Ore Deposit Models #14. Volcanogenic Massive Sulphide Deposits Part 2: Genetic Models

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Introduction

Since Oftedahl (1958) revived the idea that volcanogenic massive sulphide (VMS) deposits were formed on the sea floor, more articles have been published on the genesis of VMS deposits than any other deposit type. This article is intended as a summary of current opinions on the genesis of VMS deposits, rather than a review of the progression of scientific thought by which these opinions have been reached (see reviews by Sangster, 1972; Sangster and Scott, 1976; Solomon, 1976; Franklin *et al.*, 1981 for this background). Current ideas on the topic are highly influenced by studies of hydrothermal systems and sulphide accumulations at modern submarine spreading centres. Following this research trend, this articles places emphasis on these studies of modern sea-floor sulphide accumulations and their applicability to an understanding of the genesis of ancient VMS deposits.

A genetic model for a mineral deposit type is an attempt to give a rational and consistent explanation of the characteristics of the deposit type in terms of physical and chemical processes. Characteristics of VMS deposits were described in Part 1 of this article (Lydon, 1984a). Discussion here will be limited to those processes and related geological aspects that have been of the most concern in the recent literature and include: (i) processes of sulphide accumulation which form the massive sulphide lens and which in turn control the morphology, texture, mineralogical zonation, etc. of the sulphide body; (ii) processes in the immediate footwall of proximal VMS deposits that give rise to the hydrothermal alteration pipe and stockwork ore; (iii) reasons for fluid flow in the hydrothermal system, which in turn

help explain the geological setting and distribution of VMS deposits; and (iv) origin and nature of the hydrothermal fluids, which in turn determine the source of the ore constituents and the chemistry of the sulphide ores.

Accumulation of sulphides

Historical perspective. The debates of the 1950s and 1960s resulted in a consensus that VMS deposits were formed on the sea floor by the accumulation of sulphides precipitated from hydrothermal fluids. The main evidence in support of this opinion came from observations on well-preserved proximal-type deposits (*i.e.*, those deposits which formed immediately around a hydrothermal vent, Plimer, 1978; Franklin *et al.*, 1981), and, as illustrated by figure 9 and figure 2 of Lydon (1984a), includes:
(i) The presence of sedimentary structures within the massive sulphide lens of which graded-bedding, cross-bedding, and the intercalation of fragmental with laminated sulphide lithologies are the most convincing. The descriptive papers in Ishihara (1974) illustrate classic examples from the Kuroko deposits of Japan.
(ii) The stratigraphically upper contact of the massive sulphide lens is sharp and conformable with hanging wall rocks.
(iii) The massive sulphide lens is commonly laterally continuous with an horizon of chemical and/or clastic metalliferous sediment. Examples are the Key Tuffite of the Matagami area (Roberts, 1975) and the C contact exhalative sediment of the Noranda area (Gibson *et al.*, 1983), which are both pyritic tuffaceous cherts.
(iv) The massive sulphide lens is commonly rooted in a discordant footwall hydrothermal alteration pipe, interpreted to represent the uppermost part of the hydrothermal conduit. The upward termination of the conduit at the horizon of concordant sulphides indicates that ore-forming hydrothermal activity was confined to the time interval between deposition of the footwall rocks and the deposition of the hanging wall rocks.

Sato (1972) postulated that a hydrothermal solution discharged into seawater would behave in one of three ways, depending on its initial temperature and density and its subsequent degree of mixing with seawater (Figure 1):
Type I or highly saline hydrothermal solutions whose densities are greater than cold seawater at all degrees of mixing.
Type II solutions that, although initially less dense than seawater, at some stage in the mixing process pass through a density maximum which is greater than that of cold seawater.
Type III solutions that are initially less dense than cold seawater and which remain buoyant at all degrees of mixing.

Following the prevalent perception of the time that any deposition on the sea floor must follow the laws of sedimentary super-

position, Sato (1972) suggested that each of his three ore solution types would give rise to deposits with a characteristic morphology. Type I solutions would give rise to brine pool deposits that characteristically have a tabular or sheet-like morphology (see figure 9 for morphology types). Type II ore solutions would give rise to deposits with a conical or mound-like morphology, which is typical of proximal deposits. Precipitates from his Type III ore solutions would be dispersed by the buoyant plume and would only form a veneer of large lateral extent from the plume fall-out.

Despite the large volume of literature on the genesis of VMS deposits, relatively few papers have addressed the problem of the mechanisms of sulphide accumulation. Prior to the discovery of the mound-chimney sulphide deposits on the East Pacific Rise (EPR) (Francheteau *et al.*, 1979; Hekinian *et al.*, 1980), mechanisms by which sulphides accumulated were most frequently visualized as analogous to those for the Red Sea brine pool metalliferous sediments (Miller *et al.*, 1966; Degens and Ross, 1969) or were based on the buoyancy models of Sato (1972), whereby sulphides were precipitated from the hydrothermal fluids after discharge from the vent and accumulated as heavy gelatinous muds (Sangster, 1972). For example, Hutchinson and Searle (1971) interpreted the VMS deposits of Cyprus to be brine pool muds, whereas it appears to be implicit in genetic models of the Japanese Kuroko deposits by Kajiwara (1973), Sato (1973), Large (1977) and Urabe and Sato (1978) that the sulphides accumulated as fallout from hydrothermal plumes of Sato's (1972) Type II hydrothermal solutions. Experimental studies of buoyant hydrothermal plumes (Turner and Gustafson, 1978; Solomon and Walshe, 1979a) also carried with them the assumption that sulphides accumulated from plume fall-back and formed mounds of sulphide gel around the vent (Solomon and Walshe, 1979a).

In contrast, studies of modern mound-chimney deposits emphasize that sulphides in proximal deposits accumulate as rigid edifices. It is not being suggested that studies of the modern sulphide deposits by themselves have completely revolutionized geological thought on the accumulation of VMS deposits, because many of the current concepts, including the rigidity of proximal sulphide lenses, were previously widely appreciated by at least the mineral exploration community (*e.g.*, Simmons *et al.*, 1973; Spence, 1975). What these studies on modern sulphide deposits have accomplished is to provide, by documentation and observation in a natural experimental laboratory, the scientific confirmation of processes that already existed as concepts in the minds of exploration geologists, and to bring new details of the phenomena and processes, together with the concepts, into the mainstream of scientific literature.
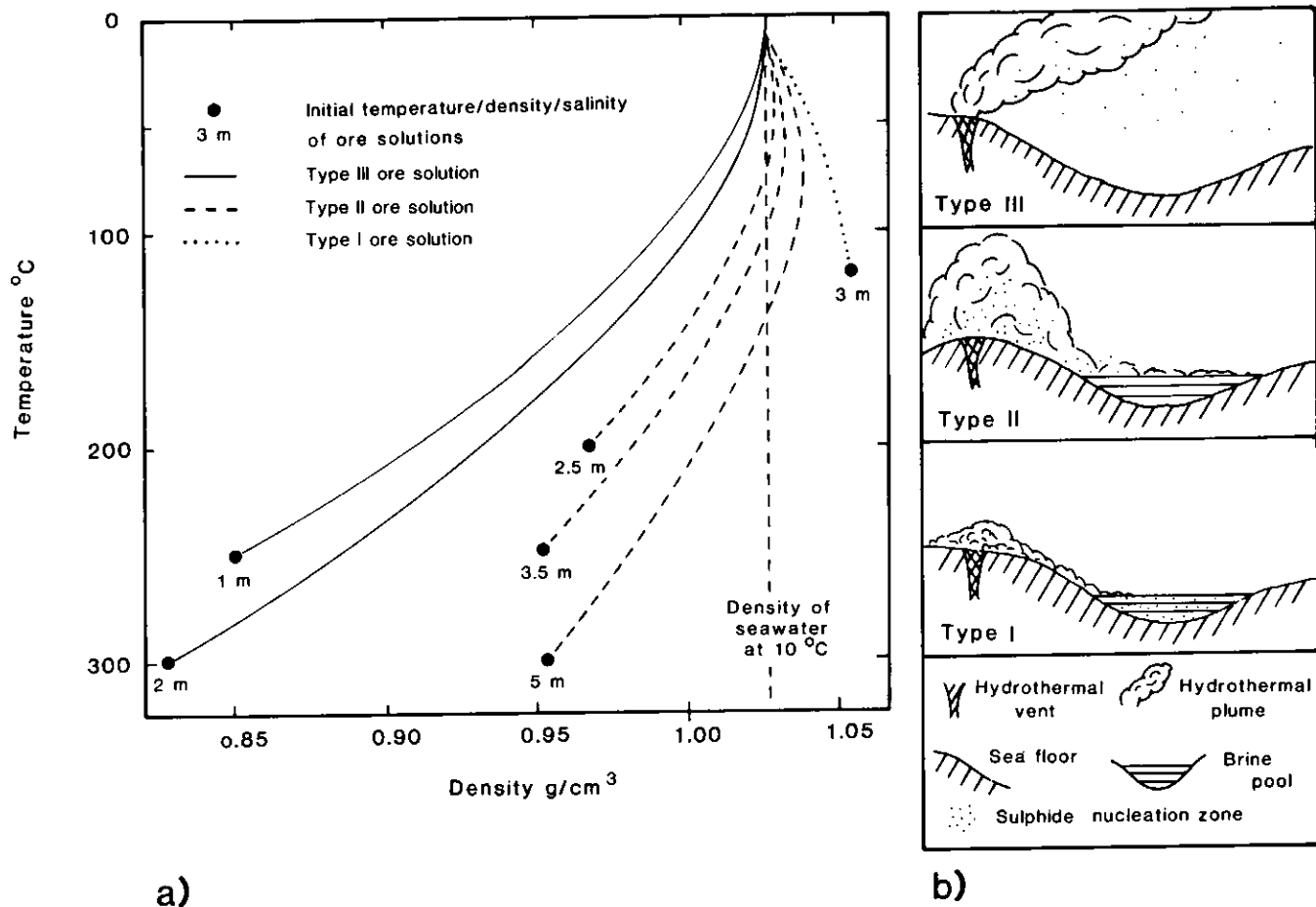
a)

b)

Figure 1 (a) (upper left) *Density-temperature relationships of hot NaCl solutions mixed with seawater at 10 °C (after Sato, 1972) illustrating the definition of Sato's (1972) three types of hydrothermal solutions.*
(b) (upper right) *Schematic representation of the buoyancy behaviour of and sulphide precipitation from Sato's (1972) three types of hydrothermal solutions.*

Table 1 The compositions (in mg·kg⁻¹) of some natural metalliferous hydrothermal solutions compared with modern seawater. References: *Salton Sea:* Helgeson (1968); *Red Sea:* Shanks and Bischoff (1977); *Kuroko:* Pisutha-Arnond and Ohmoto (1983) (maximum concentrations in fluid inclusions); *East Pacific Rise (EPR),* *Seawater:* Janecky and Seyfried (1984) (EPR, 21°N, average); *Southern Juan de Fuca Ridge (SJFR):* Von Damm and Bischoff (1987) (SJFR, Plume vent).

	Salton Sea	Red Sea	Kuroko	EPR	SJFR	Seawater
Temp (°C)	340	60	320	350	224	2
pH	5.5	5.5	4.5	3.5	3.2	8.0
Na	53000	92600	17500	9800	18300	10790
K	16500	1870	5000	1000	2020	395
Ca	28800	5150	4400	860	3860	413
Mg	10	764	510	< 1	< 1	1280
SiO_2	400	60	?	960	1400	10
Cl	155000	156000	40400	17335	38640	19355
SO_4	10	840	?	< 1	-50	2745
H_2S	30	?	?	221	63	< 1
ΣCO_2	500	140	8800	282	?	103
Fe	2000	81	6	100	1045	< 1
Mn	1370	82	?	34	197	< 1
Zn	500	5.4	3	7	59	< 1
Cu	3	0.3	5	1	< 0.1	< 1
Pb	80	?	3	< 1	?	< 1
Ba	250	0.9	?	13	?	< 1

Modern submarine hydrothermal activity. Aspects of modern sulphide deposits at submarine spreading centres have been reviewed by Rona (1984) and Franklin (1986). As of 1984, with only about 1% of the 50,000 km length of oceanic ridges having been explored at the detail necessary to detect hydrothermal activity, about 60 hydrothermal fields had been discovered (Rona, 1984). The majority of known sites are in the Eastern Pacific, where most vents occur in the median valley of the ridge crest and the hydrothermal fluids emanate directly from a volcanic (mainly basaltic) substrate. At some sites, notably those of the Guaymas Basin in the Gulf of California, Middle Valley at the northern end of the Juan de Fuca Ridge and the Escanaba Trough adjacent to

1. Initiation of hydrothermal discharge and chimney growth

2. Collapse of old chimney and growth of new chimneys

3. Growth of mound by accumulation of chimney talus and defocussing of hydrothermal discharge

4. Decrease of mound permeability and intramound sulphide precipitation, replacement and remobilization

LEGEND:

Chimney talus

Sulphide infilling, replacement and/or remobilization

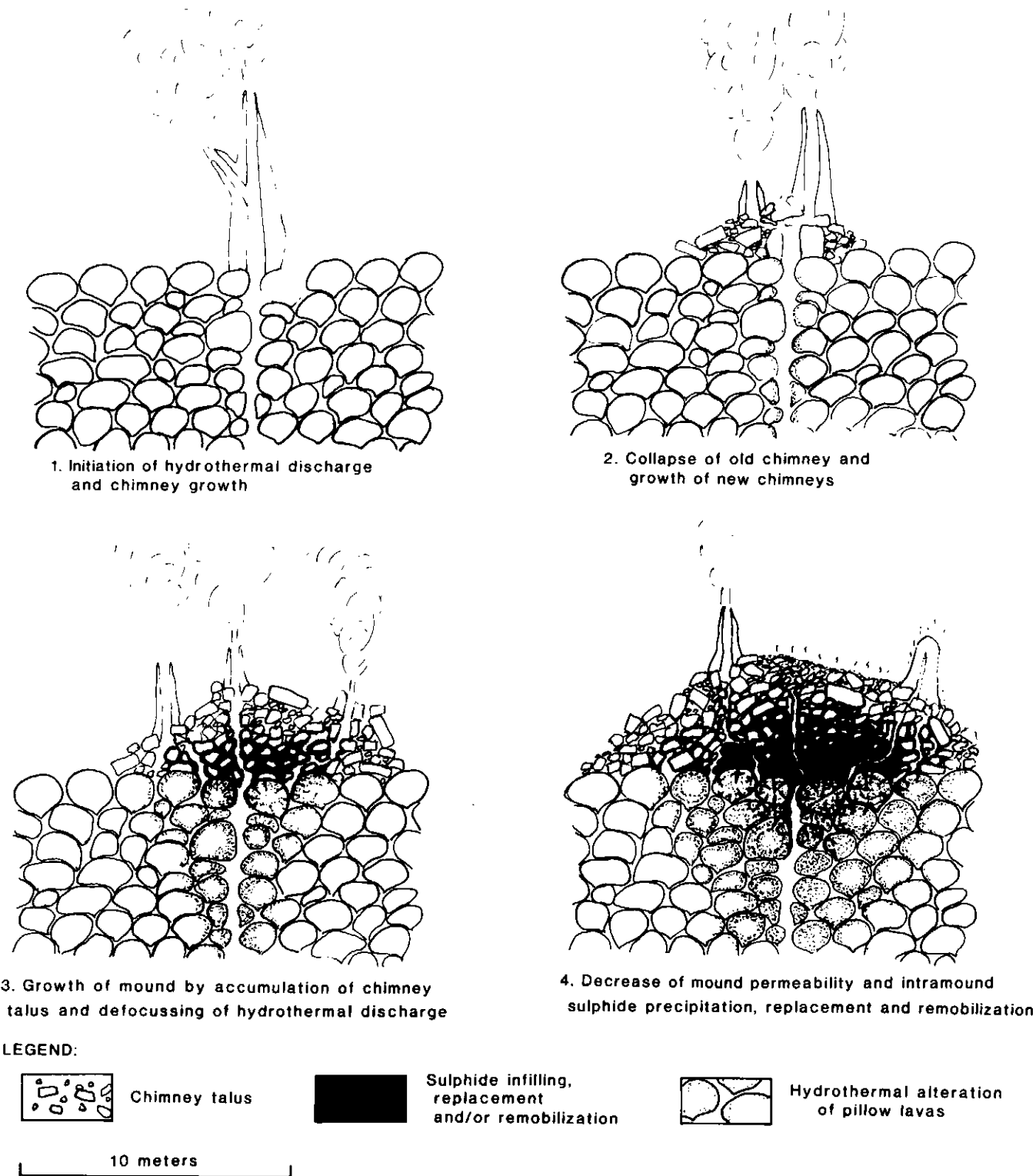Hydrothermal alteration of pillow lavas

10 meters

Figure 2 Schematic representation of the growth of a modern mound-chimney sulphide deposit. (Based on the descriptions by Hekinian and Foquet, 1985; Goldfarb et al., 1983; Jonasson et al., 1986).

the Gorda Ridge, hydrothermal discharge is through a sediment cover as much as 500 m thick. In addition to the median valley of the ridge crest, seamounts have also proved to be a favourable setting for high temperature hydrothermal discharge and sulphide deposition (Lonsdale et al., 1982; Hekinian and Fouquet, 1985; CASM, 1985).

