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Volcanic-associated massive sulphide deposits—an update.

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Abstract

Volcanic-associated massive sulphide deposits are classified according to their metal contents into copper-zinc, zinc-copper-(lead) and zinc-lead-copper groups. The first group includes deposits formed primarily in a basaltic domain, and under deep water; the second formed in shallower water, also with basalt as a significant footwall component; the last formed in areas dominated by felsic volcanic and/or sedimentary rocks. Alteration pipes are primarily chloritic for the Cu-Zn deposits, quartz-sericite-carbonate for the Zn-Cu-(Pb) deposits, and quartz-sericite-chlorite for Zn-Pb-Cu deposits; lower semiconformable alteration zones (LSZ) are, for the first two groups respectively, silicified, and carbonatized; little is known regarding this aspect of the third group.

Active metalliferous hydrothermal vents occur in at least four environments on the sea floor; 1. abundant but very small deposits occur in volcanically active intermediate to fast spreading ridges such as 12°N and 21°N on the East Pacific Rise; 2. larger deposits (up to 1 million tonnes) are forming in volcanically inactive, or mature ridge crests; 3. very large deposits (up to 2 million tonnes) occur on off-axis seamounts; 4. highly sedimented ridge crests have the potential for the largest deposits, as sulphides may form within sedimentary domes, thus protected from oxidative destruction by the sediments.

Sulphide mounds form by 1. initial precipitation of anhydrite on a bacterial or tube-worm substrate, 2. overgrowth of sulphides on the anhydrite, and 3. replacement of early-formed sulphides by higher-temperature minerals as the mound grows and is heated from within by temporarily trapped high temperature fluids.

From direct measurements of the seafloor hydrothermal fluids as well as from experimental data, it has been determined that in basaltic terrains, a metalliferous fluid can develop only at temperatures in excess of about 400°C, under low water/rock ratio conditions. The specific gravity of a fluid of this temperature is dependent on the total pressure, in turn a function of water depth. The velocity at which this fluid exits onto the sea floor is controlled by the density difference between this fluid at the base of the hydrothermal reservoir and the sea floor. This difference is much greater for deposits forming at depths of 2 500m than for those at 1 000m. Thus the exit velocity for fluids in the former regime is much greater than for fluids in the latter. The higher the exit velocity, the greater the amount of cold seawater that is drawn down around the vent. This cold water is the source of the magnesium that forms the chloritic pipe associated with the Cu-Zn deposits. Deposits which formed under shallower water do so from fluids exiting at lower velocities; cooling of this ore fluid in the absence of a large volume of refluxing seawater would produce a silicified, sericitized alteration pipe.

Silicification of the LSZ probably occurs where the hydrothermal fluid is rapidly superheated by a new influx of magma into a subvolcanic intrusion, driving the fluid composition past the silica solubility maximum, and inducing rapid precipitation of quartz. Carbonatization of the LSZ occurred where the hydrothermal fluid reached the two-phase boundary above the critical point, possible only where the water is relatively shallow; a CO_2 rich vapour phase probably separated and moved up rapidly through the footwall rocks to form carbonate in the immediate subsurface through mixing with unmodified seawater.

Introduction

During the past 10 years, many comprehensive reviews of the geological environments and genetic models of volcanic-associated massive sulphide deposits have been published (e.g. Sangster and Scott, 1976; Solomon, 1976; Klau and Large, 1980; Franklin et al, 1981; Lydon, 1984a). Also, many new studies have been published on individual deposits or massive sulphide districts, including a major volume on the results of a comprehensive examination of the Kuroko district (Ohmoto and Skinner, 1983). Perhaps the most scientifically significant finding of the past decade in relation to this deposit type has been the discovery of the active high-temperature (~400°C) hydrothermal vents on the spreading ridges of the eastern Pacific Ocean, with their attendant accumulations of copper-zinc massive sulphide deposits (e.g. Edmond et al, 1979). At these vents, a variety of massive sulphide deposits are forming, providing the scientific community with a unique opportunity to study the ore-forming process directly, thus avoiding some of the difficulties encountered in interpreting observations and measurements made on preserved deposits. The student of volcanic-associated massive sulphide deposits must remember, however, that the seafloor deposits represent a rather specific member of a complex spectrum of deposit subtypes, and that conclusions drawn from these studies have somewhat limited application to other members of this spectrum. Deposits in the active spreading ridges may not have a totally direct analogy with massive sulphide deposits preserved in the geological record. However, many of the physical and chemical characteristics which control the composition of the ore-forming fluid are

not directly dependent on the tectonic environment; the temperature of the fluid, the water/rock ratio of the environment in which the metals enter the ore-forming fluid, and the mineralogical composition of the rocks in the reaction zone are the principal controls.

With the wealth of new information available on massive sulphide deposits, only a few aspects may be dealt with in a brief review of this type. It will concentrate primarily on two aspects, alteration of the footwall rocks and the seafloor hydrothermal vents.

Alteration associated with these deposits is important not only because it represents various aspects of the history of formation of the deposits, but also because altered rocks usually extend over a sufficiently large area to be useful as an exploration guide. The form and composition of the alteration zones seem to be in part a function of both the physical nature and composition of the footwall rocks, as well as in part a function of the composition of the oreforming solutions.

Many new observations of the active seafloor hydrothermal vents have been made over the past year, but little summary information is available. These data are important in modifying our genetic models, but also are of use in judging the economic significance of these discoveries.

