapidly and repeatedly to higher levels in the basin. The second and third roles should be familiar to readers acquainted with modern models for sedex mineralization.

#### Sources of Metals

Presuming that adequate mechanisms of

long-range metal transport exist, as outlined above, we still need to identify plausible ultimate sources of metals. The principal proposals include: 1) the *leaching of metals from footwall sediments (or basement)* by evolved (warm, saline) basin waters, 2) the formation of metalliferous *metamorphic ore brines* during deep burial of footwall strata, and 3) the formation of *magmatic-affiliated ore brines* in intra-cratonic rift environments. Each of these possibilities is supported by particular features observed in one or more major SCD deposits (see below).

*Leaching of metals* from deep basin or basement was suggested by Davidson (1965) and advocated by Wedepohl *et al.* (1978). The latter concluded from lead isotopic ratios that the ore metals of the Kupferschiefer were ultimately derived from Precambrian basement rocks or their detrital equivalents in the overlying Rotliegende red beds. Rose (oral communication, 1986) also suggested, reasonably so, that most SCDs could be formed by leaching as little as 5 ppm copper from the large volume of red beds that typically underlie SCDs.

In many cases, the footwall red beds contain an abundance of labile clasts in which copper is a significant trace constituent (Zielinski *et al.*, 1983; Walker, 1989; see Table 2). Copper may also adhere temporarily to clay particles and to amorphous or poorly crystalline goethitic iron oxides typically formed during the diagenetic reddening of sediments that produces red beds. Copper from all these red bed sources could be released to form stable soluble metal-chloride complexes in the co-existing warm saline pore water. Lustwerk and Rose (1983) found that, although most footwall red beds at Redstone contain an expected 20 ppm or more Cu, some samples contained essentially no copper and would seem, therefore, to have been leached of most of their original trace copper contents.

In addition to red bed sources of copper, anomalous amounts of copper are common in other footwall lithostratigraphic units. For example, at White Pine, the Portage Lake Volcanics underlying the red beds of the Copper Harbor Conglomerate contain the famous Keweenaw native copper deposits, some 30-120 km along strike to the northeast of White Pine (W.S. White, 1968; Weege and Pollack, 1972), and minor amounts of native copper mineralization also occur in patchy chloritic zones within the Copper Harbor Conglomerate directly beneath the White Pine mine area (Ensign *et al.*, 1968). Is this copper mineralization contemporaneous with the stratigraphically higher White Pine deposit, and were both deposits derived from a common copper source? If so, what common source? Or was the native copper mineralization a protore for subsequent solution and redeposition as a sulphide-dominated SCD in the basal Nonesuch Shale?

There is little doubt of some genetic rela-

**Table 2** Copper content of common labile minerals in first-cycle sandstones (from Walker, 1989).

Mineral	Number of Analyzed Samples	Average Cu Content (ppm)
Pyroxene	90	120
Biotite	660	86
Amphibole	40	78
Magnetite	250	76
Plagioclase	108	62
Potassium feldspar	70	1-20

tionship between the native metal and sulphide deposits, and, indeed, the entire Keweenaw district, including White Pine, is known as a single copper-silver province extending over much of the Lake Superior district (Turneaure, 1955). Certainly, sufficient amounts of metals for the complete Keweenaw district could be found in the very thick, widespread, rift-filling clastic and volcanic units underlying both the native copper and White Pine areas. Similarly, at Redstone, the regional strata underlying and enclosing the Transition Zone deposits have even been labelled the "copper cycle" because of high background copper contents (Aitken *et al.*, 1973), and, thus, adequate sources of footwall copper undoubtedly existed there as well.