The temperature of the hydrothermal fluids ranges from 400°C at some vents to just a few degrees above ambient seawater at others. The highest temperature fluids are considered to be pristine hydrothermal fluids (i.e., fluids which have equilibrated with reservoir rocks at pressure-temperature conditions close to the maximum values of the hydrothermal system), whereas those at lower temperatures are usually mixtures of pristine hydrothermal fluid and pore water (mainly seawater) that has become entrained into the hydrothermal conduit in the subsurface. The hydrothermal fluids (Table 1) have salinities up to twice that of modern seawater (3.2 wt.% NaCl), and, as predicted by Sato (1972) for his Type III solutions, form buoyant plumes on discharge. The Red Sea brines, with salinities seven times that of seawater, discharge at temperatures of over 200°C (Schoell, 1976), and, like Sato's (1972) Type I solutions, collect as brine pools in the deepest parts of the axial valley. Recent evaluation (Turner and Campbell, 1987) of the problem addressed by Sato (1972) suggests that all high temperature (>300°C) fluids will be initially buoyant in seawater, but if their salinities are greater than about 7 wt.% NaCl will show reversing buoyancy on mixing with seawater. This means that all the vent fluids of the Eastern Pacific that have been studied to date are of Sato's Type III solutions, but visual observations (Lonsdale et al., 1982) and data from fluid inclusions (Delaney and Cosens, 1982; Stakes and Vanko, 1986) suggest that fluids with salinities high enough to form reversing plumes like Sato's Type II solutions do in fact exist in the modern oceanic crust.

Active sulphide deposition on the ocean floor is confined to high temperature (>200°C but more commonly >300°C) vents. Sulphide deposits formed from buoyant hydrothermal fluids are characterized by sulphide chimneys that rise from a basal mound of sulphides (Figure 2). The most-studied area to date is the East Pacific Rise (EPR) at 21°N (Spiess et al., 1980), where a typical mound-chimney combination has been estimated to contain about 1000 tonnes of metal (Rona, 1984) or about 2000 tonnes of sulphide. At 13°N on EPR, more than 80 separate sulphide deposits have been recognized along a 20 km segment of the axial graben, but it has been estimated that collectively they do not contain more than 20,000 tonnes of sulphide (Hekinian and Fouquet, 1985). Perhaps the largest mound-chimney deposit discovered to date occurs in the TAG hydrothermal field on the Mid-Atlantic Ridge

at 26°N, where a single deposit has been estimated to contain 4.5 million tonnes of sulphide (Rona et al., 1986). Current unpublished speculation is that sulphide deposits of sediment-covered segments of ridges at Middle Valley (Davis et al., 1987) and Escanaba Trough (Zierenberg et al., 1986) may be significantly larger. Deposits of the mound-chimney type have only been grab-sampled, which does not allow an accurate estimate of their ore grades (see Rona, 1984). The largest sulphide deposits known at present on the modern ocean floor are the metalliferous sediments of the Red Sea brine pools. The Atlantis II deposit consists of about 100 million tonnes of sulphide/oxide sediment containing 2% Zn, 0.4% Cu, 90 g·t⁻¹ Ag, 0.8 g·t⁻¹ Au (Blissenbach and Nawab, 1982) and about 0.1% Pb (Lowell and Rona, 1985).

Perhaps the most unexpected discovery with regard to modern submarine hydrothermal vents is the associated prolific biota and their food-chain based on chemosynthetic

bacteria (Grassle, 1983; Jannasch, 1983). Megafauna of the hydrothermal vents are characterized by vestimentiferan tube-worms and giant clams in the Eastern Pacific (Desbruyeres and Laubier, 1983), by shrimps and anemones in the mid-Atlantic (Rona et al., 1986), and by large gastropods in the Manus Basin, Papua New Guinea (Both et al., 1986). Traces of these megafauna, notably tube casts of vestimentifera, are preserved as textural relicts in chimney sulphides.

Accumulation of modern sulphide chimneys and mounds. Growth of a sulphide chimney (Figure 3) is initiated by the precipitation of anhydrite in the narrow vertical zone of high thermal gradient between the buoyant hydrothermal fluid and surrounding cold seawater (Haymon, 1983). Anhydrite precipitates from seawater at this thermal interface because its solubility decreases with increasing temperature. Modern seawater precipitates anhydrite when it is heated (without evaporation) to 130°C (Haymon and
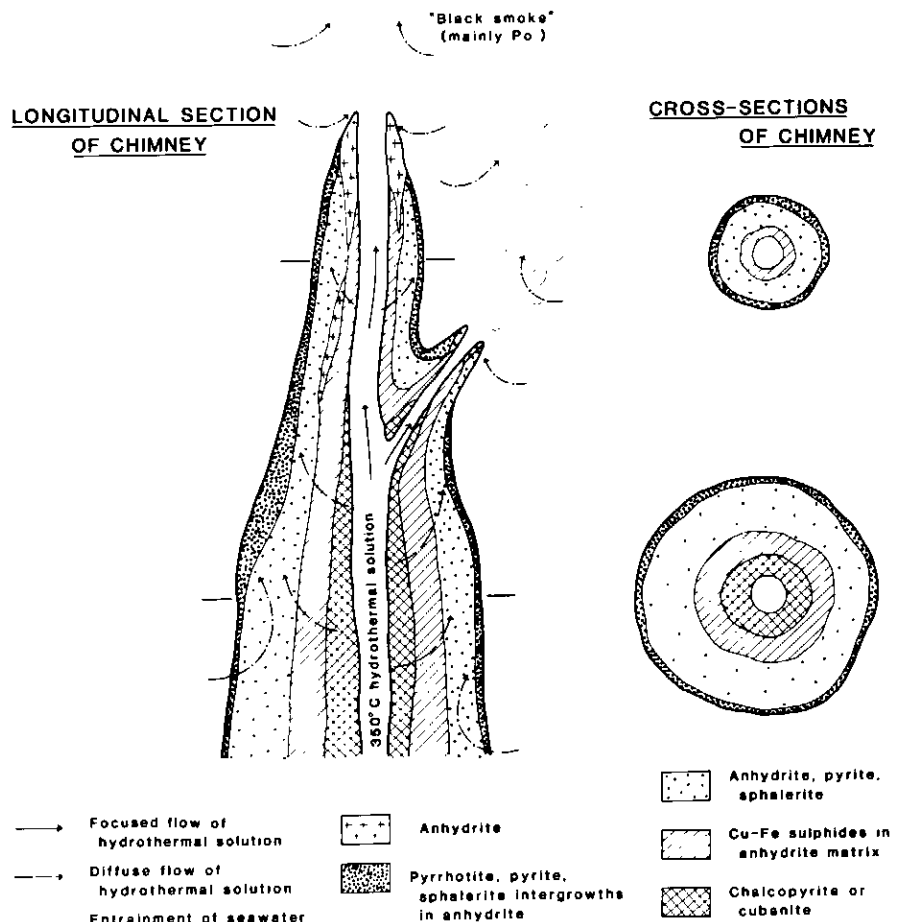

Figure 3 *Characteristics of mineral zonation of a modern "black smoker" sulphide chimney. (After Haymon and Kastner, 1981; Haymon, 1983).*

Kastner, 1981). The porous wall or collar of anhydrite that forms at the thermal interface continues to grow upward around the hydrothermal jet for as long as high temperature flow is sustained. Although some calcium may be contributed by the hydrothermal fluids, sulphur isotope analyses indicate that sulphate of the anhydrite is derived from seawater (Styrt et al., 1981).

Most of the hydrothermal fluid flows upward along the central conduit of the anhydrite collar and discharges into the surrounding seawater. However, a small proportion (< 1%) of the hydrothermal fluid flows through the porous anhydrite wall. In doing so, the fluid descends a steep physicochemical gradient from high temperature (> 300°C), acidic (~ pH 3.5), reduced (H_2S > > SO_4) conditions on the inside of the wall, to conditions approaching the low temperature (2°C), alkaline (~ pH 7.8), oxidized (SO_4 > > H_2S) nature of ambient seawater on the outside of the wall. Minerals precipitated from the hydrothermal fluid due to this physicochemical gradient are trapped in the pore spaces of the anhydrite wall, so that, as the anhydrite collar on top of the chimney extends upward, the walls of the lower part of the chimney gradually thicken by the precipitation of sulphides in the interior portions and anhydrite in the exterior portions. A mature chimney structure has a characteristic concentric zonation from chalcopyrite (± isocubanite ± pyrrhotite) on the inside, via a zone dominated by pyrite, sphalerite and wurtzite in an anhydrite matrix, to an exterior zone of anhydrite with minor sulphides, amorphous silica, barite, magnesium hydroxysulphate-hydrate (MHSH), and talc (Spiess et al., 1980; Haymon and Kastner, 1981; Haymon, 1983; Oudin, 1981, 1983; Goldfarb et al., 1983; Tivey and Delaney, 1986).

Mathematical modelling indicates that the zonation is predominantly due to the temperature decrease across the wall, rather than to a chemical gradient, and that the cooling is probably brought about more by mixing of the hydrothermal fluid with cold seawater than by conductive heat exchange (Janecky and Seyfried, 1984; Bowers et al., 1985). In detail, sulphide precipitation in the chimney walls is a complex process, in which reversals of the pressure gradient across the wall, due to the dynamics of high velocity flow within an irregular hydrothermal conduit, plays a dominant role in causing oscillation of the thermal and chemical profiles (Tivey, 1986). Mineral precipitation in any small volume of chimney wall may therefore consist of intermixed mineral assemblages that collectively reflect a wide range of physicochemical conditions. In the longer term, mineral zone boundaries migrate outward with time, so that lower temperature assemblages are replaced by higher temperature assemblages (Haymon, 1983; Goldfarb et al., 1983). Anhydrite is eventually dissolved by the sulphate-free hydrothermal

fluids in the interior zones of the chimneys, and by cold seawater in the exterior zones as the chimney cools (Haymon and Kastner, 1981), leaving a sulphide assemblage in which opaline silica is the dominant gangue mineral (Oudin, 1983; Tivey and Delaney, 1986).

The vertical growth of a sulphide chimney has been measured at 8 cm per day (Hekinian et al., 1983) and has been estimated to be as much as 30 cm per day (Goldfarb et al., 1983). Ultimately the chimney becomes mechanically unstable and collapses to form a mound of chimney talus, on which chimney growth begins again (Figure 2). Repetition of this process eventually gives rise to a mound which completely covers the original vent orifice and causes diversion of hydrothermal flow to multiple discharge sites on the mound. Individual chimneys formed at the different discharge points evolve at different rates, and on the same mound "white smokers", "snowballs" and "dead" chimneys may co-exist with the "black smoker" vents (Speiss et al., 1980). "White smokers", which precipitate white clouds of barite, silica and minor pyrite (Rona, 1984), are chimneys in which hydrothermal precipitation has sealed open orifices and decreased the permeability of the chimney walls. The lower flux of hydrothermal fluid through these low permeability walls allows more intra-chimney cooling by seawater entrainment and by heat conduction, so that fluid exit temperatures in the range 100-330°C are lower than those of black smoker chimneys. In the eastern Pacific at least, these less active chimneys sustain the most prolific growth of tube worms, which may become so densely packed as to form a spherical mass of white tubes ("snowballs"). Pseudomorphs of the worm tubes are a common textural feature in chimney sulphides (Speiss et al., 1980; Haymon and Kastner, 1981; Oudin and Constantinou, 1984).

The growth of the basal mound (Figure 2), which can be envisaged as the coalescence of adjacent chimneys into larger edifices (Goldfarb et al., 1983; Hekinian and Fouquet, 1985; Tivey and Delaney, 1986; Alt et al., 1987), is fundamentally due to the same principles which govern chimney growth. The major difference is that in mound growth a horizontal blanket of chimney talus carries out the function of the vertical porous anhydrite wall in chimney growth. Defocussing of hydrothermal discharge by the mound of chimney talus over the original vent orifice promotes advective/conductive cooling and sulphide/silica precipitation in the outer part of the mound (Tivey and Delaney, 1986). These hydrothermal precipitates decrease the permeability of the mound in much the same way as a white smoker chimney evolves, and by constricting fluid channelways through cementation of chimney talus forms a surface crust of low permeability (Goldfarb et al., 1983). In constraining fluid escape, the low-permeability

crust causes the high-temperature fluids to circulate within the mound, which leads to the upward migration of isotherms within the mound and consequently to the replacement of previous sulphides by higher temperature mineral assemblages. The creation of new fluid channelways by hydraulic, seismic or tectonic fracturing of the mound in turn initiates the growth of new chimneys, and mound growth continues by repetition of the process for as long as high temperature hydrothermal flow is sustained.

This model for mound growth is supported by several lines of evidence. The fact that high temperature hydrothermal fluids circulate within the mound can be demonstrated by rupturing of the mound crust (Goldfarb et al., 1983), or breaking open inactive chimneys (Hekinian et al., 1983; Von Damm et al., 1985), which results in the immediate emission of "black smoker" fluids. That cooling of some of the hydrothermal fluid takes place within the mound is indicated by the differences in exit temperatures of fluids at different orifices of the same mound. That sulphide precipitation takes place within the mound-chimney edifice is demonstrated by the loss of metal sulphide components in the effluent from white smokers that co-exist on the same mound as black smokers.

Seafloor sulphides are chemically very unstable in modern seawater, and rapidly oxidize upon cessation of hydrothermal activity to form ochreous deposits dominated by hydrated iron oxides (Hekinian et al., 1980; Haymon and Kastner, 1981; Alt et al., 1987). Unless the sulphide deposits are quickly covered by a volcanic flow, they are unlikely to be preserved as sulphides in the geological record.

Principles of chimney-mound accumulation. The accumulation of sulphides from modern black smoker vents is an extremely inefficient process. It is estimated that more than 99% of the metal carried by hydrothermal fluids (that have not mixed with seawater or otherwise cooled in the sub-surface) is dispersed in the water column by black smoker plumes (Rona, 1984), and eventually becomes incorporated into distal marine sediments (e.g., Boström and Peterson, 1966; Boström, 1983). Metalliferous components from the hydrothermal fluid have been detected in the water column at distances of more than 750 km from its source (Rona, 1984).