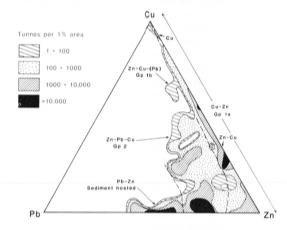
Classification of massive sulphide deposits has been dealt with at length by Franklin et al. (1981). and Lydon (1984a), as well as in earlier reviews by Hutchinson (1973) and Sangster (1972). Following the axiom that the best classification system is that which is applied with a minimum of necessary interpretation of the geological setting or quantitative measurement of various geological criteria (e.g. abundance of lithologies), the system established by Franklin et al. (1981) and further refined by Lydon (1984a) will be followed. This requires only that the deposit to be classified fits the criteria of being concordant and stratiform (at least in part), that it occurs in volcanic or volcaniclastic rocks, and that its copper, zinc and lead contents be known. The classification is based on the last mentioned compositional characteristics. Figure 1 illustrates the non-continuous nature of the compositions of these deposits, which are divided into two groups, (1) copper-zinc, and (2) zinc-leadcopper deposits. The copper-zinc group includes all of those deposits formed in environments dominated by basalt, such as the Pre-Cambrian shields, the Norwegian Caledonides, the ophiolite areas of Cyprus and Oman, the Besshi district of Japan, and the seafloor deposits of the eastern Pacific Ocean. The lead-zinc-copper group includes deposits in environments dominated by either felsic volcanic rocks or volcaniclastic sedimentary strata. The deposits of the Iberian Pyrite Belt, the Green Tuff region of Japan, the Bathurst (New Brunswick) district in Canada, and the Tasman Geosyncline of Australia are representative of this latter group. In the Irish context, the Avoca deposit of County Wicklow is probably in the copper-zinc group, although its geological setting is poorly established due to the extreme deformation and alteration of its associated wallrocks.

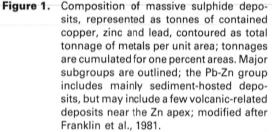
Since implementing this twofold classification system in 1981, an additional subgroup (1b) within the copper-zinc group has become evident. A few deposits within the Pre-Cambrian Shield of Canada have a higher lead content than that which is typical of the latter group; these are typified by the Mattabi (7.98% Zn, 0.83% Cu, 0.76% Pb, 90 g/t Ag) and Kidd Creek (6.00% Zn, 2.46% Cu, 0.2% Pb, 70 g/t Ag) deposits in the Superior Province, and deposits in the Hackett River area of Slave Province (6.83% Zn, 0.32% Cu, 1.19% Pb, 190g/t Ag) (Franklin and Thorpe, 1982).

Most of these have unusually high Pb/Zn ratios, compared with other copper-zinc deposits, but do not fall in the compositional range defined by Lydon (1984) for the zinclead-copper group. Also, most of the deposits in this subgroup have unusually high silver contents in comparison with all other deposits.

Alteration

Since the early descriptions of alteration at Noranda, Quebec (Price, 1953), attention has been focussed on this phenomenon, initially as it provided a useful exploration guide, and more recently because its mineralogical, chemical and isotopic characteristics have provided a window through which the chemical and physical characteristics of the mineralizing process may be interpreted. Alteration occurs in two stratigraphic positions, relative to the palaeoseafloor on which the sulphides accumulated. Best known are the alteration pipes, which occur immediately below the massive sulphide zones; these have a wide range of mineralogical characteristics, which are partially a function of the composition and physical characteristics of the host rocks and the ore-forming fluids, and partly, apparently, a function of the depth of water under which the deposits formed. Less well known, but very important from a genetic





as well as from an exploration viewpoint, are the "lower, semi-conformable" alteration zones (Franklin et al., 1981) which occur several hundreds of metres or more below the massive sulphide deposits, and may represent in part the "reservoir zone" (Hodgson and Lydon, 1977) where the metals and sulphur were leached (Spooner and Fyfe, 1973) prior to their ascent to, and expulsion on, the seafloor. The types and characteristics of alteration are summarized in Table 1.

Alteration pipes

Although alteration pipes may be reasonably divided

Deposit Type 1a. Cu-Zn	Pipe	Lower semiconformable		
	Well-defined Mg-chlorite core, marginal halo of sericite.	Intensive silicification approx. 1km below deposit.		
1b. Zn-Cu (-Pb)				
2. Zn-Pb-Cu	Poorly to moderately well-defined silicic and sericitic core, with a broad outer zone of Mg- and Fe-chlorite.			

Types of alteration associated with volcanic-associated massive sulphide deposits

Table 1. Summary of alteration types.

into three groups, each based on its dominant mineral assemblage, the distinction may be less clearly defined than indicated by Franklin et al. (1981). As also described by Urabe et al. (1983), deposits of each of the two major compositional groups have alteration pipes distinguished by somewhat specific mineral assemblages and zonation patterns. Some of the more significant recent observations are described below.

(1a) Copper-zinc deposits: Numerous recent studies of alteration pipes associated with copper-zinc deposits have confirmed the association of distinctly-zoned, chlorite core-sericite rim zonation (Fig. 2). For example, Larson (1984) documents a pipe at the Bruce deposit in the Proterozoic rocks of Arizona that is very similar to the pipe described by Riverin and Hodgson (1980) at the Millenbach mine near Noranda, Quebec. Aggarwal and Nesbitt (1984) describe a talc-enriched alteration pipe beneath the Chu Chua deposit in Palaeozoic rocks of British Columbia that is generally similar to the talcose pipe described beneath the Mattagami Lake deposit, in northern Quebec, by Roberts and Reardon (1978) and Costa et al. (1983). At the Mathiati deposit in Cyprus (Lydon, 1984b) chloritization also characterizes the pipe zone.

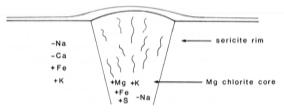


Figure 2. Schematic distribution of mineral assemblages and chemical changes associated with alteration pipes under copper-zinc massive sulphide deposits that formed in deep water (>2 000m).