In another leaching model, Renfro (1974) proposed that SCDs could form during the intense *evaporative pumping* that is characteristic of coastal (or inland) sabkha environments. Under hot, arid climatic conditions, two contrasting types of water would meet beneath an actively forming sabkha sediment (commonly a microbial-laminated carbonate): 1) oxidized, acidic, meteoric water which had leached metals from buried continental red beds inland of the sabkha platform, and 2) alkaline, sulphate-bearing seawater from offshore. Biogenic sulphate reduction in the fetid sabkha carbonate units would deposit influxed metals. While this concept does account for the noted affiliation of some SCDs with sabkha sediments, it does not explain the overprinting of a single cupriferous zone across a stack of interbedded red bed/sabkha units, as seen at Redstone. Secondly, it does not allow for mineralization except during evaporitic pumping at an active sabkha surface, and is thus incompatible with textural interpretations of mineralization overprinted after a significant degree of early diagenesis. Thirdly, it does not account for SCDs not associated with sabkha-type sediments. Finally, it cannot readily explain the leaching and transport of metals from the proposed red bed source because the water arriving from the continental direction should be essentially fresh meteoric water and, thus, incapable of dissolving significant quantities of metals.

Low-temperature remobilization of background quantities of metals from distant

*down-dip portions of the ore horizon* itself has also been suggested for White Pine and possibly other SCD deposits. Could progressive deep burial of extensive carbonaceous, pyritic, grey beds release significant amounts of metals (e.g., the 100-200 ppm Cu common to pyritic portions of the Nonesuch Shale) and form local ore-grade concentrations in up-dip portions of the same strata? This concept has never been substantiated, nor is it likely to be. In the presence of a pyritic precipitant and abundant reductants, base metals are notoriously insoluble and, hence, very immobile.

A number of researchers have proposed, however, that *metamorphogenic ore solutions* could form during advanced metamorphic dehydration of suitable footwall units. Not only could large amounts of water be released during prograde metamorphism from the greenschist and amphibolite facies, but those waters should also be rich in chloride. They could, therefore, leach significant amounts of metals from large volumes of rocks during metamorphism. From the combined studies of Stoiber and Davidson (1959), Jolly (1974), and Livnat *et al.* (1983), the immense volumes of deeply buried mafic volcanic rocks should produce metamorphic brines capable of forming native copper ores along up-dip aquifers in the Keweenaw district, as well as combined sulphide/native copper ores at the base of the Nonesuch Shale in the White Pine area.

Finally, the common association of SCDs with rift settings (see, for example, Sawkins, 1982, 1990; Brown, 1984; Jowett, 1986b, 1989; Maynard, 1991) suggests a *possible deep magmatic source of metals (and/or heat)*. Annels (1984, 1989) advocated a deep magmatic source for the Chambishi ores in Zambia, based mainly on lithostratigraphic and structural evidence for a rift setting, the occurrence of high-level, sill-like intrusions at Chambishi, numerous indications of high-temperature ore deposition (estimated to exceed 250°C), and a complex (magmatic?) suite of trace metals (Ni, Ag, Au, As, Mo, U, W, Bi and Te) associated with these Cu-Co ores.

At White Pine, the Keweenaw rift is filled by an extraordinarily thick sequence of mafic volcanic flows (possibly exceeding 20 km in thickness; Sutcliffe, 1991) intercalated with red beds and felsic volcanic units at upper

stratigraphic levels. Could this immense amount of pre-Nonesuch Shale magmatic activity have terminated with the generation of late magmatic ore-forming fluids, which then circulated upward to the base of the Nonesuch Shale? The chief arguments against this concept are the simple, low-temperature, ore mineralogy and the lack of expected high-temperature, hydrothermal, alteration zones. But if high-temperature magmatic fluids are ruled out, there should still have been a large amount of latent magmatic heat and an anomalously high geothermal gradient in this rift zone during the early history of the Nonesuch Shale. Thus, prior magmatic activity in the rift could have contributed indirectly to the subsequent formation of the White Pine deposit by thermal circulation of ore-forming solutions of deep magmatic or other origins.

Although many SCDs show evidence of at least some footwall igneous activity, the proposal of a direct magmatic "telethermal" (in the sense of the Lindgren-Graton school) source of metals remains highly tentative and will probably continue so until demonstrated otherwise. The attractive linkage between SCD genesis and the anomalous heat associated with continental rifting (see above), however, can be extended to the global scale, as described below.

#### AFFILIATIONS OF SCDs WITH CONTINENTAL RIFT BASINS AND RIFT BASIN HEAT

Anomalously high geothermal gradients typically form in continental rift zones in response to hot asthenosphere rising into the thinned crust. Magmas normally form under depressurized conditions within the rift, and the accompanying heat could play a prominent role in generating and circulating SCD-forming fluids at higher levels in the crust.