The vertical flow rates of hydrothermal fluids that exit at temperatures of 350°C from single vents with orifice diameters of 2.7-4.7 cm have been measured as 1.0-2.4 m·s⁻¹ (Converse et al., 1984). The most common size of sulphide particles in the black smoker plume is 1-3 μm (Mottl, 1986) and these have settling rates of about 2.0×10^{-5} m·s⁻¹. Thus, only in the absence of ocean currents could there be any appreciable accumulation of sulphides in the vicinity of the hydrothermal vent (Cathles, 1983; Converse et al., 1984; Campbell et al.,

1984), a prediction in keeping with the scarcity of plume fall-back sediment in the vicinity of modern black smoker vents, and a confirmation of Sato's (1972) prediction for his Type III hydrothermal solutions.

The near-vent accumulation of large quantities of sulphides in the modern submarine environment would therefore appear to depend upon the paradoxical requirement that a mound of sulphide be developed over the vent. Once established, the mound has the capacity to grow by the precipitation of sulphides within the mound and by the accumulation of chimney talus on its surface for as long as high temperature hydrothermal flow is maintained. The role of the porous anhydrite collar in initiating sulphide accumulation in the first place is therefore of paramount importance in understanding the accumulation of sulphides from buoyant seafloor hydrothermal fluids.

As can be easily demonstrated in the laboratory by injecting dilute sulphuric acid into a beaker of calcium chloride solution, anhydrite forms a rigid, though fragile, mass of interconnected acicular and tabular crystals, even when it nucleates rapidly. It is

1. Initial hydrothermal eruption.
   Accumulation of eruption breccia over hydrothermal vent.

2. Decrease of eruption breccia permeability by intraclast precipitation of sulphides etc.
   Initiation of surface sulphide accumulation by crust formation, plume fallback, and chimney talus.

3. Recurrence of hydrothermal eruption.
   Hydrothermal eruption breccia contains sulphide clasts.

4. Further recurrence of hydrothermal eruption.
   As the mound grows:
   Increase in the proportion of sulphide clasts in eruption:
   Hydrothermal discharge becomes increasingly diffuse:
   Recrystallization and redistribution of sulphides within the mound.

LEGEND:

Lithic clasts

Sulphide clasts

Breccia with sulphide infilling of interstices

Massive sulphide, chimney talus, plume fallback, surface crust, fine particulates fluidized from mound interstices.

Focused discharge from sulphide chimney
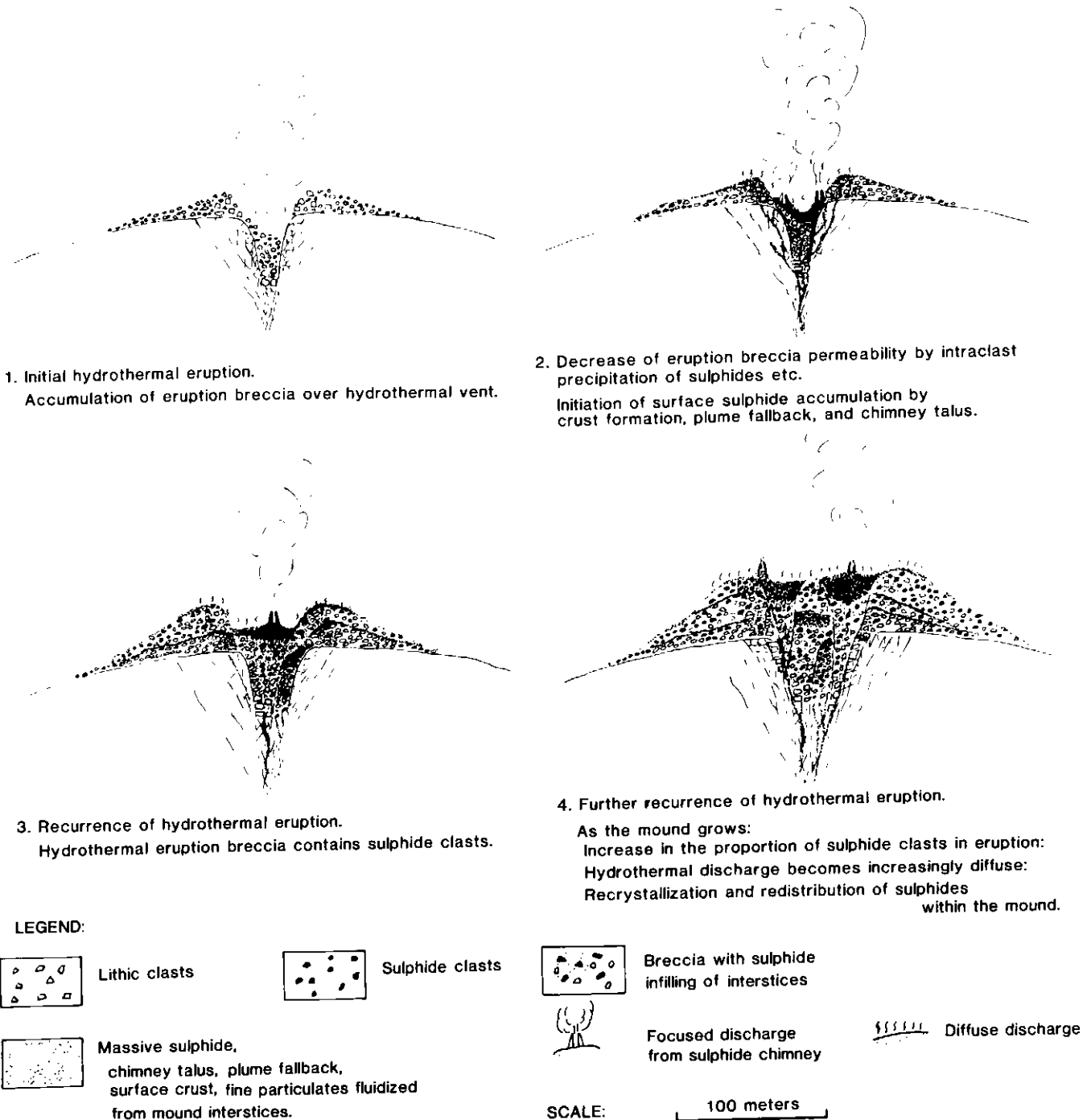
Diffuse discharge

SCALE: 100 meters

Figure 4 Schematic representation of the growth of a proximal VMS deposit formed by a recurrently eruptive hydrothermal vent. The final stage of the progression is illustrated by Figure 5.

presumed that the anhydrite collar of modern hydrothermal vents precipitates in a similar fashion since it commonly exhibits similar acicular and tabular crystal habits (see mineral texture descriptions by Haymon and Kastner, 1981). This porous network of anhydrite crystals serves three main functions in promoting the accumulation of sulphides:

(1) It impedes the upward flow of any buoyant hydrothermal fluid that enters its latticework. It thus promotes near-vent degeneration of the hydrothermal fluid (e.g., mixing with entrained seawater; cooling by conduction) and consequently near-vent nucleation of sulphides. The lower velocity of the fluid within the anydrite wall permits a higher proportion of precipitated sulphides to remain at the nucleation site rather than being mechanically transported in suspension by the rapid movement of the hydrothermal jet of an open vent.

(2) It provides a substrate upon which hydrothermal precipitation can take place by crystal growth.

(3) It acts as a filter in trapping sulphide particles suspended in the hydrothermal fluid. Its filtering capacity may be expected to increase with time, as the diameter of fluid passageways decrease due to hydrothermal precipitation.

The common denominator to these three functions is diffuse hydrothermal discharge through a porous medium. It is this defocussing of hydrothermal discharge by a porous barrier that is the main factor in maximizing the cooling of the hydrothermal fluid close to the sea floor and the enhancement of near-vent accumulation of precipitates.

Sulphide accumulation in VMS deposits. The general similarities (e.g., mineralogy, ore mineral zonation, wall rock lithologies) between modern mound-chimney sulphide edifices and ancient proximal VMS deposits are so strong, that drawing direct analogy between the two is almost unavoidable. The discovery of chimney fragments and fossil worm tubes in ophiolitic VMS deposits of Cyprus (Oudin and Constantinou, 1984) and Oman (Haymon et al., 1984) certainly suggests that the mode of accumulation of sea-floor sulphides, at least as far back as the Cretaceous, involved mound-chimney edifices much like the modern ones. Furthermore, the size and inferred tonnage of sulphide mounds discovered recently on the Mid-Atlantic Ridge (Rona et al., 1986; Honnorez et al., 1986) indicate that deposits with physical dimensions comparable to an average ancient VMS deposit (Lydon, 1984a) can be accumulated by the apparently inefficient sulphide-depositing hydrothermal process at modern sea-floor spreading centres.

Fluid inclusion studies of a variety of proximal deposits, particularly from Cyprus (Spooner and Bray, 1977) and Japan (Pisutha-Arnond and Ohmoto, 1983 and references therein), indicate that ore solutions for VMS deposits typically had maximum temperatures of $300 \pm 50°C$ and salinities up to twice those of modern seawater. These temperature-salinity relationships indicate that the ore fluids would be highly buoyant in seawater if they reached the sea floor in an unmodified state (Solomon and Walshe, 1979a, b) and would behave in a similar fashion to the fluids of the modern high-temperature vents.

As discussed above, the main prerequisite for the accumulation of a proximal type VMS deposit is the establishment of a porous barrier over the hydrothermal vent which causes diffuse discharge of the hydrothermal fluids and initiates the accumulation of sulphides. Although the interference between adjacent plumes from a multiple-orifice vent would allow the accumulation of a high proportion of precipitates (Solomon and Walshe, 1979a, b), plume fall-back itself (Eldridge et al., 1983) would not appear to be a prime candidate for initiating the growth of a sulphide mound, as this would mean the effect preceding the cause.

Recognizing the beneficial qualities of a porous anhydrite wall in modern sulphide chimneys for promoting initial sulphide accumulation, Campbell et al. (1984) suggested that some volcanogenic massive sulphide deposits form beneath an anhydrite cap. As realized by the authors, the weakness in this suggestion is that, with the exception of the Kuroko deposits, anhydrite/gypsum is rare in ancient VMS deposits, even considering that much of the original anhydrite may have been dissolved by
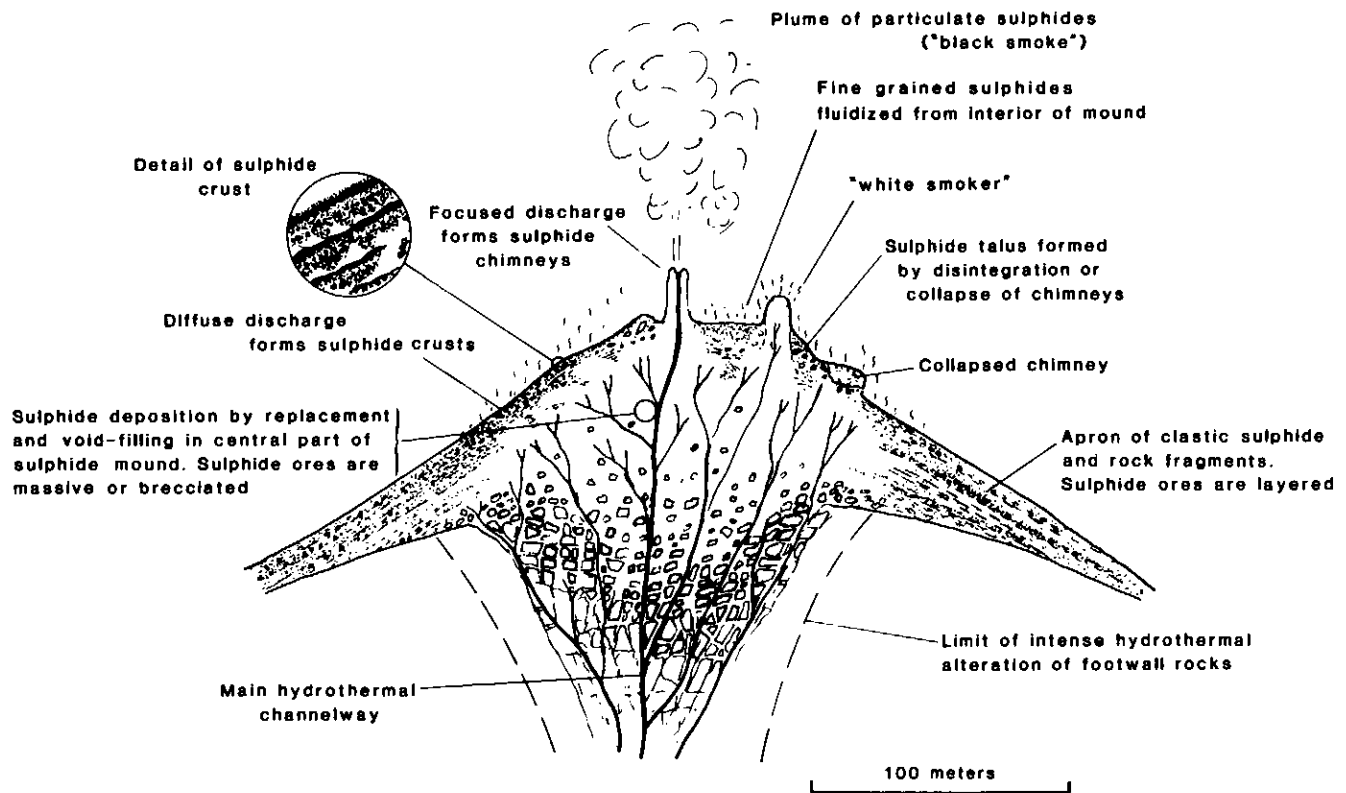

Figure 5 *Schematic representation of some processes of sulphide accumulation in a proximal VMS deposit.*

digestion in later ore fluids or by aging in cold seawater on the ocean floor, as is the case with modern sulphide mound deposits (Tivey and Delaney, 1986). The typical siting of Sekko ore (anhydrite/gypsum) below and/or adjacent to sulphide ore (e.g., Lambert and Sato, 1974; Hirabayashi, 1974; Shikazono et al., 1983) does suggest a genetic link between the two ore types in the case of Kuroko deposits, presumably involving the mixing of ore fluids with seawater at an early stage of hydrothermal activity (Sato, 1972, 1973; Shikazono et al., 1983), and the anhydrite may indeed have served as an initial, largely sub-surface, porous blanket which caused subsequent diffuse hydrothermal discharge at the surface.

For the majority of proximal VMS deposits, however, a layer of fragmental rocks over the hydrothermal vent is a much more likely candidate to have fulfilled the role of the porous anhydrite wall in modern sulphide chimneys rather than a cap of anhydrite itself. Fragmental rocks have long been recognized as being an intimate associate of VMS deposits (e.g., Gilmour, 1965; Boldy, 1968) and have been affectionately termed "millrock" (Sangster, 1972). By their definition of having a footwall stockwork zone, proximal VMS lenses invariably repose on breccias or brecciated rock. The fragmental rocks may have had a magmatic (Burnham, 1983), phreatic (Horikoshi, 1969; Clark, 1983), or hydrothermal (Henley and Thornley, 1979; Lydon, 1986) explosive origin or be talus accumulations (Hekinian and Bideau, 1986).

Of these possible diverse origins to the mound or blanket of breccia within which sulphide accumulation is initiated, perhaps the most common one is hydrothermal eruption, caused by early stage explosive discharge of the ore-forming hydrothermal system (see Discussion). Consistent with this interpretation, the stockwork zone represents a hydrothermal breccia pipe, formed by repeated episodes of hydraulic fracturing and by concomitant precipitation of hydrothermal minerals in fractures and hydrothermal alteration of the clasts. The volume expansion required by the dilatant hydraulic fracturing is accommodated by the upward displacement of the fragmented rocks of the breccia pipe and their eruption at the surface (Lydon and Galley, 1986). This gradual upward displacement of breccia clasts accounts for the gradational nature (in terms of sulphide:wall rock ratio) of the lower contact of the massive sulphide lens, the downward decrease in sulphide grade in the stockwork zone, and at least in part for the polymictic clastic apron surrounding the massive sulphide lens described in Part 1 of this article (Lydon, 1984a).