Several of the above studies have demonstrated that silicification is a more prevalent feature of alteration pipes beneath copper-zinc massive sulphide deposits than previously suggested. Lydon (1984b) indicated that the core of the alteration pipe beneath the Mathiati mine is both silicified and chloritized, with a surrounding zone of chloritic alteration. Alabaster and Pearce (1985) similarly indicate that quartz-chlorite stockworks occur below the Lasail deposit in the ophiolite region of Oman. Aggarwal and Nesbitt (1984) demonstrate that the Chu Chua deposit has a core zone of talc alteration, surrounded by a silica-pyrite alteration halo. Silicification is not ubiquitous, however, as neither Walford and Franklin (1982) nor Costa et al. (1983) describe any silica addition. In fact, in the most intensely chloritized zones, the rocks have undergone silica loss.

The deposits in the Devonian volcanic rocks of the West Shasta greenstone belt stand out as having atypical alteration for copper-zinc deposits. Reed (1984) notes that the alteration pipes are developed in rhyolite, and consist of silicified stockworks with chlorite as a less common alteration product. These pipes extend downward at least 200m below the deposits, continuing into the underlying mafic volcanic rocks.

The chemical composition of alteration pipes is predictable from their mineralogical attributes. MgO increases towards the centre of most pipes, reflecting both an increase in absolute abundance of chlorite (Riverin and Hodgson, 1980) and an increase in Mg content of chlorite in the same direction (e.g. Urabe et al., 1983). Reed (1984) notes that although the chlorite compositions in the alteration zones beneath the West Shasta deposits are Mg-rich, the primary wall rock composition exerts some influence on this, with alteration chlorite in mafic rocks having a higher Mg content than that in felsic rocks. Sodium is generally very depleted in these alteration zones, reflecting the virtually total destruction of feldspar. Potassium is locally slightly enriched in the sericite halo. Interestingly, Reed (1984) established that the alteration sericite is anomalously enriched in sodium, a feature also noted at the Mattabi deposit (described below). Perhaps Na-enriched sericite has been overlooked in other deposits, and might provide an indication of hydrothermal activity. Alumina is generally considered to be immobile, although at the Mattagami Lake deposit (Roberts and Reardon, 1978), some alumina must have been removed to enable the formation of talc. Costa et al. (1983) and Aggarwal and Nesbitt (1984) suggest that some of the talc at the Mattagami Lake and Chu Chua deposits, respectively, is a direct precipitate on the seafloor (cf. Lonsdale et al. 1980, for actively precipitating talc in the Guaymas hydrothermal field). Finlow-Bates and Stumpfl (1981) indicate that in the intense hydrothermal alteration regime typical of most pipes, even the supposed "immobile elements" such as Zr and Ti are redistributed.

Most of the deposits with the "typical" chlorite-core alteration pipes were formed in relatively deep water, based on a limited amount of volcanological data. For example, deposits in both the Noranda and Mattagami Lake areas are immediately associated with pillowed rocks with little vesicularity (e.g. Millenbach andesite, Noranda) and/or massive to vitriclastic felsic tuff, with an absence of pumice (Roberts and Reardon, 1978). Hydroexplosion breccias are generally absent in the immediate vicinity. At West Shasta, however, Reed (1984) notes that the rocks are locally coarse fragmentals, with a considerable pumice component. These latter deposits may have formed in relatively shallow water, compared to the aforementioned deposits. The relation of alteration assemblage to depth of water during the period of sulphide accumulation is further demonstrated with the deposits described below.

(1b) Zinc-copper (-lead) deposits: Although deposits of this subgroup are not numerous, they include the supergiant Kidd Creek deposit (>100Mt), as well as five deposits in the Sturgeon Lake, Ontario, area (Franklin et al., 1977). All occur in volcanic sequences with almost equal amounts of felsic and mafic footwall rocks. The Sturgeon Lake and Kidd Creek deposits have large massive sulphide zones in comparison with their amounts of "stringer" or alteration-pipe sulphide, but the occurrences elsewhere in Superior Province consist almost entirely of stringer or vein-type sulphides.

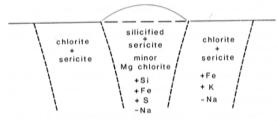


Figure 3. Schematic distribution of mineral assemblages and chemical changes associated with alteration pipes under zinc-copper (-lead) deposits that formed in moderately shallow (1 000-2 000m) water.

The alteration pipes associated with this group of deposits (Fig. 3) are not as clearly defined on a mineralogical basis as those of the other groups. Studies by Franklin et al. (1975), Groves (1984), and Friske (1985) in the Sturgeon Lake area illustrate the following aspects: the core of the alteration zone, immediately below the deposits, consists of highly silicified rocks, with chloritoid, sericite, up to 10% siderite, and alusite, and minor Mg-chlorite, all developed as irregular pod-shaped zones up to several tens of metres in width and thickness. Kyanite occurs near the ore in quartz-sulphide veins. Silicification is controlled by palaeofractures, producing a grid-pattern of alteration in the immediate ten metres below the deposit. Sodium is almost completely removed, and as with the sericite in the alteration associated with the copper-zinc deposits, the sericite in the sodium-depleted rocks beneath the Mattabi deposit is enriched in sodium. The immediate footwall rocks at the Onaman Lake occurrence (Osterberg, 1985) are similarly silicified, but contain abundant kyanite and andalusite. Immediately adjacent to the core zone of the alteration at both Mattabi and Onaman Lake, sericite is dominant.

Beneath the silicified zone at Mattabi is an area of very carbonatized and sericitized rock. The pipe is defined on the basis of the presence of siderite (Franklin et al., 1975), and has, in addition, abundant chloritoid, pods of sericite, and some chlorite. Outside the pipe, the carbonate abundance is similar to that within the pipe (typically 15%), and is stratiform, extending for six to eight kilometres away from the deposit; the carbonate species is ankerite or ferrodolomite in this more distal zone, however. The alteration pipe cuts across this carbonate zone, and extends for at least several hundreds of metres beneath the deposit.