The suggested linkage of SCDs with rift basin environments has a parallel in the rather recent recognition that sediment-hosted submarine exhalative (sedex) Pb-Zn deposits are closely associated with continental rift environments (Large, 1980, 1983). Borrowing the sedex model, Brown (1981, 1984) suggested a so-called pene-exhalative SCD model in which hot, copper-dominant, metalliferous solutions would ascend along syn-sedimentary faults and "exhale", not onto the rift basin floor, but into major aquifer units such as the footwall red beds of SCD deposits. The red bed reservoir of cooling ore solution could then mineralize the basal grey beds across the redoxcline, as described earlier. As with a direct magmatic source of metals, the pene-exhalative concept can be disputed due to the lack of evidence for high-temperature alteration and the simple, low-temperature, ore mineral assemblages in most SCDs. But could the fluids have cooled and attained an oxidizing nature in the extensive footwall red beds? Have we overlooked subtle low-temperature

alteration patterns? Has the polymetallic character of most SCDs been too often ignored?

Further hints of possible linkages between SCDs and continental rift environments can be seen in the many allusions to this affiliation in recent publications on SCD deposits. Rift basin controls for several prominent SCD occurrences were reviewed by both Jowett (1989) and Maiden (1989). As well, several interpretations of SCD mineralization in the recent GAC volume on stratiform copper deposits (Boyle *et al.*, 1989) refer to continental rift settings for SCDs. Various recent texts relating mineral deposits to tectonic environments (e.g., Sawkins, 1990) also associate the origins of SCDs with processes operating in rift environments.

#### AFFILIATIONS OF SCDs WITH HOT, ARID ENVIRONMENTS

Kirkham (1989) proposed a still more specific environmental control over SCD genesis. First, he recalled that SCDs are commonly associated with both red beds and evaporitic units (Davidson, 1965; Renfro, 1974). Evaporitic units in the stratigraphic section assure that the basin pore solutions would be saline and capable of extracting metals from the red beds. Next, from plots of the global occurrence of SCDs and evaporite deposits through geologic time, Kirkham demonstrated that SCDs and evaporites have formed predominantly under hot, arid to semi-arid climates, which on a global scale occur mainly within 20-30° of the contemporaneous paleoequator (see Fig. 12, for the Permian period, for example). It is also pertinent that, like evaporites, the formation of red bed sediments is also favoured by hot, arid paleoclimates (Walker, 1989; Glennie, 1989). This spatial association of SCDs with

evaporites, red beds, and hot, arid/semi-arid paleoenvironments focusses particular attention on basins formed at these low latitudes, and, thus, a knowledge of paleopoles and paleoclimates could be a useful exploration guide for locating new SCD deposits.

Finally, it is probably not coincidental that many SCDs are associated jointly with 1) evaporites and red beds formed at low paleolatitudes, and 2) continental or re-entrant rift environments. The restricted marine or lacustrine environments typical of such rift basins are, in fact, excellent for evaporite formation if located in hot, arid environments. Although all SCDs cannot be forced into this mold, it is perhaps appropriate from our current understanding of SCDs to suggest that the exceptions are hybrid deposits, and that a general genetic model can be built upon the conjunction of continental rifts with hot, arid climates.

#### DISTRIBUTION OF SCDs THROUGH GEOLOGIC TIME

Several analyses have been made to determine if there is a preferred distribution of SCD mineralization through geologic time (e.g., Meyer, 1981, 1988; Sawkins, 1983; Kirkham, 1989). Because the total population of significant occurrences is rather limited, it can be expected that most conclusions are correspondingly tentative. For example, considering only those examples mentioned in this paper, there is a clear abundance of SCD mineralization in the Late Proterozoic (e.g., Central African Copperbelt, White Pine, Redstone, Troy, Adelaidean) and again in the Permian (Kupferschiefer, Creta). There are also, however, deposits in the Early to Middle Proterozoic (Udokan, Kona Dolomite) and in the Early Paleozoic (Aynak, Timna). A particularly large number

of mostly minor SCD occurrences is found in red beds of the Carboniferous, but, aside from the large Dzhuzkazgan deposit of the CIS, most are of little economic significance, and many, in fact, would be more accurately classified as continental red bed deposits rather than as SCDs (endnote 1).