Barton (1978) recognized that much of the ore deposition of Kuroko deposits took place by episodes of open space filling and replacement that alternated with episodes of fracturing and slumping of the sulphide ores.

Further elaboration of his study and concepts (Eldridge et al., 1983) resulted in a model for ore deposition that is similar in essential details to that shown for the modern mound-chimney deposits in Figure 2. Salient points of the model by Eldridge et al. (1983) are that, once initiated, the sulphide mound itself acts as a porous medium over the vent to promote diffuse hydrothermal discharge, and that the "semi-sealed outer sulfide rind" (Eldridge et al., 1983) or the "thin thermal and mechanical blanket" (Barton, 1978) are equivalent to the "low permeability crust" of modern sulphide mounds (Goldfarb et al., 1983) in allowing advective, convective or conductive cooling of the ore fluid within the sulphide mound and the consequent subsurface precipitation of sulphides. Thus, just as with modern mound-chimney edifices, the Kuroko deposits are envisaged to have accumulated both by the addition of clastic sulphide from above (plume fall-out, chimney talus) and by open space infilling and replacement within the mound.

Essentially the same general conclusions were reached by independent and earlier studies of the Archean deposits of the Noranda area (Simmons et al., 1973; Spence, 1975; Riverin and Hodgson, 1980; Knuckey et al., 1982). Although the concepts derived from the Noranda examples have been used in exploration strategy since the early 1960s (Gilmour, 1965), they have not been so elaborately discussed in the literature as those derived from the modern mound-chimney or the Kuroko deposits. A major difference in emphasis has been the role of explosive volcanic and hydrothermal activity, considered important by the "Noranda" school but not, with some exceptions (e.g., Horikoshi, 1969; Clark, 1971, 1983), by the mainstream "Kuroko" or "modern chimney-mound" schools.

In summary, and with reference to Figure 4 and Figure 5, the model for the accumulation of ancient proximal VMS deposits which incorporates most salient points of current thought visualizes:

(1) The discharge of hydrothermal fluid from a focussed vent into a pile of fragmental rocks, which most commonly is a blanket or mound of lithic hydrothermal eruption breccia produced by the initial explosive discharge of the ore-forming hydrothermal system, or in some cases and more fortuitously, may be pre-existing magmatic, phreatic or talus breccia.

(2) Defocussing of hydrothermal flow by the fragmental pile which enhances advective, conductive or adiabatic cooling of the hydrothermal fluid within the mound and thus the precipitation of sulphides and other hydrothermal minerals. Fine particulates fluidized from the interior may accumulate at the mound surface.

(3) Hydrothermal flow becomes more diffuse as channelways within the mound become more restricted by hydrothermal precipitation,

which in turn increases the efficiency of sulphide precipitation within the mound. Formation of a low permeability crust by conductive or advective cooling of the mound exterior allows only diffuse, low velocity discharge across the mound surface which tends to maximize the rate of accumulation of hydrothermal particulates formed by quenching in the overlying water column.

(4) Renewed episode of fracturing, hydraulic or otherwise, and perhaps hydrothermal eruption, allows that discharge of hydrothermal fluids from major new channelways as focussed buoyant hydrothermal plumes form new sulphide chimneys but also disperses the dissolved components in the overlying water column. Reversing buoyancy plumes would minimize this dispersal of suspended sulphide particles.

(5) Subsequent repetition of Stages 2-4 leads to growth of the mound by the internal creation and filling of fractures, by crust formation, and by the surface accumulation of eruption products, chimney talus and fallback of plume particulates.

Massive sulphide lenses formed by these mechanisms are most likely to be conical or mound-like in morphology, with maximum lateral extent:thickness ratios (aspect ratio) typically in the range 3:1 to 5:1. Downslope transportation of sulphides as slump breccia flows or slide sheets (Schermerhorn, 1970) initiated by gravitational instability or hydraulic lifting (Eldridge et al., 1983; Cathles, 1983) might be expected to produce transported deposits with different morphologies (Lydon, 1984a, fig. 9).

Deposits with a sheet-like morphology (aspect ratio 10:1) are more likely to be formed by processes that more closely follow the laws of sedimentary superimposition than do the proximal mound deposits. The most obvious case where this mode of accumululation occurs is in brine pools formed by high density ore solutions (i.e., Sato's (1972) Type I solutions). Turner and Gustafson (1978) described situations in which initially buoyant plumes that are discharged into a submarine depression may pond below a picnocline (i.e., a variant of Sato's Type II solutions). Since the ponding of the hydrothermal effluent prevents not only the dispersion of plume particulates but also insulates them from the oxidizing effects of normal seawater, sulphide accumulation under these circumstances is more efficient than in the proximal mound type of accumulation. It is thus perhaps significant that the largest VMS deposits, such as Kidd Creek (Coad, 1985) and Brunswick No.12 (van Staal and Williams, 1984) tend to have high aspect ratios.

Zonation in the massive sulphide lens
Mineralogical and chemical zonation.
The increase in Zn:Cu ratio upward and outward from the core of the massive sulphide lens is one of the most definitive

characteristics of VMS deposits. The similarity of the ore mineral assemblages and the polarity of their zonation (from the core of the sulphide structure to the seawater interface) to those of modern sulphide chimneys suggests similar controls on sulphide precipitation and deposition in both cases.

Based on evidence from ancient VMS deposits, it has been suggested that the characteristic zonation patterns reflected the effects of local physicochemical gradients on mineral precipitation from, and alteration by, an ore fluid (e.g., Riverin and Hodgson, 1980; Knuckey et al., 1982), rather

than changes in the composition or temperature of the pristine ore fluid with time (e.g., Solomon and Walshe, 1979a). This view is supported by sophisticated computer models of mineral deposition from aqueous solutions similar in composition to the EPR 21°N vent fluids (Janecky and Seyfried, 1984; Bowers et al., 1985; Reed, 1983). Furthermore, this computer modelling indicates that it is indeed the progressive local cooling of the solutions, rather than other physicochemical changes such as dilution, oxidation, or pH change (e.g., cf. Large, 1977), that causes the Cu-dominant to Zn-dominant zonation. The only constraints on reproducing the sequential sulphide mineral assemblages that mark the zonation are that in the initial solution:

(i) the concentrations of Fe, Cu and Zn are within one or two orders of magnitude of one another; (ii) the metals are in solution dominantly as chloride complexes; (iii) molality dissolved H_2S > molality total dissolved metal; (iv) activity H_2S >> activity SO_4 at chemical equilibrium (i.e., the solutions are in a very reduced oxidation state).

The reason for this invariability in the sequential Cu-dominant to Zn-dominant sulphide assemblages produced by the cooling of polymetallic, reduced, acidic, sulphurous aqueous solutions is due to the relative solubilities of chalcopyrite and sphalerite as a function of temperature under these conditions (illustrated in Figure 6). The solubility of chalcopyrite in a chloride-bearing aqueous solution in equilibrium with an iron sulphide is dominantly a function of temperature. If 0.1 mg·kg⁻¹ Cu in solution is taken as the minimal concentration necessary to precipitate chalcopyrite, then the lower temperature limit for chalcopyrite deposition is above 300°C for solutions from EPR 21°N vents (Janecky and Seyfried, 1984), but may be as low as 150°C in solutions with higher chloride concentrations, lower p_{O_2}, higher metal to sulphide ratio and higher Cu:Fe ratios (e.g., Large, 1977). The solubility of sphalerite (and galena) in chloride solutions is much less temperature dependant than that of chalcopyrite (Figure 6), and significant concentrations of Zn and Pb in solution invariably extend to lower temperatures than does that of Cu under comparable physicochemical conditions. The degree of separation of Zn (and Pb) from Cu in sequential precipitation along the cooling path of a reduced solution depends upon the degree of undersaturation of Zn (and Pb) in the initial solution. The relative position of maximum iron sulphide deposition in the cooling sequence is dependant on the concomitant pH and p_{O_2} profile.

Contours of Cu:Zn ratios in a proximal VMS deposit can therefore be taken to represent an approximate average isotherm pattern (Figure 7). It is only approximate because, as noted above for modern sulphide chimneys, mineral zone boundaries probably oscillated with time, and the overall
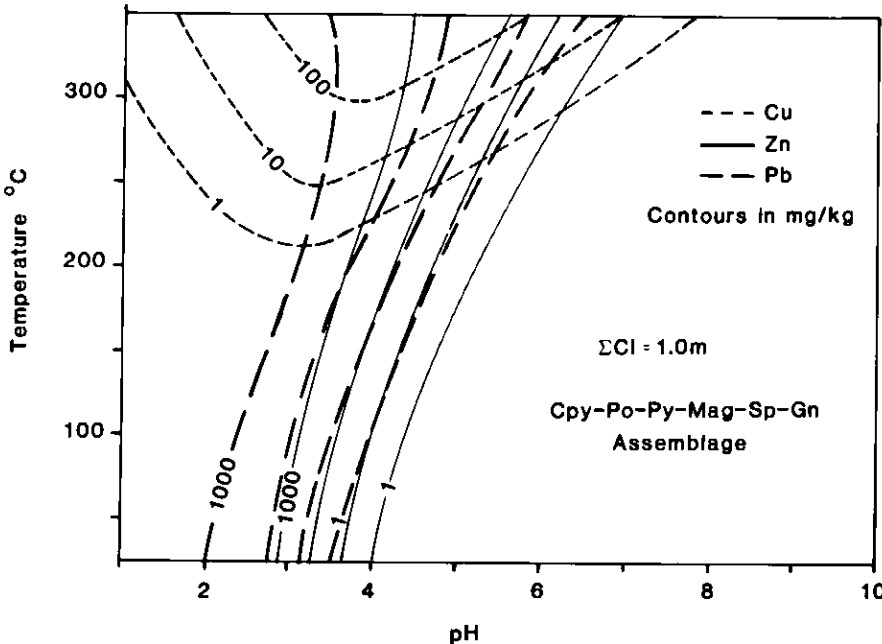

Figure 6 *Sulphide solubility patterns due to chloride complexing. Calculated total metal concentrations (in mg·kg⁻¹) in a 1 m NaCl solution in equilibrium with a chalcopyrite-pyrite-pyrrhotite-magnetite-sphalerite-galena assemblage. Note that the sulphur content of the solution ranges from < < 1 mg·kg⁻¹ at low pH and low temperature to > 10,000 mg·kg⁻¹ at high pH and high temperature. The isothermal decrease in chalcopyrite solubility with decreasing pH at low pH is due to the decrease in activity of Cl⁻ as the relative proportion of chloride complexed with metals increases. (Data from Helgeson, 1969; and Crerar and Barnes, 1976).*
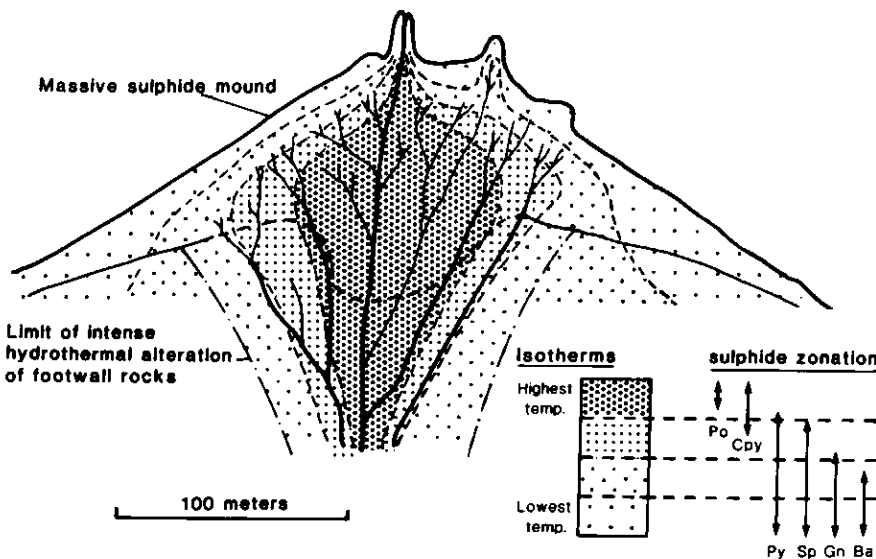

Figure 7 *Idealized sulphide zonation of the proximal VMS deposit illustrated in Figure 5 showing the direct relationship between sulphide zonation and average maximum isotherms if the ore metals were present in the ore fluid dominantly as chloride complexes.*

growth pattern entails the upward and outward expansion of isotherms within the sulphide mound, resulting in the replacement of sphalerite by chalcopyrite in the core and the relative concentration of zinc in the mound crust, chimneys and plume fallback (Eldridge et al., 1983). The preservation of a consistent Cu:Zn zonation pattern implies that a proximal sulphide mound was essentially a rigid edifice. The argument for this conclusion, supported by the steep-sided morphology of conical mounds (Simmons et al., 1973), is that since the zonation is due to a chemical evolution of the fluid, a porous rigid framework is necessary to support and maintain the spatial configuration of precipitates from the fluid.

Little is known of gangue mineral zonation in VMS deposits. In proximal deposits, silica appears to be a pervasive cement throughout the mound (e.g., Costa et al., 1983). The precipitation of silica from solution requires cooling without dilution, such as by conductive or adiabatic cooling (Janecky and Seyfried, 1984). Barite, when present, is concentrated in the upper parts of the deposit and seawater sulphate appears to be involved in its precipitation (e.g., Watanabe and Sakai, 1983; Kowalik et al., 1981). Silicates may be added to the mound by fluidization or eruption from the footwall, lithic fall-out from above, or by hydrothermal precipitation. Talc, formed by the mixing of ore fluid with seawater (Lonsdale et al., 1980; Costa et al., 1983; Aggarwal and Nesbitt, 1984; Bowers et al., 1985) may be the most common primary hydrothermal silicate.

Sulphides accumulated by mechanical processes, including the clastic apron of proximal mounds and deposits with a high aspect ratio morphology, tend to lack a pronounced or consistent zonation. Sheet-like or layered deposits (e.g., Brunswick No.12, Rosebery) generally have high aggregate (Zn + Pb)/Cu ratios and probably largely consist of the lower temperature sulphide precipitates of plume or brine-pool fall-out (Solomon and Walshe, 1979a; Green et al., 1981). Sediments containing a significant proportion of iron oxides, manganese oxides, or silica, including "tuffaceous exhalites" such as the Tetsusekiei associated with the Kuroko deposits, are sometimes spatially associated with the sulphide deposits. These sediments may reflect marginal or terminal oxidation of brine pools as in the Red Sea (e.g., Pottorf and Barnes, 1983), distal products of the progressive oxidation of a buoyant hydrothermal plume (Large, 1977; Kalogeropoulos and Scott, 1983), or products of contemporaneous or later low temperature hydrothermal discharge.

Evidence for the sea-floor oxidation of VMS deposits is scarce, which is surprising considering the rapidity with which sulphides of modern sea-floor sulphide mounds are oxidized. The most popular examples cited for sea-floor oxidation of ancient VMS deposits are the ochres of some deposits of

Cyprus (Constantinou and Govett, 1972, 1973), but even in these cases it appears that at least some of the ochres were formed by post-burial oxidation of sulphides by circulating ground water (Lydon, 1984c). The general absence of oxidized cappings to VMS deposits may imply that one of the conditions for preservation (and perhaps accumulation) of VMS deposits is insulation from the oxidizing effects of normal seawater. This insulation may be provided by anoxic bottom conditions, developed during times of ocean stratification or induced by the ponding of sulphurous ore solutions, or by almost instantaneous burial of the sulphide deposit. Another possibility is that burial metamorphism, in tending to equilibrate the diverse mineral assemblages of the primary deposit, may have resulted in sulphidation of oxidation products.