The alteration beneath the siderite deposits in the Michipicoten volcanic belt near Wawa, Ontario is very similar to the alteration at Sturgeon Lake (Morton and Nebel, 1984), with a pipe characterized by siderite, chloritoid and sericite beneath the Helen deposit. Siderite gives way to ankerite away from the core zone, concomitantly with an increase in sericite content. Beneath many of the other iron deposits in the Wawa area, siderite alteration is stratiform, however, and discrete pipes cannot be defined. Base metals are notably absent from the Wawa deposits, although, in the northeastern part of the Michipicoten greenstone belt, a zinc-lead occurrence at Kozak Lake occurs in the same stratigraphic position (Lockwood et al., 1985).

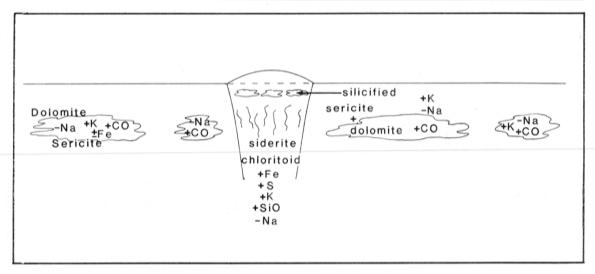
One volcanological characteristic common to all of the deposits with carbonate-rich, chloritoid-bearing alterationpipes is that they are all contained within sequences that have substantial amounts of subaerial volcanic products within a few hundred metres of the deposits. At Mattabi, the immediate 150m of succession below the massive sulphide zone was deposited under no more than 500m of water (Groves, 1984). The volcanic rocks more than 500m below the deposit formed subaerially. Morton and Nebel (1983) demonstrated that the strata beneath the Wawa deposits also were formed subaerially, as illustrated by abundant hydroexplosion breccia and non-welded pyroclastic flows.

(2) Zinc-lead-copper deposits: Although deposits of this group are amongst the largest volcanic-associated massive sulphide deposits in the world (e.g. the Iberian Pyrite Belt; Bathurst, New Brunswick; Green Tuff belt of Japan), their alteration remains less well documented than that for the other groups. This is in part because of the degree of deformation (e.g. Bathurst), although the Japanese deposits have been described thoroughly (Urabe et al., 1983; Date et al., 1983; Bryndzia et al., 1983).

The zonal pattern of alteration beneath the Kuroko deposits established by Shirozo (1974) is applicable to most of the Kuroko deposits. The core of the alteration pipe is composed of sericite,quartz and pyrite. This is surrounded by a chlorite-quartz-sericite zone, which gives way outwards to a mixed layer clay-sericite-chlorite-quartz assemblage, then an albite-sericite-chlorite-quartz assemblage, and finally, in the outermost parts of the alteration pipe, to a kaolinite-quartz-sericite \pm chlorite \pm albite zone (Urabe et al., 1983) (Fig. 4). A similar alteration pattern was documented for the Seneca deposit (Urabe et al., 1983).

The chemical composition of the alteration associated with the zinc-lead-copper deposits again reflects the mineralogical zonation. The chlorite compositions in the chloriterich halo are more iron rich than the chlorite from the core zone of the pipes associated with the copper-zinc deposits, but chlorite in the former group also has an increasing Mg content towards the centre of the pipe. Hashiguchi et al. (1981) and Date et al. (1983) demonstrate that sodium has been removed over virtually all of the alteration zones mentioned above, as well as from a broad semi-conformable zone extending for approximately 200m away from the orebody.

Alteration assemblages under other deposits of this group have been reviewed in Franklin et al. (1981). Silicific-





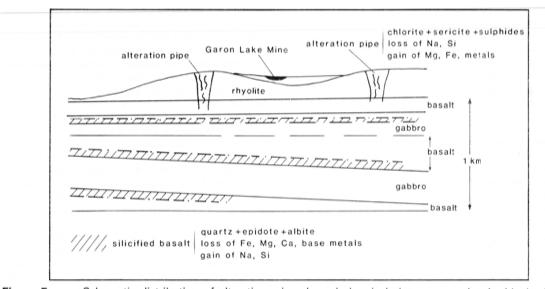
Schematic distribution of mineral assemblages and chemical changes associated with alteration pipes under zinc-lead-copper deposits.

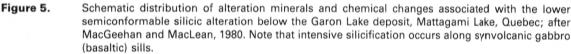
ation and sericitization dominate most of these, and chlorite, where present, tends to be more Fe-rich than that associated with deposits of the copper-zinc group.

Lower semiconformable alteration zones

Compressed metamorphic isograds in the lower parts of the ophiolite sequences at Cyprus (Gass and Smewing, 1973) and in East Liguria, Italy, were explained by Spooner and Fyfe (1973) as being due to increased heat flow through convective heat transfer away from the cooling intrusion at the base of these sequences. They observed fracturecontrolled high temperature alteration (epidote-actinolitequartz), and attributed this to water-rock reactions at temperatures of up to 400°C. These zones are common, but not pervasive, in the footwall rocks at Cyprus. Spooner (1977), in furthering the research on these zones using petrochemical, as well as strontium (Spooner et al., 1977a) and oxygen (Spooner et al., 1977b) isotopic studies, identified them as representing the zone of high temperature hydrothermal reaction, under low water-rock ratio conditions, where the metals and sulphur entered into the oreforming solution.