The most obvious temporal control on SCDs appears to be their restriction to sedimentary basins formed after the Earth's atmosphere became oxygen-rich, *i.e.*, after the "oxyatmversion" event of about 2.45-2.22 billion years ago (Roscoe, 1973, 1991). This observation should not be surprising, since the low-temperature transport of copper in basin brines is favoured under oxidizing conditions.

#### CONCLUSIONS

##### A General Genetic Model

The overprint model described here consists essentially of: a footwall source (basin-filling red bed and/or volcanic strata, metamorphosed basement rocks, or deep magmatic fluids) which releases metals to a warm or even hot brine; an oxidized aquifer (footwall red beds) and/or deep-reaching rift basin faults, which allow circulation of the metaliferous brine across thermal and/or hydraulic gradients; and a fine-grained, reducing, S-rich, host rock on the hangingwall side of a chemically distinct redoxcline.

The source lithology need not be similar for all SCDs, for it can be argued that, given sufficient volume, the amount of metal required can be found in almost any lithology. Nevertheless, the most probable sources would seem to be those commonly associated with a continental rift basin setting, *i.e.*, red beds which typically underlie SCDs, with or without bimodal intrusions and/or extrusions which are commonly present at deep levels in major rift basins.

The metals (essentially copper, with minor to major amounts of silver, lead, zinc, cobalt, molybdenum, etc.) are carried as metal-chloride complexes in the warm, oxidized, chloride-rich, sulphide-poor brines. The aqueous component may be evolved connate, recharge, metamorphic and/or magmatic water, and the dissolved salts, attaining molar concentrations, are presumably produced by partial or complete equilibration with the lithologies encountered at the elevated temperatures found deep within a rift basin setting. The oxidized character of the solutions would be assured, at least within the footwall red beds, by equilibration with hematite.

Basin-scale circulation of ore solutions may be induced by the anomalous crustal heat in the rift setting, possibly aided by the heat of local high level intrusions of hot magmas or salt diapirs or by latent heat from rapidly buried extrusions. Rapid burial of sediments could also release important amounts of heat below the montmorillonite-illite transition. Gravity-driven convection is

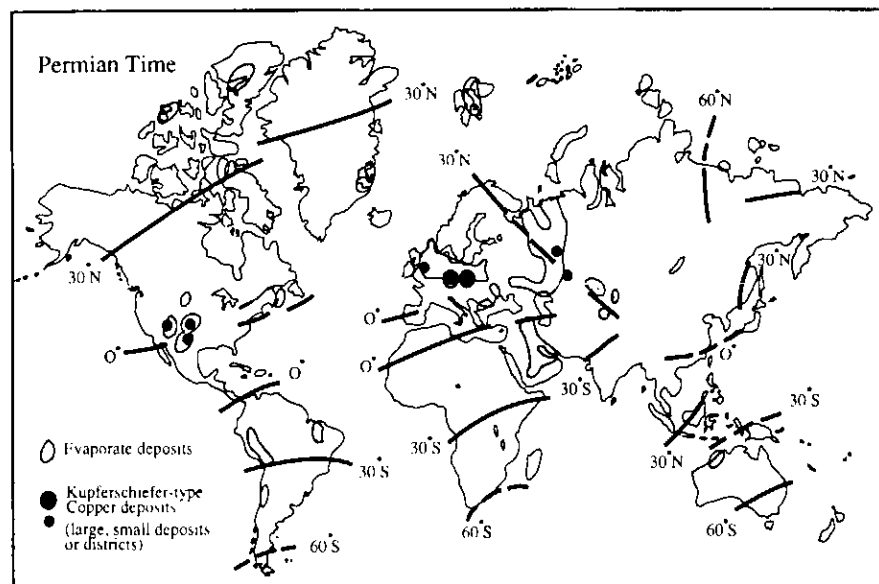


Figure 12 Global correlation of major and minor sediment-hosted stratiform copper deposits with low paleolatitudes and evaporite deposits for Permian time. From Kirkham (1989).



also conceivable. In all cases, sufficient solution could recirculate between source rocks and host rocks to explain the amounts of metal deposited. Although a recently deposited, unconsolidated sediment may be the most common host, some deposits may form after lithification, probably coincident with late structural and thermal perturbations within the basin.