The primary zonation pattern is susceptible to post-burial modification. In the Cyprus deposits, the primary Zn:Cu zonation is locally reversed by the deposition of secondary copper sulphides from oxidized ground water at the redox boundary between sulphide ore and unmineralized lavas (Lydon, 1984c). Mobilization of sulphides during penetrative deformation and metamorphism can result in stockwork-like veins and also distort the primary zonation patterns (van Staal and Williams, 1984).

Textural zonation. Due to the facility with which sulphide minerals anneal, recrystallize and re-equilibrate, only rarely is any semblance of the complex and intricate micro-

scopic textural detail of a pristine VMS deposit preserved in a deposit that has undergone even lower greenschist metamorphism. Only in the youngest VMS deposits, such as those of Cyprus, Oman and Japan, are microscopic textures preserved that are comparable to those of modern mound-chimney sulphides.

However, in the least metamorphosed and deformed ancient VMS deposits, primary macroscopic textures can often be discerned, especially where the form of the texture is marked by a radical change in bulk chemical composition (e.g., lithic clast in sulphide matrix; sphalerite vein in massive pyrite). The general correlation that the pyrrhotite-, pyrite- or chalcopyrite-rich core of a proximal massive sulphide lens tends to be massive or show brecciated textures, whereas the sphalerite- or pyrite-rich outer parts of the lens tend to preserve banded, bedded or clastic textures and structures, is directly related to the mechanisms of sulphide accumulation described above. Ore accumulation in the core is mainly by deposition in fractures and channelways from circulating fluids that are contained by the outer low permeability crust. The sustained high temperature fluid circulation in the core leads to annealing and chemical homogenization even while the deposit is on the sea floor. The outer part of the mound, accumulated by crust formation or clastic processes, is not so pervasively subjected to this high temperature reworking of the sulphides, and hence tends to retain its original inhomogeneities.
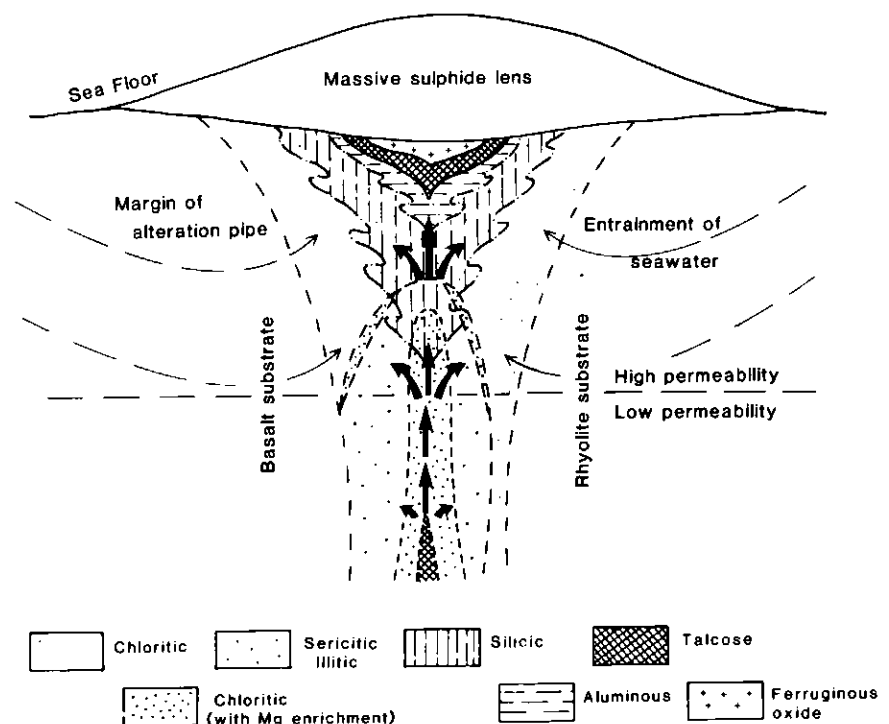

Figure 8 *Composite representation of the various alteration assemblages that have been reported for alteration pipes of VMS deposits. See text for explanation and discussion.*

Due to the tendency for obliteration of primary textures by metamorphism, the significance of many remnant textural features of ancient VMS deposits has probably gone unrecognized. For example, monomineralic patches and bands of sphalerite in massive pyritic ore probably represent the infilling of hydrothermal channelways and fractures, respectively, within the sulphide mound (see some comparative photographs in Lydon, 1984b).

Zonation of alteration pipe
There is consensus that the footwall hydrothermal alteration pipes of proximal VMS deposits represent the conduits for the upward flowing ore fluids (Franklin et al., 1981), but probably a lack of consensus on generalization of its characteristic features (Lydon et al., 1984). A composite of the various features reported for VMS alteration pipes is shown schematically in Figure 8.

Studies of the least metamorphosed Archean Cu-Zn deposits (see summaries in Franklin et al., 1981) show that in terms of silicate mineralogy the alteration pipes are characterized by chloritic cores and sericitic margins, though as Riverin and Hodgson (1980) point out, in some cases the chloritic core may top out upward so that the alteration assemblage immediately below the massive ore is dominantly a sericitic facies (usually sericite-chlorite-quartz) (Figure 8). A magnesium enrichment in the core of the alteration pipe can often be demonstrated (e.g., Riverin and Hodgson, 1980; Knuckey and Watkins, 1982; Walford and Franklin, 1982). A similar configuration occurs in the alteration pipes of Cu-Zn deposits in Cyprus where most commonly choritic cores are surrounded by illite or illite-smectite peripheries (Clark, 1971; Lydon and Galley, 1986). However, in some cases, such as the Pitharokhoma deposit (Richards et al., in press), illitic alteration dominates the entire alteration pipe. At the Mathiati deposit, at least, magnesium enrichment is confined to a narrow zone around the periphery of the chloritic part of the alteration pipe (Lydon and Galley, 1986), which may be analogous to a narrow zone of high-Mg chlorite, approximately coinciding with the transition between chalcopyrite-dominant and sphalerite-dominant stockwork mineralization, observed by the author at the Archean Millenbach deposit.

The same range of features can be observed in the Cu-Zn-Pb type of deposit. For example, chloritic alteration with magnesium enrichment occurs beneath the La Zarza deposit in Spain (Strauss et al., 1981) whereas quartz-sericite dominates the alteration below Kuroko deposits (Shirozo, 1974). Chlorite which occurs outside of the quartz-sericite zone below Kuroko deposits is ubiquitous in footwall rocks for at least several kilometres away from the sulphide mineralization (Date et al., 1983), and probably should not be

considered to indicate a "reverse zonation" of alteration (Franklin et al., 1981, p. 607; Urabe et al., 1983) on the scale at which hydrothermal alteration pipes are usually defined.

The chlorite to sericite (or illite) zonation has been interpreted to represent a decreasing thermal gradient (Riverin and Hodgson, 1980; Lydon and Galley, 1986). This interpretation is consistent with the sulphide zonation pattern of the alteration pipe which characteristically consists of a relatively chalcopyrite-rich core and sphalerite-rich margins. This pattern, as discussed above, is diagnostic of an outward-decreasing thermal gradient. It is also consistent with experimental seawater-basalt interaction, which indicates that the transition between potassium loss from and potassium addition to basalt occurs in the range 150-200°C (Seyfried and Bischoff, 1979).

If the thermal gradient from core to margin of the alteration pipe is due to subsurface mixing of the ore fluid with ambient waters at the margin of the hydrothermal plume (Lydon and Galley, 1986), then the ratio of sericite (or illite) to chlorite reflects the average degree of mixing that has taken place at that site. If this is correct, then the upward culmination of the chloritic zone depicted in Figure 8 reflects the tendency of hydrothermal plumes to collapse upward due to the entrainment of subsurface waters in a permeable substrate. The low temperature thermal springs of the Galapagos Ridge (Edmond et al., 1979) are thought to represent the discharge of such a collapsed hydrothermal plume, its original sulphide load having been deposited in the sub-surface to give a stockwork deposit analogous to that encountered by DSDP Hole 504B (Alt et al., 1986).

Potassium added to the rock in the form of alteration sericite could have been derived from seawater and the ore fluid (Lydon and Galley, 1986) and/or from that released by the process of chloritization in the core of the alteration pipe (Riverin and Hodgson, 1980). Consistent with experimental seawater-basalt interaction (e.g., Hajash, 1975; Mottl and Holland, 1978; Seyfried and Bischoff, 1979) and the magnesium-free nature of modern pristine hydrothermal fluids emanating from basalts (von Damm et al., 1985), magnesium added in the uppermost or peripheral parts of the alteration pipe is most likely contributed by entrained seawater (Roberts and Reardon, 1978; Lydon and Galley, 1986). The preferential addition of magnesium in the core of the alteration pipe and in sulphide vein selvages implies a derivation from the ore fluids (Riverin and Hodgson, 1980), which likely means either a minor amount of seawater Mg having been entrained into the hydrothermal fluid at depth or else the pristine ore fluids contained Mg and were therefore generated in a feldspar-free lithology (e.g., completely chloritized/epidotized basalt, argillaceous sediments or ultramafic rocks).

Immediately below the massive sulphide lens, the ubiquitous chloritic and/or sericitic alteration (or precursor/successor assemblages) may be supplanted or superimposed by hydrothermal mineral assemblages of contrasting composition. The range includes siliceous (e.g., Shirozo, 1974; Lydon and Galley, 1986), aluminous (e.g., Nilsson, 1968; Walford and Franklin, 1982), carbonate (e.g., Franklin et al., 1975); Deptuck et al., 1982), talcose (Roberts and Reardon, 1978; Aggarwal and Nesbitt, 1984), and ferruginous oxide (e.g., Knuckey and Watkins, 1982; Richards and Boyle, 1986) assemblages. Although Figure 8 implies that these particular mineral assemblages are confined to the uppermost parts of the alteration pipe, this is only a speculative interpretation. Metamorphism, structural complexity and lack of access to alteration pipes away from economic grades of mineralization in most VMS deposits has not allowed studies that unequivocally relate these mineral assemblages to the near-surface part of the hydrothermal discharge vents.

Some of the iron oxide in ferruginous units immediately below the massive sulphide lens originated as early accumulations of oxidized plume fall-out prior to the establishment of anoxic bottom conditions and the stabilization of sulphides (Lydon and Galley, 1986; Richards and Boyle, 1986). Similarly, accumulation of talc may have occurred at the sea floor during the initial discharge of silica-saturated hydrothermal solutions into magnesium-bearing seawater (Costa et al., 1983; Aggarwal and Nesbitt, 1984). Talc-actinolite may have also formed just beneath the massive sulphide lens due to rock alteration by the shallow entrainment of magnesium-bearing seawater into the hydrothermal conduit (Roberts and Reardon, 1978). Boiling of the hydrothermal fluids, causing cooling of the ore solutions without dilution by entrained seawater, would lead to the enhanced precipitation of silica (Lydon and Galley, 1986), and, particularly when the solutions contained dissolved CO_2, other minerals which are dependent on acidity for their solubility (Drummond and Ohmoto, 1985). Adiabatic cooling could also give rise to aluminous mineral assemblages (Riverin and Hodgson, 1980) as could high acidity created by oxidation of sulphurous ore solutions.

Based on a study of fluid inclusions in the upper part of the stockwork zone of Kuroko deposits, Pisutha-Arnond and Ohmoto (1983) demonstrated a waxing and a waning temperature of the hydrothermal system. Time-dependent zonation is difficult to separate from space-dependent zonation in most VMS deposits. This difficulty, combined with the complexities of mineral assemblage genesis noted above, emphasize the caution necessary before drawing generalizations on the nature of the ore fluid and the hydrothermal history of the VMS deposit based on observations in the upper part of an alteration pipe.

Types of hydrothermal systems

As illustrated in Figure 9, a specific hydro-thermal system may be a composite of various end-member types in which both the hydrothermal fluids and the energy for fluid circulation are derived from diverse sources. Discussion here is limited to the three main models that have been applied to the genesis of VMS deposits.

Convection cell models. The existence of hydrothermal convection cells in modern oceanic crust is well established. First postu-lated to explain the discrepancy between the measured and theoretical heat flow of oceanic ridges (Palmason, 1967; Lister, 1972), and later predicted by mathematical models of the heat budget (Wolery and Sleep, 1976; Crane and Normark, 1977), they were confirmed by the discovery of high temperature hydrother-mal vents at oceanic ridges (Francheteau *et al.*, 1979). Supported by the reality of the phenomenon, a convection cell model is cur-rently the most popular hydrodynamic model for the formation of VMS deposits.

Spooner and Fyfe (1973) suggested that waters which penetrate and react with oceanic crust could form VMS deposits on their return to the sea floor. This convection cell model was first specifically applied to the VMS deposits of Cyprus (Heaton and Shep-pard, 1977; Spooner, 1977). The fundamental concept in this model is that subsurface waters, dominantly of seawater origin, are caused to convect by a magmatic heat source and leach the ore components from the rocks along their flow path. In its applica-tion to specific areas, the postulated magma-tic heat source is tailored to suit the local geological setting of the VMS deposit under discussion. Suggested heat sources have included rhyolite domes or plugs (*e.g.*, Ohmoto and Rye, 1974), sub-volcanic sills (*e.g.*, Campbell *et al.*, 1981), felsic plutons (*e.g.*, Cathles, 1983), and, of course, spread-ing ridge magma chambers of both ancient ophiolites (*e.g.*, Spooner, 1977) and the mod-ern oceanic lithosphere (*e.g.*, Lowell and Rona, 1985).

The convection cell scenario has been mathematically modelled by a variety of tech-niques employing a spectrum of basic assumptions. However, all calculations point to the conclusion that if the ore fluids contain the same concentration of base metals as pristine black smoker fluids of the EPR (*i.e.*, 10 ppm Zn + Cu) there is not enough heat in a reasonably sized magmatic body to form an average sized VMS deposit (about 6 million tonnes sulphide).

Cathles (1978, 1983) modelled Kuroko hydrothermal systems on the basis of assum-ing a magmatic heat source at an initial tem-perature of 700°C and hydrothermal flow through a porous medium. He found that even if the ore fluid contained 1000 ppm Cu, the average sized rhyolite plug commonly associated with Kuroko deposits was several orders of magnitude too small to convect sufficient fluid to supply the amount of cop-per in an average Kuroko deposit (Cathles, 1978). To form the 4.5 million tonnes of base metal resources of the Hokuroku basin from >300°C fluids containing 100 ppm Cu + Zn + Pb would require an intrusive dyke 40 km long, 3.25 km high and 1.3 km wide, provided that all the dissolved metal accumulated at the sea floor discharge site (Cathles, 1983). The deposits could have formed in less than 5,000 years as a result of intrusive pulses in a spreading environment (Cathles, 1983). Similarly, with a minimum requirement of 78 km³ of felsic magma to heat enough >300°C fluid containing 100 ppm Cu + Zn to form the Noranda deposits, the composite Flavrian "granite" was permissibly the heat source (Cathles, 1983).