Subsequently, two important studies, both in basaltdominated terrains, have demonstrated that this high temperature reaction may have caused pervasive alteration under many massive sulphide districts. MacGeehan and MacLean (1980) described a major zone of silicic alteration beneath the deposits on the northern limb of the major anticline at Mattagami Lake. Gibson et al. (1983) describe a different form of silicification beneath the deposits in the Millenbach-Amulet area near Noranda. In addition to these





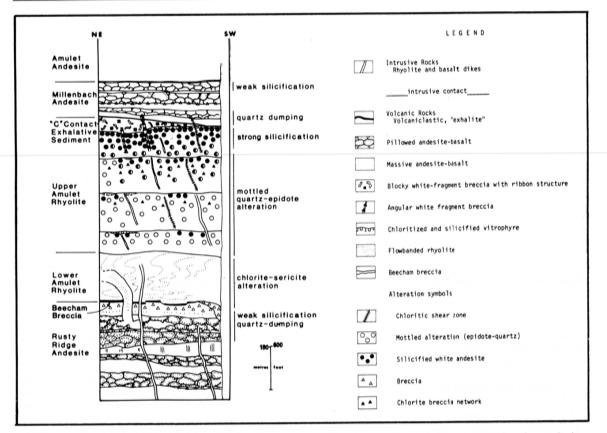


Figure 6. Alteration of the highly silicified mafic volcanic rocks in the Amulet Rhyolite Formation, beneath the Amulet-Millenbach group of deposits, Noranda, Quebec; from Gibson et al., 1983.

documented occurrences, a zone of silicification similar to that at Mattagami Lake has been noted in Proterozoic basalts several hundred metres (stratigraphically) beneath the massive sulphide deposits at Snow Lake, Manitoba (Skirrow, R. G., pers. comm.).

The alteration at Mattagami Lake occurs several hundred metres below the Garon Lake deposit, and is in a section of the footwall stratigraphy characterized by many synvolcanic basaltic sills (Fig. 5).Immediately adjacent to each sill, primarily on its upper surface (stratigraphically) the basalt is intensely altered by silicic veinlets, mantled by quartzalbite and quartz-epidote. These intensely altered zones are a metre or more in width. Adjacent to them, for at least several metres, the basalt is spilitized with secondary albite, epidote, quartz and some chlorite (MacGeehan, 1978). Stratigraphically higher, immediately below the Garon Lake deposit, a typical chlorite-core alteration pipe has formed. MacGeehan and Maclean (1980) determined that the spilitized rocks have gained silica and sodium, and have lost base metals. The alteration pipe, however, is very similar to the typical Noranda pipes described by Riverin and Hodgson (1980). MacGeehan and MacLean (1980) interpret the zones of silicification as the "reservoir" zone, i.e. the source of metals and sulphur for the ore-forming solution.

Gibson et al. (1983) describe a zone of highly silicified basalts in the Amulet Rhyolite Formation approximately 200m below the ore horizon of the Millenbach and Amulet orebodies (Fig. 6). Less pervasive silicification extends to approximately 800m below this horizon. Within the uppermost zone of alteration, the rocks are not only pervasively silicified (their "quartz-dumping" zone) but the silicified rocks have subsequently been brecciated. Below the uppermost zone, the basalts have pervasive quartz-epidote alteration. The entire 600m altered section is albitized, and actinolite is present in the less intensely silicified areas. Near the NE- and NW-striking faults that were the synvolcanic fractures that controlled the hydrothermal discharges onto the palaeoseafloor, the rocks are chloritized, and are compositionally similar to the alteration pipe described by Riverin and Hodgson (1980). Gibson et al. (1983) demonstrated that the chloritic alteration is later than the silicification, and they interpret the silicification as an early, deep-level alteration, formed at moderately high temperature, and representing both a "cap" to the reservoir and also possibly a part of the metal source zone. This zone was breached by the synvolcanic faults, and the high temperature fluids escaped to form the sulphide deposits on the seafloor. During the escape, the uppermost silicified zone was brecciated.

In comparing the silicification zones at Mattagami Lake and Noranda, the former is more clearly related to a zone of high temperature interaction between a hydrothermal fluid and the basalt, as the individual silicified areas are immediately adjacent to basaltic sills. The source of heat for the latter silicic alteration is not as clear, although suggested by Gibson et al. (1983) to be a combination of the cooling flows and a major subvolcanic intrusion near the base of the local volcanic sequence. Both the Noranda and Mattagami Lake alteration zones are similar to that described in Cyprus by Spooner (1977). These zones may be an essential consequence of developing a hydrothermal system in basaltic sequences, and thus are an important exploration guide.

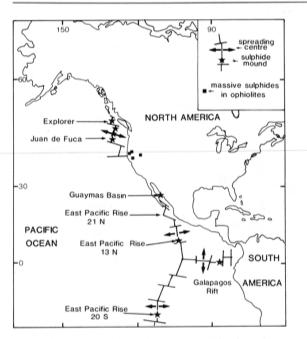


Figure 7. Distribution of active metalliferous hydrothermal centres in the eastern Pacific Ocean.

Lower semiconformable alteration zones of such a pronounced nature have not been located under either the zinc-copper (-lead) (type lb) deposits or the zinc-leadcopper (type 2) deposits. A laterally extensive zone of carbonate-enriched, sodium-depleted rock occurs on either side of the deposits at Sturgeon Lake (Franklin et al., 1977; Friske, 1984), and may be typical of the rocks adjacent to many of the type lb deposits. This zone contains the large areas of ankerite and ferruginous dolomite described above, as well as irregular zones of chloritoid-sericite alteration, and is typically 50m thick away from the deposits (Groves, 1984). The carbonate was emplaced prior to the formation of the alteration pipe, and may have sealed the reservoir in a manner similar to that ascribed to the silicification zone at Noranda (Gibson et al., 1983). No studies of non-pipe alteration beneath the zinc-leadcopper deposits have been completed. On the basis of lead isotope studies, however, Fehn et al. (1983) suggested that the pre-Nishikurozawa rocks, including the Palaeozoic basement to the Green Tuff belt, were the source of the metals for the Kuroko deposits.