At the depositional site, the host rock must be physically and chemically suitable for metal emplacement. First, the host sediment should be permeable to ore solutions by infiltration and/or locally by diffusion. The route of local metal influx is indicated by the local configuration and zoning of the overprinted mineralization. In general, laterally broad, subvertically stacked zones of Cu → Pb, Zn, Cd sulphide mineralization signal local entry across the base of the sub-horizontal host beds, whereas C-shaped configurations suggest entry along the more permeable beds of the stratigraphic section.

Second, the host should initially contain sufficient sulphur to form ore-grade, disseminated mineralization over economically interesting stratigraphic thicknesses. Note that introduced, overprinted mineralization may occupy only a fraction of the grey beds suitable for mineralization. Also, the pre-ore sulphur may be concentrated initially as fine-grained, disseminated pyrite (or as more primitive iron sulphides) and/or as sulphates (gypsum/anhydrite) which can be reduced to sulphide before or while ore metals enter the host sediment. Reduced sulphur could also be provided by hydrocarbons migrating through the host strata. Sulphur may also be introduced as dissolved sulphate within the ore-forming brine itself.

Sulphate reduction generally results from bacterial activity in the newly deposited, organic matter-rich muds, most commonly forming syndiagenetic iron sulphide from dissolved sulphate diffusing from overlying basin water into the uppermost levels of carbonaceous basin sediments. Evaporitic sulphates such as gypsum or anhydrite may also be attacked by bacteria to produce sulphides in recently formed sabkha-type sediments. Alternatively, sulphate may be reduced inorganically by high temperature reactions involving hydrocarbons.

The precipitation of metals in previously prepared (sulphide-rich) hosts is essentially a chemical event which takes place across a well-defined redoxcline. Metals are typically deposited immediately upon encountering any previously formed, more soluble sulphide. This reaction results in sulphide replacement textures and in the local overprinting of disseminated metal sulphides on extensive, commonly pyritic, host rocks. The cupriferous zone is formed upstream of other metals (Pb, Zn, Cd, etc.) and an unmineralized pyritic zone extends downstream (into the hangingwall) throughout the remainder of the favourable host rock.

The most common lithologies hosting SCDs are 1) fine-grained, pyritic, carbonaceous, clastic units (especially dark grey or greenish mudstones, siltstones, sandstones) directly overlying coarse-grained red beds, and 2) microbial-laminated, sabkha carbonates, *i.e.*, carbonaceous evaporitic carbonate units (especially formed in marginal basins or sabkhas) also deposited over red beds. The red bed to grey bed transition commonly marks a basin-wide transition from continental to marine environments.

Finally, there is a notable affiliation of SCDs with sediments formed in hot arid climates. The common occurrence of evaporites in the host section, especially sabkha-type beds, indicates low rainfall and long periods of high evaporation. "Black shales" also signal the deposition of anoxic clastic units requiring no annual inversions of basin water as typically occur in lakes and seas at high latitudes. The formation of thick, rift-type red beds is also favoured by rare torrential rains carrying coarse debris into rift basins from adjacent horst blocks. Kirkham (1989) emphasized that SCD mineralization is closely affiliated with evaporites which are commonly located within 30° of the paleoequator.

#### Metallotects for SCDs

In this concluding section, a list of major geological guides to SCD mineralization (metallotects) is presented, beginning with the global scale and terminating with local, map-scale features. The principal question is: given the analysis of favourable SCD environments described above, what geologic features could guide an exploration geologist toward the discovery of new sediment-hosted stratiform copper deposits? The principal features appear to be:

1) Until demonstrated otherwise, SCDs appear to be restricted to sedimentary basins formed after the oxyatmoverion of about 2.4-2.2 Ga. They should not be expected in Archean basins.

2) Based on the common association of SCDs with rift basins, the tectonic setting should be one of extensional tectonics, particularly intra-cratonic rifts or the trailing edges of separated continental blocks. While this criterion is not (yet) universally supported, the continental rift environment has become a recognized crustal setting for most major SCDs, just as these rifts have themselves become recognized as a significant metallogenic feature of the Earth's crust.