Using a discrete fracture model for hydro-thermal convection at mid-oceanic ridges, Cann and Strens (1982), Cann *et al.* (1985), Strens and Cann (1986) concluded that heat stored in solid rock within 1 or 2 km of the surface would not allow the formation of a VMS deposit. They found that discharge above 300°C could be sustained only for 10² years, which is comparable to the estimated
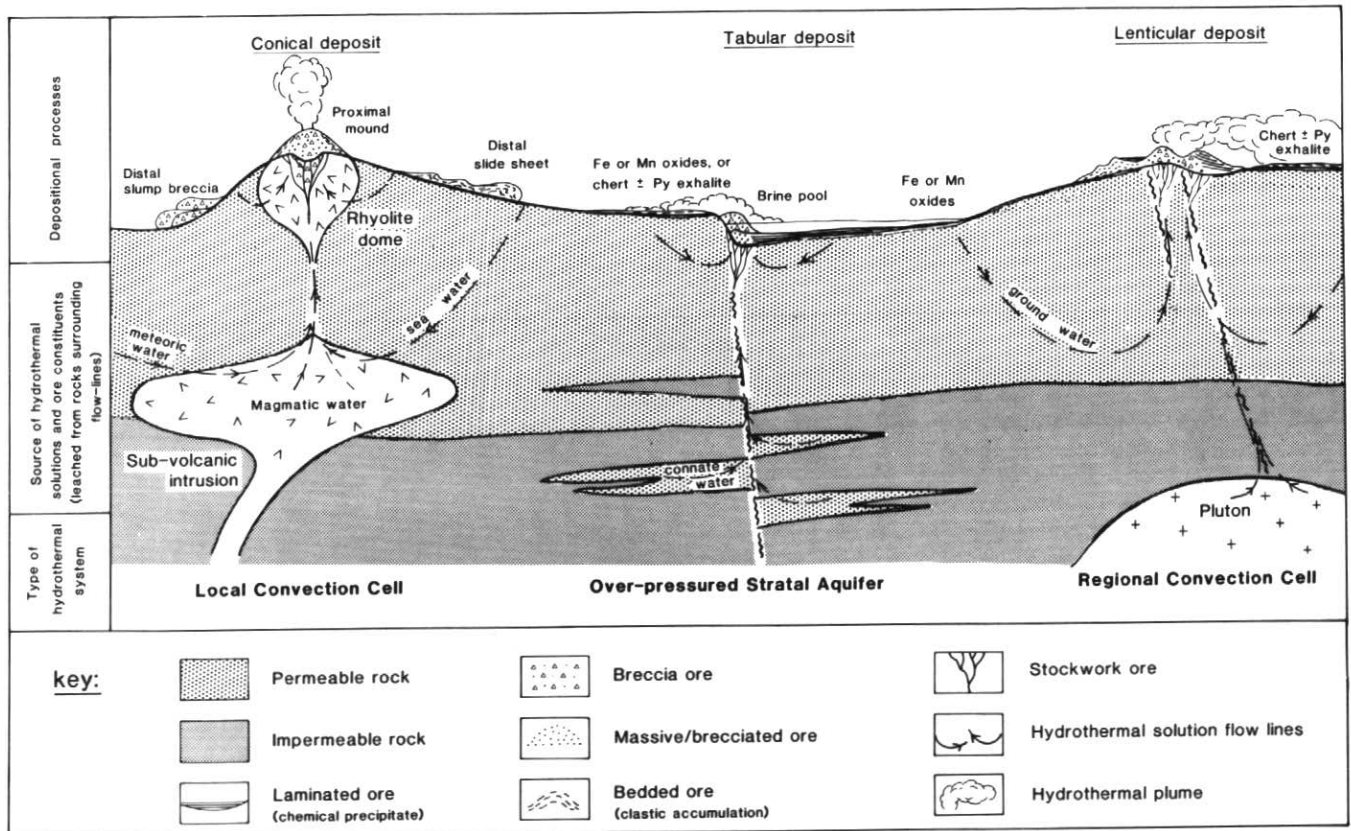

Figure 9 *Schematic representation of some major features of genetic models for VMS deposits. Note that the portrayed linkages between various factors represent only some of the many possible combinations, e.g., a brine pool deposit can be formed by the discharge of a local convection cell driven by a cooling pluton.*

10^1-10^2 years for modern black smoker vents (Macdonald et al., 1980). Cann and his co-authors suggested that the heat must be extracted from a convecting magma chamber and calculated that ore fluids at 350°C containing 115 ppm Fe requires the crystallization of 30 km^3 of basaltic magma to form a 3 million tonne iron sulphide deposit. The deposit could accumulate in 4000 years assuming 70% accumulation of the sulphides at the sea floor hydrothermal vent.

Using thermal balance considerations, Lowell and Rona (1985) also concluded that the heat content of permeable rocks in oceanic crust was insufficient to form a 3 million tonne sulphide deposit assuming 100 ppm metal concentration in the hydrothermal fluid and 100% efficiency of sulphide accumulation at the hydrothermal vent. However, the same deposit could be formed under the same assumptions, if the heat was extracted from the roof of a vigorously convecting magma chamber. As with the models of Strens and Cann cited above, the essence of this model is a twinned convective system, in which heat is supplied to the base of a hydrothermal convection cell by a magmatic convection cell across a thin-plated gabbro at the roof of the magma chamber. A positive feature of this model is that since the heat exchange site does not migrate with time, the spatial configuration of the hydrothermal convection cell may remain stable for an extended period.

It is apparent from the above selection of convection cell models, that enormous volumes of magma, whether crystallized or not, are required to form an average VMS deposit. The numbers quoted are close to the best-case scenarios, in that it is assumed that all the ore metals transported by high-temperature fluids are precipitated as distinct sulphide deposits. Taking into account the low probability of high temperature discharge being confined to just a few vents and the inefficiency of sulphide accumulation from a buoyant hydrothermal plume, as demonstrated by the modern black smoker vents, it would seem that to account for the formation of the larger VMS deposits by discharge from hydrothermal convection cells, the ore fluids would have had to contain considerably more than 100 ppm total metal.

Magmatic hydrothermal models. There has been the suggestion, but little corroboration, that the ore fluids for VMS deposits are derived from the volatiles of magmas. For example, Urabe and Sato (1978) suggested a magmatic origin for ore fluids for Kuroko deposits largely on the grounds of spatial association with rhyolite domes and weaknesses with alternative models. Bryndzia et al. (1983) favoured a magmatic component in Kuroko ore fluids to explain elevated salinities (up to 1.9 times greater than seawater) in fluid inclusions, whereas Sawkins and Kowalik (1981) expressed a similar sentiment for ore fluids of the Buchans orebodies

based on considerations of lead isotopes and the lead budget. The perception that VMS deposits can be related to particular igneous suites, particularly the most differentiated products of a calc-alkaline magma (Sangster, 1972; Solomon, 1976), may also be construed as inference of a magmatic affiliation. Although the magmatic model does not seem to have current support, perhaps the concept should not be dismissed. The geochemical data of Perfit and Fornari (1983) and Perfit et al. (1983), for example, could be interpreted to reflect the loss of large quantities of sulphur and base metals during a high p_{H_2O} stage of magmatic fractionation.

Stratal aquifer model. Although this model has been proposed for VMS deposits (Hodgson and Lydon, 1977; Gibson et al., 1983), it has found much more favour in genetic models for the sedimentary-exhalative class of sulphide deposits (e.g., Walker et al., 1977; Badham, 1981; Lydon, 1983; Sawkins, 1984; Lydon, 1986). In a sense this is informative, because as Gilmour (1976) has pointed out, the only major difference between some volcanogenic massive sulphide deposits and some sedimentary-exhalative deposits is the lithology of their host rocks. If sedimentary-exhalative sulphide deposits can be formed without the involvement of large volumes of magmas, then it would seem logical that some VMS deposits may have been formed in a similar way.

In the stratal aquifer model, it is visualized that the ore fluids originate as the pore waters of a porous rock unit (the "aquifer") which have been prevented from migrating during burial and compaction by an overlying impermeable barrier (the "cap-rock"). Progessive burial causes heating of the pore fluids along the geothermal gradient and an increase in pore-fluid pressure above hydrostatic pressure. Depending upon the mechanical strength of the cap-rock, pore-fluid pressure may approach or exceed lithostatic pressure. Eventual hydraulic or mechanical fracturing of the cap-rock, perhaps triggered by tectonic activity (e.g., Sibson et al., 1975), allows the upward release of the over-pressured pore waters along fracture zones. Once cross-stratal permeability is established, a short-lived successor convection cell may be initiated, which is driven by the heat stored in rocks of the aquifer.

A unique feature of the stratal aquifer model is that it allows the surface expulsion of very large quantities of fluid within a short time. A modest modern example of the phenomenon may be the expulsion of about 10^{10} kg of saline ground water within a few months of the 1966 initiation of the Matsushiro swarm earthquakes (Tsuneishi and Nakamura, 1970). An attraction of the model is its minimal energy requirements. Since a cap-rock is by definition also a thermal insulator, an over-pressured hydrothermal aquifer actually conserves heat that would

otherwise be lost by conduction and convection. Only the normal conductive heat flow of a volcanically active area is required to heat the pore fluids of the aquifer to more than 300°C within 1 km of the surface (McNitt, 1970). In a convection cell model, much of the heat content of a magmatic body is transferred at low temperature during the waxing and waning stages and by peripheral hydrothermal flow. Another positive feature is the minimal water:rock ratio of the stratal aquifer system, which in turn maximizes the capacity of the hydrothermal solution to attain high concentrations of metal by the leaching of the aquifer rocks (see below). The model is also geologically very realistic in terms of the volume requirements of the aquifer. For example, the 4.7 × 10^{13} kg ore fluid containing 100 ppm ore metal estimated by Cathles (1983) to be necessary to form the Noranda deposits could be contained by a 300 m thick aquifer of 15% porosity occupying an area of 900 km^2, which is about the thickness and area (Cathles, 1983) occupied by the semi-conformable alteration zone underlying the deposits (Gibson et al., 1983). The increasing recognition of semi-conformable alteration zones stratigraphically below the favourable ore horizon in different VMS districts of Canadian greenstone belts (e.g., Franklin et al., 1975; MacGeehan and Maclean, 1980; Gibson et al., 1983; Bailes et al., 1987) may be evidence that the stratal aquifer model has wide applicability.

As noted near the beginning of this article, the largest modern sulphide mounds may be those of the Middle Valley and Escanaba Trough areas, where turbidite sediments infilling the axial valleys cap the underlying basalt substrate. It may not be coincidence that the seismic profile of Middle Valley (Davis et al., 1987, fig. 5) is remarkably similar to figure 12 of Lydon (1986) which, in illustrating a genetic model for the Irish sedimentary-exhalative deposits, depicts 500 m of argillaceous sediments capping arenaceous sediments of a fault-controlled trough. The lithologies may be different in the two areas, but the thermal and hydrodynamic roles they play are probably identical.

Distribution of VMS deposits. There is no obvious advantage to any one of the above genetic models in explaining the areal distribution of VMS deposits. The hydrothermal discharge vents are most commonly localized by fracture systems (Gilmour, 1965; Sangster, 1972; Scott, 1978) which serve only to focus the hydrothermal discharge and have no direct bearing on the mechanisms by which the hydrothermal fluids were generated. The tendency of VMS deposits to occur in clusters can perhaps be most readily rationalized in terms of a convection cell model or a magmatic model, in which the cluster represents the annular distribution of hydrothermal discharge above a cooling pluton (Cathles, 1983). However, the same distribution patterns can also be explained by

the stratal aquifer model, noting that the volcanic stratigraphy of many VMS clusters can be interpreted in terms of a resurgent caldera (Hodgson and Lydon, 1977; Ohmoto, 1978; Ohmoto and Takahashi, 1983), that the range of caldera diameters is comparable to that of VMS clusters (Sangster, 1980), and that collapse calderas represent one of the most favourable environments in volcanic terrains for the development of stratal hydrothermal reservoirs (Hodgson and Lydon, 1977).

The stratal aquifer model probably best explains the phenomenon of "the favourable horizon". A single tectonic pulse can initiate synchronous discharge from different geopressured aquifers over a relatively wide area. Because high volume hydrothermal flow from a geopressured aquifer would be expected to be a single episode of relatively short duration, ore deposition over the entire mining district would likely be restricted to a narrow stratigraphic interval. However, this argument is not definitive, because as the calculations of Cathles (1983) indicate in the Noranda case, the Flavrian pluton could have driven the convective circulation of sufficient quantities of high-temperature fluid to have formed the VMS deposits in just a few thousand years, if the permeability of the pluton and the regional country rocks were within a permissible range. Certainly, insofar as interpretation based on zircon U-Pb ages allow, the Flavrian pluton is co-eval with volcanic rocks that contain the favourable horizon at Noranda (Mortensen, 1987). The preference of the stratal aquifer over the convection cell model to explain the favourable horizon phenomenon depends on the time interval that the favourable horizon represents (i.e., whether it represents perhaps 10^1-10^3 years versus 10^3-10^5 years, respectively).

A difficulty with the convection cell model is that, if hydrothermal convection is an integral part of submarine volcanism, as the evidence from the modern ocean floor and the predictions based on mathematical models suggest, then every submarine volcanic centre would be expected to have its attendant hydrothermal convection cells. The model in its simplest form therefore does not appear to rationally explain, for example, the distribution of VMS deposits in the Abitibi Belt, where, as described in Part 1 of this article (Lydon, 1984a), of the nine volcanic complexes identified only four contain VMS deposits. Perhaps in its application to the genesis of VMS deposits of significant size, the convection cell model requires qualification as to a minimum size and maximum depth of the heat source, such as large subvolcanic sills (Campbell et al., 1981), and a specific range to the regional permeability of the volcanic pile that plutonic heat source intrudes (Cathles, 1983).

Generation of ore fluids.

The consensus is that the hydrothermal fluid that emanates from modern submarine spreading ridges is seawater that has reacted with basaltic rocks as it is circulated through oceanic crust by a convection cell. The model is supported by experimental seawater-basalt interaction (e.g., Hajash, 1975; Mottl, 1983a, b; Seyfried and Bischoff, 1981), computer modelling (Reed, 1983) and observations on sea-floor basalts (Humphris and Thompson, 1978; Thompson, 1983).

The chemical evolution of the seawater (Table 1), as it is heated in the presence of basalt, is dominated in the early stages by the removal of sulphate, which precipitates as anhydrite due to temperature increase. The major cationic exchange is dominated by the loss of magnesium to the basalt in exchange for calcium. Magnesium is also removed above 250°C as MHSH (Bischoff and Seyfried, 1978) causing high acidity in the fluid. High acidity may also be created by epidote formation and by sodium fixation during retrograde cooling when silica activities are high (Seyfried and Janecky, 1985; Shanks and Seyfried, 1987). Potassium is lost to basalt at low temperature, but leached from it above 150°C (Seyfried and Bischoff, 1979). The result is a sulphurous Na-Ca-Cl fluid containing ppm concentrations of Fe, Mn, Zn and Cu (Table 1).

Oxygen and hydrogen isotope data for hydrothermal minerals and for water from fluid inclusions in minerals associated with VMS deposits (e.g., Ohmoto and Rye, 1974; Heaton and Sheppard, 1977; Beaty and Taylor, 1982; Pisutha-Arnond and Ohmoto, 1983) allow the interpretation that the hydrothermal fluids were seawater, possibly containing a component of magmatic and/or meteoric water, that had undergone isotope exchange by reaction with rocks. The elevated salinities of ore fluids generated within oceanic crust can be explained by a variety of processes. Rock hydration reactions by consuming water will concentrate chloride in the pore fluid. For example, a rock of 4% porosity absorbing 4 wt.% water by clay alteration would increase the salinity of the pore fluid by a factor of 2.7 (Cathles, 1983). Phase separation of the NaCl-H_2O fluid under high temperature and pressure conditions produces a brine with salinities two to three times that of seawater (Bischoff and Pitzer, 1985). This chloride brine may be formed and discharged during active hydrothermal venting or may collect in the sub-surface to form a brine reservoir that is tapped later (Von Damm and Bischoff, 1987; Gallinatti, 1984). Ore fluids for VMS deposits associated with sedimentary rocks could attain high salinities simply by the dissolution of evaporites, as in the case of the Red Sea brines, or by a process of ion filtration by argillaceous lithologies (Graf, 1982). Similarly, ore fluids in basaltic rocks could possibly achieve high salinities by the dissolution of

a speculative $Fe_2(OH)_3Cl$ phase formed by experimental seawater-basalt reaction at low water:rock ratios (Seyfried et al., 1986).