Seafloor deposits

Since the discovery of the metalliferous sediments in the axial trough of the Red Sea in 1965 (Miller et al., 1966), and of massive sulphide deposits on the East Pacific Rise (Francheteau et al., 1979; MacDonald et al., 1980), much research effort has been directed towards measuring the compositions of the metalliferous fluids and the sulphide precipitates, and towards establishing the physical and chemical conditions that enabled the formation of high temperature metalliferous brines. Comprehensive papers have been published on each of the discovery areas, including the 21°N (Speiss et al., 1980; Goldfarb et al., 1983) and 13°N (Hekinian and Fouquet, 1985) areas on the East Pacific Rise, the Galapagos Rift (Corliss et al., 1979) and the Guaymas basin in the Gulf of California (Lonsdale et al., 1980). Recent discoveries of hydrothermal activity have been made at least as far south as 20°S on the East Pacific Rise, and northwards along the Juan de Fuca and Explorer Ridges (Fig. 7). Using the submersibles ALVIN and PISCES, many of these new sites were examined closely for the first time during the summer of 1984 (Normark et al., 1984; Merge Group, 1984; Hammond et al., 1984; Scott et al., 1984).

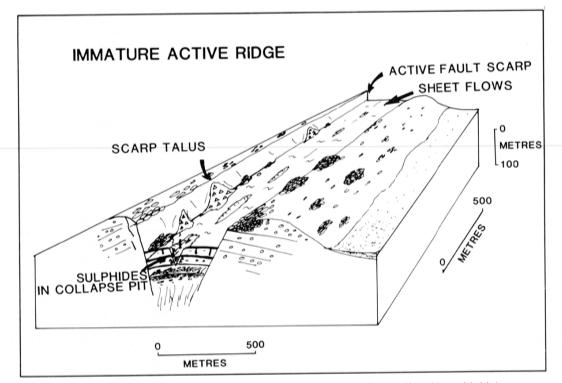
Descriptions of these new discoveries, together with observations on seamounts near 12°42'N on the East Pacific Rise permit the development of a more comprehensive classification of seafloor environments than was first evident from the Galapagos, 13°N and 21°N discoveries.

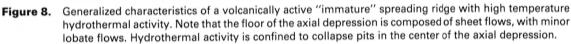
The seafloor hydrothermal deposits may be divided into four groups, based on their geological setting (Table 2). Each of these has a different morphology, and deposits within each vary considerably in size. By combining the observations made in all four environments, a general model for the formation of a sulphide mound can be developed.

Setting	Environment	Sulphide morphology		
1. Immature Ridge	Volcanically active, well-defined central cleft; sheet flows dominate over pillow lavas; collapse pits common in axial zone.			
2. Mature Ridge	Volcanically inactive, highly faulted and fissured zone with distinctive marginal fault zones; pillowed volcanic rocks dominant.	ginal faults.		
3. Seamounts	Distinctive mounds of pillow lavas, cut by major fault zone.			
4. Sedimented Ridges	Volcanically active ridge crests, with sedi- mentary basins (500-1 000m deep) cut by sills; sediments are actively faulted and loc- ally domed by hydrothermal activity.			

Characteristic of modern seafloor massive sulphide deposits

Table 2. Classification characteristics of modern seafloor massive sulphide deposits.





(1) Deposits in immature, actively spreading ridges

The hydrothermally active areas at 13°N and 21°N, and also the southern Juan de Fuca (Normark et al., 1982; Normark et al., 1984) typify these settings. Figure 8 summarizes the features observed in these areas. The rate of spreading varies from 12cm per year at 13°N (Hekinian et al., 1983), to 6cm per year at 21°N and the Juan de Fuca Ridge (Larson, 1971). The rise axis in each area is well defined, typically 3 to 6km wide, with an elevation of 80m (21°N, Speiss et al., 1980) to 250m (13°N, Hekinian et al., 1983) above the rise flanks. The crest usually has an equally well defined central axial graben 100 to 1000m wide and 20 to 50m deep. The graben walls are generally steep normal faults, with abundant talus piles. The floor of the graben is generally smooth, composed of sheet and lobate flows. In the hydrothermally active area, the axial zone is typically elevated (Ballard et al., 1981) relative to the adjacent ridgecrest areas, where hydrothermal activity is absent. The sheet flow areas in the southern Juan de Fuca Ridge are actually the tops of drained-out lava lakes. Each sheet flow top is supported on lava pillars, each about 1 to 2m in height. Commonly, three or four such lava sheets, each separated by 1 to 2m of water-filled space, have been observed; below these, the sheets have collapsed to form a thick sequence of in situ breccia. Collapse pits are common along the central active zone of the graben (Normark et al., 1983). The margins of the central graben are typically composed of pillow basalts. Eruptions of pillow lavas apparently have occurred penecontemporaneously with formation of sheet and lobate flows; the stratigraphy of the graben zone is thus complex. All rocks are very fresh, with little or no sediment cover, and all basalt surfaces are fresh and glassy.

The hydrothermal vents in these active spreading centres are located primarily in the central part of the axial graben (Speiss et al., 1980; Ballard et al., 1981; Normark et al., 1983). Speiss et al. (1980) noted that the fissures that controlled the hydrothermal activity are oriented at about 15° to the trend of the axial graben. In the southern Juan de Fuca area, Normark et al. (1983) noted that most of the hydrothermal activity is localized in axial collapse pits.

The hydrothermally active areas contain two vent forms, the high temperature vents (> 250°C) that are emitting prolific sulphide particulates in many cases (black smokers), and low temperature vents (typically 5°C to 30°C) emitting clear water or, less commonly, white particulates (sulphates) forming a milky effluent (white smokers). In addition, warm water is being emitted from clusters of tube worms ("snowballs", cf. Speiss et al, 1980). Fluids from the high temperature vents have a considerable temperature range, from 250°C to 400°C (Merge Group, 1984). White smokers have temperatures of up to 330°C (Speiss et al., 1980), and there is some overlap in the temperature range of these with black smokers. Furthermore, vents within a single area may have quite different temperatures and attendant precipitation products. The fluids are escaping from the black smokers at a rate of 1 to 5 metres per second (MacDonald et al., 1980).