3) The recognition of a strong correlation between SCDs, evaporites and red beds formed at low paleolatitudes (within 20-30° of paleoequator positions) adds a second global-scale guide to favourable SCD environments. Particular attention should be given, therefore, to continental rifting that occurred at low paleolatitudes.

4) More locally, the rift basin should be a well-developed crustal feature containing thick sequences of red beds and possibly showing evidence of bimodal extrusive (or even intrusive) igneous activity.

5) The oxidized footwall strata must be overlain or intercalated with grey bed units of at least mineable thicknesses and of broad lateral extent. Mineralization is typically located in the basal grey beds immediately above (or laterally adjacent to) the readily visible redoxcline transitional from red bed units.

6) The grey beds should have abundant original sulphides (and/or organic constituents to assure *in situ* reduction of sulphates) to precipitate influxed metals. Sabkha- and marginal-basin carbonates and pyritic "black shale" horizons are the most common hosts.

7) The stratigraphic column may include extensive evaporitic units. Note, however, that evaporites may be absent due to local meteoric leaching.

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#### ENDNOTES

<sup>1</sup> Also known as "Kupferschiefer-type" mineralization. This type-locality name is avoided here, however, because the Kupferschiefer deposits are not adequately representative of the wide variation in characteristics among generally recognized members of the SCD family.

<sup>2</sup> Discontinuous (lenticular) stratabound continental sandstone-hosted (red bed) copper deposits are not discussed in this paper.

<sup>3</sup> The term "diagenetic model" has been used for this new concept, but should be discouraged because it suggests that the mineralization resulted from a reconstitution of elements already present in the host sediment and does not adequately recognize the importance of an influx of metals from (distant?) outside sources. The expression "diagenetic timing", however, is appropriate.

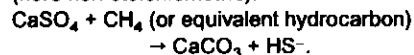
<sup>4</sup> For simplicity, the term "downstream" is used in a general sense to indicate the direction of flow of solutions, metals and ore-forming constituents toward and across the redoxcline into reduced strata, whether or not the flow is, in fact, across or along stratigraphy.

<sup>5</sup> Where the mineralized rock does not presently contain carbonaceous matter, it may have lost organic matter during diagenesis, or the required reductant was transitory, as in the case of a fluid hydrocarbon.

<sup>6</sup> The distinction between marine and lacustrine environments is still generally inconclusive for many deposits, and usage of the term "marine" should not imply exclusion of large scale, saline, lacustrine sediments.

<sup>7</sup> Holomictic lakes, in which the water overturns periodically, do not retain permanently anoxic deep-basin waters. In northern climates, for example, overturning of fresh water bodies commonly results from cooling of upper level lake water as winter approaches.

<sup>8</sup> High temperature (~300°C; Trudinger and Williams, 1982) inorganic reduction with hydrocarbons (e.g., methane) is the only known alternative to low temperature biogenic activity for the reduction of sulphate to sulphide. The inorganic sulphate → sulphide reaction is kinetically immobile at low temperatures and only occurs spontaneously at temperatures far above those expected during the formation of most SCDs. Annels (1974, 1989) considered this inorganic mechanism to have been important in Zambian strata where he expected ore solutions to have been hot, and where he observed anhydrite nodules replaced by a quartz-calcite assemblage, apparently by the reaction (here non-stoichiometric):



<sup>9</sup> While carbonaceous sediments themselves may contain "anomalous amounts" of many trace metals (e.g., Cu, Pb, Zn, Cd, Ag, Co, Ni, Mo, As, Hg, U, Th, Bi, Cr, V), these amounts are typically anomalous only by comparison with non-carbonaceous lithologies. In fact, the majority of ppm-level metals in grey beds may be attributed to metals carried by bonding to organic matter (Rose, 1989).

<sup>10</sup> The evaluation of various mechanisms controlling the diffusion of metals, salts and water molecules across very fine-grained sediments is a highly complex but important aspect of infiltration-diffusion studies. The interested reader should refer to papers on "semi-permeable membranes", "ultra-infiltration" and "salt-sieving" (e.g. White, 1965).

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