The $\delta^{34}S$ values of modern sulphide mound-chimney complexes range from about 1.5 to 4 ‰ (per mil) (Styrt et al., 1981; Zierenberg et al., 1984) and the sulphur is interpreted to be derived mainly from the basaltic substrate, with a smaller component derived from reduced seawater sulphate previously deposited as anhydrite (Shanks and Seyfried, 1987). Sulphur isotope values of ancient Cu-Zn VMS deposits have a similar range (Lydon, 1984a, fig. 5), which seemingly indicates that the sulphur in these deposits was likewise largely derived from the footwall mafic volcanic succession. Sangster (1976) noted that average sulphur isotope values for Phanerozoic deposits showed a sympathetic variation with co-eval seawater sulphate. The trend is almost entirely due to the Zn-Pb-Cu type of VMS deposit, which suggests that either these deposits derived their sulphur from footwall sediments, from reduced sulphur in anoxic bottom waters of a stratified ocean, or by direct reduction (bacterial ?) of seawater sulphate. The reason for the weak correlation between decreasing $\delta^{34}S$ values and decreasing Cu/Zn ratios (Lydon, 1984a, fig. 5) is not clear, but the same trend is also apparent from the core to the flanks of the massive sulphide lens in some deposits (e.g., Kajiwara, 1971).

Other isotopic tracers, including strontium (Honma and Shuto, 1979; Farrell and Holland, 1983) and lead (Doe and Zartman, 1979; Thorpe et al., 1981), also point to the ore components being derived by interaction between the ore fluid and rocks stratigraphically below the ore horizon. (Note that this does not mean the immediate footwall to the deposit, but in most cases to a depth of 0.5 to 3 km or more below the co-eval sea floor).

The most popular explanation for the aggregate metal ratios of VMS deposits is that they reflect the trace metal composition of the source rocks (e.g., Hutchinson, 1973; Solomon, 1976; Ohmoto et al., 1983). Most VMS deposits in Archean greenstone belts and Phanerozoic ophiolites, where the dominant lithologies at the time of ore deposition were of mafic composition, are of the Cu-Zn type. In contrast, the substrate to deposits of the Zn-Pb-Cu type (e.g., Kuroko deposits of Japan, Bathurst district of New Brunswick, Buchans district of Newfoundland, Pyrite Belt of Spain) consists dominantly of felsic volcanic rocks and/or argillaceous sediments. It has long been recognized that the overall range of Cu:Zn:Pb ratios of VMS deposits is about the same as that for rocks (Wilson, 1953; Wilson and Anderson, 1959). The argument that the paucity of lead in the Cu-Zn type of VMS deposits is due to the low abundance of lead in mafic rocks is widely accepted. The composition of modern sulphide mound-chimney deposits seems to

support this explanation, in that the average Zn:Pb ratios for samples from deposits resting directly on basalts is >60:1 (Rona, 1984). The abundance of lead in the Zn-Pb-Cu type of VMS is ascribed to its derivation from rocks with higher lead contents, notably felsic volcanics and sediments. Again, this view is supported by the compositions of samples from modern sulphide deposits overlying sediments of the Guaymas Basin and Escanaba Trough, which have Zn:Pb ratios as low as 3:1 (data from Hannington *et al.*, 1986; Koski, 1987). Thus, there is empirical evidence that sulphide accumulations with the ore element ratios characteristic of both the Cu-Zn and the Zn-Pb-Cu type of VMS deposits can be formed from acidic chloride solutions, and a factor in the difference between the two is the nature of the source region lithologies (note that the evidence from the Pb-rich modern sulphide deposits is that some of the ore components may be derived from the upper 500 m of the footwall succession).

Discussion
There is no doubt that the study of modern submarine hot springs and sulphide deposits, together with experimental work on seawater-rock interaction, has rapidly advanced the understanding of the genesis of VMS deposits. There also seems to be no doubt that both the modern sulphide deposits and ancient VMS deposits are products of the same fundamental processes. The main question remaining is the extent to which the analogy can be applied.

One of the main differences between modern and ancient VMS deposits is that the average amount of sulphide in the modern deposits is about two orders of magnitude smaller than in ancient VMS deposits though, as Lowell and Rona (1985) pointed out, there is overlap in the range. The reasons for this could be simply that very small VMS deposits are neglected in compilations of VMS statistics because they are not economic to mine and that few large modern deposits have been discovered because of the short exploration history of the modern ocean floor.

It is unlikely that the largest VMS deposits, consisting of more than 100 million tonnes of sulphides (*e.g.*, Kidd Creek, Brunswick No.12, Rio Tinto), were formed from ore fluids with metal concentrations as low as those in the modern vent fluids. The mathematical models indicate that the energy requirements are too large and that it would be unreasonable to expect a single convection cell to maintain the same flow paths for the length of time required to discharge sufficient fluid from a single vent site. The very large sulphide deposits therefore require either higher concentrations of metal in the ore fluid and/or a higher efficiency in the mechanism of sulphide accumulation than occurs in modern mound-chimney deposits.

Metal content of hydrothermal fluids.
Although the current consensus is that the ore components for VMS deposits are leached by the ore fluids from the sub-seafloor rock column, little attention has been given to the constraints of the leaching process itself. Lydon (1983, 1986) has pointed out that the trace metals can be considered to occur in rocks either as: (1) labile components, which include those metals that are loosely bound at the surfaces of mineral grains and those held by a grain coating of a material with high adsorption capacities (iron oxide coatings of quartz grains in red sandstones is a good example); or (2) bound components, which occur as diadochic substitutions for essential elements within the crystal structures of rock-forming minerals.

In most lithologies, the greatest proportions of trace elements occur as bound components, and can therefore only be leached during host mineral destruction. The natural destruction of a mineral may be effected either by dissolution or, more commonly, by alteration into secondary minerals. Since the amount of a bound metal that can be leached is proportional to the amount of host mineral destroyed, in cases where mineral destruction or conversion is due to mineral-solution interaction, the amount of metal leached is dependent upon the reactive capacity of the solution. For most natural water-rock interactions, the solution loses its reactive capacity (*i.e.*, chemically equilibrates with the rock) after reacting with just a fraction of its weight of rock, and therefore only low concentrations of metal can be achieved in the leachate. For example (Table 2), the reaction of seawater with a basalt to form smectite, requires a water:rock ratio of 42:1. If 50 ppm metal were leached from the basalt, the final concentration of metal in solution would be about 1 ppm minus the amount incorporated into the secondary alteration mineral assemblage. At the other end of the scale, the conversion of basalt into a chlorite-epidote-actinolite-albite-quartz assemblage (*i.e.*, typical greenschist) requires only hydration. In this case, the reactive component of the solution is the water itself and does not depend upon the supply of dissolved components. The reaction could proceed to completion at a water:rock ratio of 1:30 and result in more than 1500 ppm metal in the pore fluid if 50 ppm metal were leached from the basalt. Interpreted in terms of this leaching constraint and the specific seawater-basalt reactions involved (Table 2 and Figure 10), the 1 to 10 ppm ore metal concentration of both the experimental and the natural ocean ridge hydrothermal fluids most probably constitutes the labile component of the source rocks. If 10 ppm Zn + Cu represents the maximum labile metal available from a basalt for the water:rock ratios of a convection cell, then ore fluids generated within basaltic rocks which require a higher concentration of metal must have derived this

additional metal from the bound trace metal component of the source rock.

The most favourable circumstance for leaching the bound metal component of a rock and achieving maximum concentrations of the trace metals in the pore fluids is during thermal or barometric metamorphism of a stratal aquifer. Under these conditions, the mineral-destructive reactions are transformations of one mineral assemblage into another due to changes of temperature and/or pressure. During these mineral-mineral transformations, the bound trace metals have the opportunity to partition into the pore fluid which, in essence, is not a major reactant in the reactions. Since pore fluids in a geopressured stratal aquifer are not continually replaced, leaching of the bound trace metal will continue until the pore fluid becomes saturated with respect to the metals.
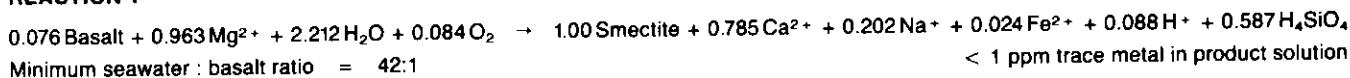
Both the reactive capacity and leaching ability of a solution increases with increasing salinity. The reactive capacity of a pore solution is largely due to the cationic concentration and the leaching ability, *via* metal complexing, is due to the anionic concentration.

It is noteworthy that the most metal-rich modern natural hydrothermal solutions are chloride-rich brines of stratal aquifers (*e.g.*, Salton Sea, oil field brines of Gulf Basin). It is also significant that these brines are saturated with respect to sphalerite and galena (Lydon, 1983; Kharaka *et al.*, 1986) and have Zn:Pb ratios in the range 3:1 to 5:1. These ratios therefore reflect the range of Zn:Pb ratios of solutions saturated with sphalerite and galena when the metals are in solution dominantly as chloride complexes and in the temperature range 100-300°C.
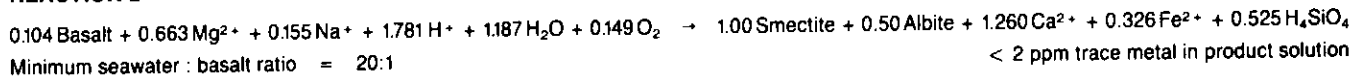
If the ore fluids for most major VMS deposits were saturated with respect to the main ore components prior to commencement of ore accumulation, then the bimodal distribution of Zn:Pb ratios of VMS deposits (Lydon, 1984a, fig. 4) may have an explanation other than the relative abundances of these metals in the source rocks. The great majority of the Zn-Pb-Cu type have Zn:Pb ratios in the range 2.5:1 to 5:1, and this strongly suggests that the pristine ore fluids were chloride-rich solutions saturated with respect to sphalerite and galena, in which the dominant metal species were chloride complexes. In turn, this implies that the ancient ore fluids contained much greater concentrations of Zn and Pb than the undersaturated fluids of modern vents. The Cu-Zn association may also be alternatively explained by metal-saturated solutions if the metals were transported mainly as bisulphide complexes. The solubilities of both chalcopyrite (Crerar and Barnes, 1976) and sphalerite (Barnes and Czamanske, 1967) as bisulphide complexes are about 100 times greater than that of galena (Giordano and Barnes, 1979) under comparable conditions.

Table 2   Some reactions involving the alteration of basalt to hydrous secondary mineral assemblages. The concentration of trace metal in the product solution is calculated assuming that a total of 50 ppm trace metal is lost from the weight of basalt which reacts with the solution. The minimum seawater:basalt ratio is calculated from the weight of seawater (containing 1350 ppm Mg) required to supply the weight of magnesium and/or water required to supply the reactants.
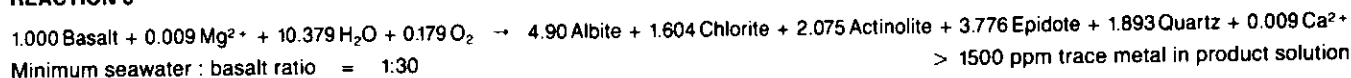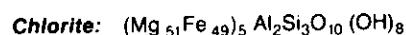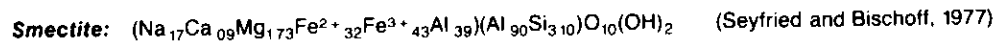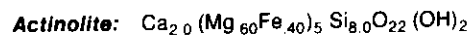
REACTION 1

0.076 Basalt $+ 0.963\,Mg^{2+} + 2.212\,H_2O + 0.084\,O_2 \rightarrow 1.00$ Smectite $+ 0.785\,Ca^{2+} + 0.202\,Na^+ + 0.024\,Fe^{2+} + 0.088\,H^+ + 0.587\,H_4SiO_4$

Minimum seawater : basalt ratio $=$ 42:1 < 1 ppm trace metal in product solution

REACTION 2

0.104 Basalt $+ 0.663\,Mg^{2+} + 0.155\,Na^+ + 1.781\,H^+ + 1.187\,H_2O + 0.149\,O_2 \rightarrow 1.00$ Smectite $+ 0.50$ Albite $+ 1.260\,Ca^{2+} + 0.326\,Fe^{2+} + 0.525\,H_4SiO_4$

Minimum seawater : basalt ratio $=$ 20:1 < 2 ppm trace metal in product solution

REACTION 3

1.000 Basalt $+ 0.009\,Mg^{2+} + 10.379\,H_2O + 0.179\,O_2 \rightarrow 4.90$ Albite $+ 1.604$ Chlorite $+ 2.075$ Actinolite $+ 3.776$ Epidote $+ 1.893$ Quartz $+ 0.009\,Ca^{2+}$

Minimum seawater : basalt ratio $=$ 1:30 > 1500 ppm trace metal in product solution

MINERAL FORMULAE

Smectite: $(Na_{17}Ca_{09}Mg_{173}Fe^{2+}{}_{32}Fe^{3+}{}_{43}Al_{39})(Al_{90}Si_{310})O_{10}(OH)_2$ (Seyfried and Bischoff, 1977)

Chlorite: $(Mg_{51}Fe_{49})_5\,Al_2Si_3O_{10}\,(OH)_8$ Approximate average compositions

Actinolite: $Ca_{20}\,(Mg_{60}Fe_{40})_5\,Si_{8.0}O_{22}\,(OH)_2$ in altered ocean floor basalts
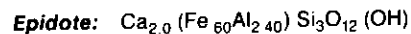
Epidote: $Ca_{2.0}\,(Fe_{60}Al_{240})\,Si_3O_{12}\,(OH)$ (Humphris and Thomson, 1978).