Individual vents or vent clusters in these actively propagating ridge-crest areas are typically confined to areas 10 to 30m wide. A minimum of 80 vent sites have been recorded in the 13°N area (Hekinian and Fouquet, 1985). The vent areas have small mounds of sulphide at their base. On the Juan de Fuca ridge (Normark et al., 1984) many of the vents and extinct chimneys are isolated, sitting directly on a fresh sheet flow, with no basal mound. The total amount of sulphide in an axial graben of this nature is small; Hekinian and Fouquet (1985) estimate 20,000t of

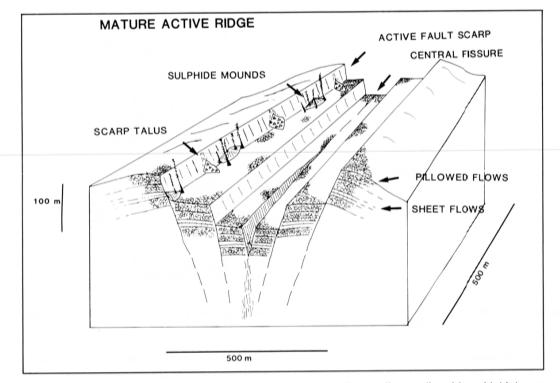


Figure 9. Generalized characteristics of a volcanically inactive "mature" spreading ridge with high temperature hydrothermal activity. Note that the area is composed of pillowed lavas, and that hydrothermal activity is present primarily along faults that are marginal to the axial depression.

sulphide collectively along 20km of axial graben at 13°N. The composition of the sulphides is highly variable (Bischoff et al., 1983). The high temperature areas are composed of copper-rich sulphide chimneys and small pyritic mounds. Slightly cooler vents, such as are dominant in the southern Juan de Fuca area (Normark et al., 1984) are exceptionally zinc-rich (Koski et al., 1982).

Other aspects of the vent sites and compositions of the sulphide chimneys and mounds are shared with those in the more mature ridge-crest areas, and will be commented on later. In summary, the highly active ridge-crests are formed primarily of sheet and lobate flows, and have all of their sulphide accumulations in the central axial cleft zone. The deposits are individually very small, and collectively not of great economic importance.

(2) Deposits in mature ridge crest areas

Recent discoveries in the Endeavour segment of the Juan de Fuca Ridge (Kingston and Delaney, 1983; Hammond et al., 1984) and the Explorer Ridge (Tunnicliffe et al., 1984; Scott et al., 1984) have demonstrated the presence of high temperature hydrothermal activity and sulphide accumulations in areas of the spreading ridges that are probably in their terminal stages of active propagation. The large accumulations of sulphides reported by Malahoff (1982) on the Galapagos ridge may also have formed in this environment. The following review is taken in part from these sources; additional observations by the author, made during the NOAA dive programme using the deep submergence vehicle ALVIN during July, 1984, are also included. Figure 9 illustrates the general features associated with sulphide deposits in this environment.

The rise associated with the mature ridge-crest areas is about 5km wide (Endeavour Ridge), but the degree of development of the central graben is variable. The graben is well defined at the Endeavour hydrothermal site, but less so on Explorer Ridge. The terrain in all of these sites is more rugged than comparable areas in the more highly active ridge crests, with many fissures, pillow mounds, and fault scarps. No well-defined central cleft has been documented. The floor of the axial zone is composed primarily of pillows, with lobate flows and sheet flows relatively rare. Talus slopes are abundant, particularly along the normal faults which bound the central graben. Most of the pillows are coated with one to two centimetres of fine-grained sediment. The basalts are less fresh than in the more active zones described above; glass is beginning to devitrify, and many pillows have thin coatings of manganese oxide (?) and iron oxides. Fresh rocks are confined to localized pillow mounds in the central regions of the graben. Most of the hydrothermally active areas are at relatively shallow depths in comparison with the hydrothermally deficient areas immediately along strike from them, and are thus in areas of somewhat exceptionally active volcanism, a feature shared with the immature ridge crests described above.

The hydrothermal vents are confined to the margins of the central graben, in contrast to the more strictly axial position of the hydrothermal activity in the highly active ridge-crest areas, and occur at the base of the marginal normal faults. They are forming during active fault movement, as sulphide mounds are commonly displaced by faults, and sulphide breccias occur at the base of faulted sections. The fault zones are evidently providing the channelways for the upwardly moving hydrothermal fluids, as most of the sulphide accumulations are either on, or immediately adjacent to, faults or related fissures.

The individual vent clusters form mounds that are 30 to 200m wide, significantly larger than the sulphide areas

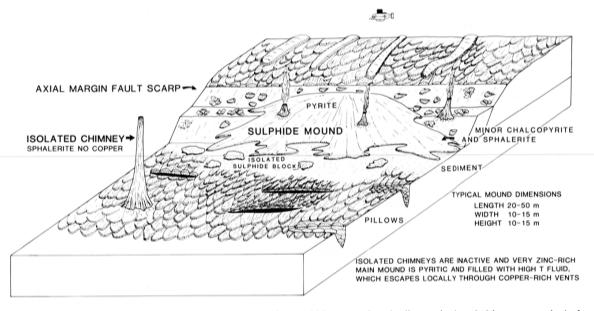


Figure 10. Generalized morphological feature of a sulphide mound and adjacent isolated chimneys, typical of a "mature" ridge-crest zone (see Fig. 9).