Albite: $Na\,Al\,Si_3\,O_8$
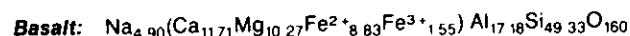
*Basalt:* $Na_{4\,90}(Ca_{11\,71}Mg_{10\,27}Fe^{2+}{}_{8\,83}Fe^{3+}{}_{1\,55})\,Al_{17\,18}Si_{49\,33}O_{160}$ Barth unit cell from analysis by Seyfried and Bischoff, 1977

Figure 10 (right) *Summary of experimental data on seawater-basalt interaction showing quenched pH and alteration mineral assemblages for experiments of more than 14 days duration (filled squares: Bischoff and Dickson, 1975; filled circles: Hajash, 1975; filled triangles: Seyfried and Bischoff, 1979; open squares: Seyfried and Bischoff, 1977; open circles: Mottl and Holland, 1978). Bars join pH measurement at the end of 14 days and at the end of the run.   Curve for chlorite-albite-(+quartz) calculated assuming 1 m NaCl and an activity of Mg^2+ equal to that for smectite-albite stability at the same temperature.   Reactions, mineral compositions, and leached metal concentrations as shown in Figure 9   Boundary between fields of H$_2$S(aq) dominance and HS- dominance: Curve A calculated from data of Brewer (1982); Curve B calculated from data of Ellis and Giggenbach (1971).*
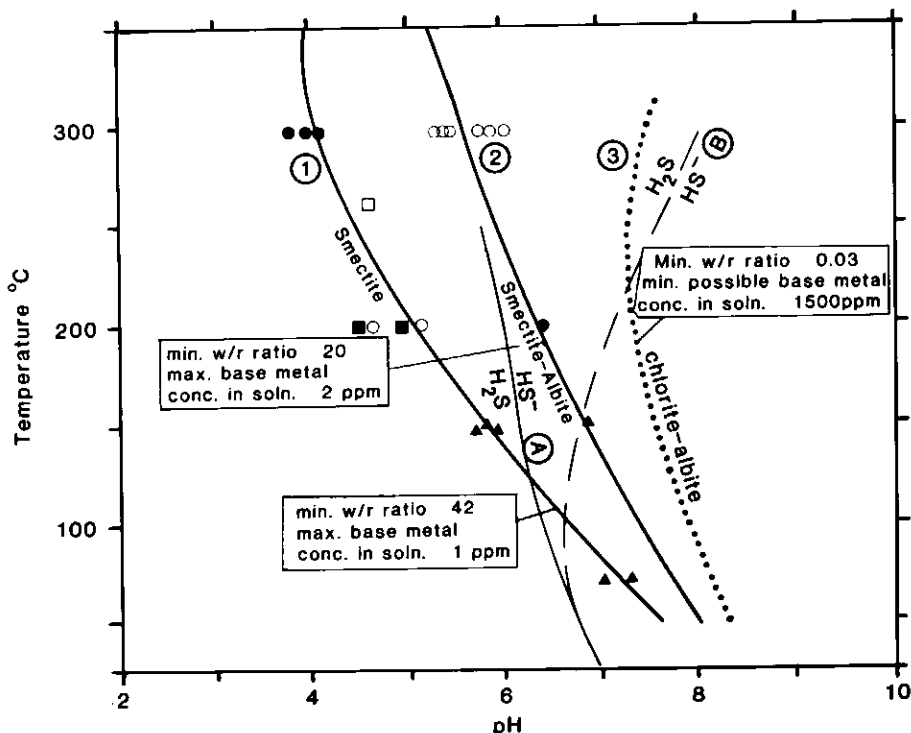
A thermodynamic evaluation of the implications of metal transport as bisulphide complexes with regard to the formation of VMS deposits is complicated by the uncertainties in the thermodynamic values for aqueous sulphur species at elevated temperatures. The maximum solubilities of both chalcopyrite and sphalerite as bisulphide complexes occur near the boundary between the fields of H_2S (aq) and HS^- dominance (Figure 11). The data of Ellis and Giggenbach (1971) (the values used most commonly in recent geological literature) indicate that these solubility maxima occur at a pH between 7 and 8 at temperatures above 200°C (Figure 10) and are separated from the field of comparable metal solubilities as chloride complexes at lower pH by a pronounced metal solubility minima. Since, at temperatures above 200°C the solubilities of both chalcopyrite and sphalerite as bisulphide complexes are relatively insensitive to temperature change but very sensitive to the sulphur content of the fluid, it would be difficult to explain the Cu-dominant to Zn-dominant zonation of the Cu-Zn type of VMS deposit if the metals were precipitated directly from bisulphide complexes.

However, the recent assessment and compilation of thermodynamic data for aqueous sulphur species by Brewer (1982) indicates that the boundary between H_2S (aq) and HS^- dominance is located at a much lower pH than reported by Ellis and Giggenbach (1971) (see Figure 10). Brewer's (1982) data base indicates that, providing the solution also contains > 1 molal chloride, the progressive desulphurization of the fluid above 200°C would cause precipitation of much of the

copper as chalcopyrite, but zinc would remain in solution as a zinc chloride complex (compare Figure 6 and Figure 11). Only on subsequent cooling of the solution would sphalerite precipitate. Thus, if Brewer's (1982) data base is correct, ore components for the Cu-Zn type of VMS deposits may be transported dominantly as bisulphide complexes (thereby suppressing the mobility of Pb), but the temperature dependent Cu-Zn zonation characteristic of the deposits (which requires precipitation from a solution in which metal chloride complexes are dominant) would still be permissible.

Whether the metals are carried as chloride complexes or bisulphide complexes depends, if the data of Ellis and Giggenbach (1971) are correct, predominatly on the pH of the fluid (and hence the mineral assemblage of the hydrothermal reservoir rocks controlling the pH — see Figure 10 for examples). On the other hand, if Brewer's (1982) data are correct, it will depend predominantly on the Cl:S ratio of the fluid.

There are some supportive arguments for a fundamental dichotomy between the chemical compositions of, and mode of metal transport in, ore fluid that formed the Cu-Zn and Zn-Pb-Cu types of VMS deposits, respectively. Only one will be given here. Barite, which is common in many deposits of the Zn-Pb-Cu type (e.g., Kuroko, Buchans) is characteristically absent from deposits of the Cu-Zn type. Significant mobilization of barium in the natural environment requires reduced acidic conditions, because under oxidized conditions it has a low solubility with respect to barite and under reduced neutral to alkaline conditions it has a low

solubility with respect to barium silicates (celsian, cymrite, hyalophane, etc.). Because the Ba:Zn ratios of average mafic, felsic and argillaceous rocks are not significantly different, the marked dichotomy of Ba:Zn ratios between deposits of the Cu-Zn type and many of those of the Zn-Pb-Cu type requires an explanation other than the trace element composition of the source rocks. On balance, the most probable explanation is that the ore fluids which formed ancient Cu-Zn VMS deposits were characteristically more alkaline than fluids which formed Zn-Pb-Cu VMS deposits, and this suggests a greater probability that the metals were transported dominantly as bisulphide complexes for the former, but as chloride complexes for the latter type. In the case of barite-free Zn-Pb-Cu deposits (e.g., Brunswick No.12), the absence of barite in ores can be explained by the lack of seawater sulphate due to anoxic bottom conditions, rather than by lack of barium in the ore fluid. However, it is extremely unlikely that the same argument can account for its characteristic absence in the Cu-Zn type of VMS deposits, because this would require that hydrothermal discharge from ancient mafic volcanic complexes occurred only at the time of stratified ocean conditions. The fact that barite is common in the modern "Cu-Zn" type of mound-chimney deposits suggests that the modern hydrothermal fluids are compositionally different, particularly with regard to their pH values, from those fluids which formed ancient Cu-Zn VMS deposits. If this is so, then the ore metal content of modern hydrothermal fluids may also not reflect typical metal concentrations of ore fluids that formed ancient VMS deposits.

Sulphide accumulation. The above discussions, particularly with regard to the size differential between ancient VMS deposits and the modern mound-chimney deposits, have suggested that ore fluids responsible for at least large ancient VMS deposits may have contained many times the concentration of ore metals than do the fluids emanating from modern vents. This, in turn, implies that the ancient ore fluids were more saline than the modern submarine vent fluids of the eastern Pacific, because the latter are close to saturation with respect to at least copper and iron sulphides (Janecky and Seyfried, 1984), and therefore an increase in metal concentration requires an increase in the concentration of the metal-complexing species (e.g., chloride). Comparison of the Juan de Fuca fluids with EPR 21°N fluids (Table 1) may illustrate this point, because in the former, despite their lower temperature (and therefore their lower Cu concentration — see slope of Cu contours Figure 6), the higher chloride concentration allows a higher zinc concentration. Elevated salinities may enhance the efficiency of sulphide accumulation by the mechanisms envisaged by Sato (1972) for the reversing buoyancy plumes of his Type II solutions (Turner and
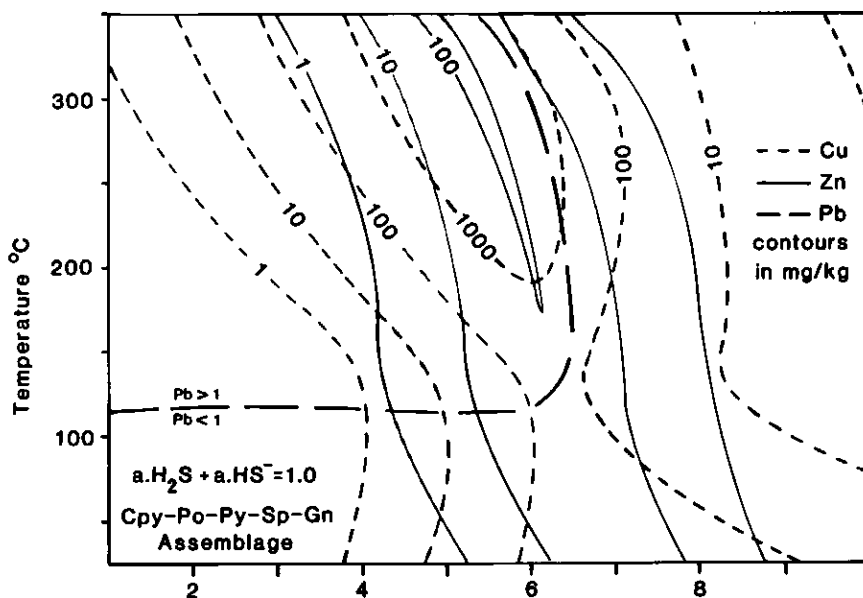

Figure 11 *Sulphide solubilities as bisulphide complexes. Calculated metal concentrations (in mg·kg⁻¹) in a solution in which the total sulphur concentration is 1 molal and which is in equilibrium with a chalcopyrite-pyrite-pyrrhotite-sphalerite-galena assemblage. Metal bisulphide thermodynamic data as listed by or extrapolated from Barnes (1979). Thermodynamic data for aqueous sulphur species from compilation by Brewer (1982).*

Campbell, 1987). The supergiant member of a VMS cluster (Sangster, 1980) could be explained if a single submarine depression acted as a collector basin for all the bottom-hugging brines discharged within a topographic catchment area that was many times larger than the area of the brine pool itself. This topographic effect could also counteract the dispersal effect of vent migration associated with a long-lived convection cell. It is noteworthy that to explain the unusually heavy oxygen isotope compositions of hydrothermal alteration associated with the Kidd Creek deposit, Beaty and Taylor (1982) suggested that the fluids were derived from an evaporitic basin or sedimentary rocks. Since modern hydrothermal fluids derived from such geological environments are typically highly saline, the involvement of a high-salinity ore fluid in forming the Kidd Creek deposits would also be consistent with the observation made earlier that the high aspect ratio of this deposit suggests deposition from a brine pool.

The origin of the fragmental rock pile over the hydrothermal vent area, suggested here to be important in the initiation of sulphide accumulation in proximal VMS deposits, has important repercussions for both genetic and exploration models. The association of fragmental rocks and submarine hydrothermal vents could be semi-fortuitous in that there may be no direct genetic link between the two. For example, hydrothermal discharge could be channelled into a pile of pyroclastic rocks by virtue of following the eruptive magma conduit, or be channelled into fault scarp talus by following the fractures of the fault system. However, in many cases, there is good evidence that the fragmental rocks (and later fragmental sulphides) are the result of hydrothermal eruption, and an integral part of the ore-forming hydrothermal system. The inverted cone-shape of the brecciated rocks of the stockwork zone, marked by an increase in the degree of brecciation and void creation upward, is typical of a hydrothermal eruption vent (Hedenquist and Henley, 1985). Eruptive fragments of footwall, stockwork and sulphide rocks that occur in the massive sulphide lens (Clark, 1983; Lydon and Galley, 1986) indicate that the ore-forming hydrothermal discharge was recurrently explosive. Consideration of the P-V energy requirements indicates that eruptive hydrothermal discharge is unlikely to take place at water depths in excess of about 1 km if the ore solutions are evolved seawater (Lydon, 1986). Explosive hydrothermal discharge may take place at much greater depths due to water exsolution from a crystallizing magma (Burnham, 1983), but in the context of the genesis of VMS deposits, this mechanism would require that the ore fluids have a substantial magmatic water component.

Eruptive hydrothermal discharge, as a common feature in the genesis of VMS deposits, gives a ready explanation to the phenomenon of the "favourable horizon". This would represent the time interval during which a growing volcanic edifice was at a water depth range of about 1 km to 300 m below the ocean surface. Below 1 km depth, hydrothermal eruption could not form a blanket of eruption breccia, and at depths much shallower than 300 m, the hydrothermal solution would have a maximum temperature of 200°C, which is too low for it to carry sufficient quantities of metal to form a significant VMS deposit. VMS deposits can, of course, form at a greater depth if the porous vent capping is other than a hydrothermal eruption breccia. In this context, it may be significant with regard to the genesis of the Corbet deposit, which occurs stratigraphically below the favourable horizon at Noranda (see Lydon, 1984a, fig. 1), to note that it was formed within a pile of previously erupted pyroclastic and volcaniclastic breccias (Knuckey and Watkins, 1982).

Conclusions

Discovery of sulphide mound-chimney deposits on the modern ocean floor has not only provided corroboration of the hydrothermal exhalative model for the genesis of VMS deposits, but has also provided new impetus and opportunity to achieve an understanding of the ore-forming processes. The most important advances have been derived from the measurements, both chemical and physical, of the ore fluids and the incorporation of this quantitative data into mathematical models of the hydrothermal system and the precipitation of hydrothermal minerals. Detailed documentation of the structure of modern sulphide chimneys and pristine ancient deposits, particularly the Kuroko deposits of Japan, have provided observations against which aspects of the mathematical models can be tested and refined.

If one concept is to be singled out for its impact on our overall appreciation of the genesis of VMS deposits, it must be that the growth of a proximal massive sulphide lens is largely due to sulphide accumulation by open space filling and replacement *within* the lens. It is this intra-mound deposition and reworking under the influence of a conductive and advective thermal gradient that produces the characteristic Cu to Zn zonation.

However, there are still many major problems for which totally satisfactory answers have yet to be given. Of fundamental importance is the nature of the hydrothermal system that most commonly forms VMS deposits. Although convection cells appear to be able to form smaller proximal VMS deposits, it may be unreasonable to suppose that a single convection cell can give rise to the larger ones like Kidd Creek, Brunswick No.12 and Rio Tinto. It may be that at least these larger VMS deposits are genetically more akin to the large-tonnage SEDEX deposits (e.g., Mount Isa, Sullivan, Howards Pass) for which a stratal aquifer model is more appropriate. Similarly, although deposition of sulphides as hard encrustations and infillings within a rigid sulphide mound appears to satisfactorily account for many of the textural features and the mineralogical zonation pattern of many proximal VMS deposits, one cannot ignore the numerous descriptions of gel-like textures and rhythmically layered sulphides in other deposits. Perhaps sulphide oozes, possibly of similar constituency to the Red Sea metalliferous muds, were an important primary component in those VMS deposits that do not so perfectly fit the idealized proximal model described here. Of paramount importance are the compositions of the ore fluids, particularly those for the largest VMS deposits. Elevated salinities of ore fluids certainly increase the probability of forming larger sulphide deposits, both through their increased metal-transporting capacity and their increased tendency to form reversing buoyancy plumes upon discharge at the sea floor which increases the efficiency of accumulation of suspended sulphide particles. Although evolved seawater is the favourite candidate, the nature or cause of its evolution into the optimal ore fluid has not been narrowed down to a single explanation. As recently discussed by Von Damm and Bischoff (1987), the evolution of seawater toward a higher chloride content alone has six plausible explanations, and to evaluate them requires more understanding of sub-surface processes than exists at present. The debate on the generation of ore fluids for VMS deposits is obviously far from reaching a consensus.

Perhaps the major conclusion that emanates from the observations and calculations of the last decade is that it is perhaps a mistake to look for one genetic model to explain all VMS deposits. From observations on modern deposits alone, it is apparent that sulphides can accumulate from buoyant plumes as well as dense brines; they can form on volcanic or on sedimentary substrates; and they can occur in the topographic lows of rift structures or on topographic highs of seamounts. There are therefore few simple "rules of thumb" that are widely applicable for the prognostication of undiscovered VMS deposits. The most important factor in such prognostication is an understanding of the fundamental processes involved in the genesis of VMS deposits, and it is only this knowledge that will allow a prediction of how these processes will express themselves in a particular geological environment.

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