described in the immature ridge-crest areas. The individual areas consist of a central mound of sulphide, surrounded by a "forest" of large, isolated chimneys which have formed on the "floor" of the central graben. The morphological features are summarized in Figure 10. The mounds are composed primarily of pyrite, with chalcopyrite and sphalerite as matrix sulphides. The outer surfaces are coated with anhydrite. Both the sulphides and the anhydrite are partially replacing dead tube worms, and also fill the interstices between pseudomorphed tube worm forms. The internal morphology of the mounds is poorly known, due to difficulty in sampling them with a submersible. Active chimneys are randomly located on the surface of the mound. These are typically much smaller than those described at 21°N (Speiss et al., 1980) or 13°N (Hekinian and Fouquet, 1985), with widths at their base of 20 to 70cm, and heights rarely exceeding 3m. Many of the active vents of these mounds have no chimney structures, but consist only of a circular opening, typically 10cm in width, with a lip of anhydrite. The chimneys have an internal lining of isocubanite which gives way outwards to pyrite with chalcopyrite and minor sphalerite. The mounds are full of high temperature fluid; breaking off pieces of the mound surface initiated a new vent. The entire surface area of the mounds away from the very localized high temperature "smokers" is emitting warm (ca. 25°C) clear water. Much of this surface area is coated with anhydrite, with bacterial mats and tube worm clusters commonly growing on it.

The isolated chimneys situated outboard of the main sulphide mound are very large, with bases typically 2m in diameter, and heights of 10 to 15m. Most of these were not observed to be active at the Endeavour Ridge site, indicating that they may have formed earlier in the hydrothermal history of the area. These chimneys are composed almost entirely of wurtzite and sphalerite, with minor pyrite and virtually no chalcopyrite.

The number of individual sites within a single ridge zone is poorly known. S. D. Scott (pers. comm.) estimates that there are at least 40 sites in the Explorer Ridge area. The largest area, Magic Mountain on Explorer Ridge, is reported to be 200m in diameter, (Northeast Pacific News, 1984) and may contain 500 000t of sulphide. Much additional mapping and sampling is required to determine properly the size of these mounds.

In summary, the areas of hydrothermal activity on mature ridge-crests are composed primarily of pillow lavas, with a thin covering of sediment, and are not presently volcanically active. The hydrothermal vents are located near the base of the normal faults which bound the central graben. The sulphides occur in mounds along these faults and as large isolated chimneys on adjacent lavas. The deposits are considerably larger than those in the more active ridge-crest areas.

(3) Deposits on seamounts

These are the most recently discovered areas of hydrothermal activity and sulphide accumulation. Sulphides have been found on a seamount six kilometres to the east of the axis of the East Pacific Rise at 12°42'N (Southeastern Seamount), and completely oxidized sulphide (?) forms, coated with 1 to 3cm of manganese oxide, were observed (CYANA cruise, February 1984) on Clipperton Seamount, 20km west of the East Pacific Rise at 12°35'N (Hekinian and Fouquet, 1985). Neither of these areas are hydrothermally active. Isolated sulphide chimneys and inactive sulphide mounds have been located in two areas of the central caldera of Axial Seamount on the Juan de Fuca Ridge.

The Southeastern Seamount adjacent to the East Pacific Rise rises about 350m above the surrounding floor, and is almost 4km in diameter at its base. It has a distinctive central caldera, but is somewhat irregular in shape, as it is cut by a fault on its western side (Fig. 11). The seamount is composed entirely of pillow lavas. The surrounding seafloor is composed of sheet flows, covered by a few tens of centimetres of sediment. Within a few hundred metres of the seamount, pillow mounds and isolated pillows become more common. On the seamount, the pillows have virtually no sediment cover.

The fault zone which partially displaces a portion of the western flank of the seamount has evidently been the fluid conduit along which the hydrothermal activity was focus-

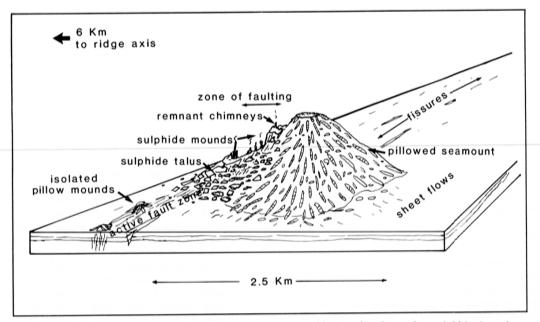


Figure 11. Generalized characteristics of a seamount with associated massive sulphide deposits.

sed. The sulphides occur as a series of mounds along the western flank, with massive sulphides on the basaltic apron, and brecciated sulphide talus forming along the fault scarps (Fig. 11). Chimney forms are preserved on the mounds. The sulphides cover an area of at least 0.25km², and with a minimum thickness of 1m at least 1Mt of sulphide are present. Thus, this single deposit is at least 50 times larger than all of the sulphide observed in the axial zone of the East Pacific Rise near 13° N.

The single published analysis of the seamount sulphides (Hekinian and Fouquet, 1985) confirms the author's observations that the sulphide is highly pyritic, but contains substantial amounts of copper (1.82% Cu, 19.05% Fe, Hekinian and Fouquet, 1985, Table 9). Atacamite is a common coating on the sulphide mounds and blocks, indicating that copper occurs throughout the seamount sulphides.

The distribution of sulphides along a fault system cutting a prominent seamount, together with the very pyritic composition, is closely analogous to the sulphide bodies at Cyprus. Lydon (1984b) has noted the development of talus sulphides adjacent to palaeo-faults cutting the Mathiati orebody. In distribution, size and grade, the Mathiati sulphides are very similar to the sulphide body observed on the Southeastern Seamount.

The sulphide bodies associated with Axial Seamount are less well documented, as each area has been examined by only a few submersible dives. As Axial Seamount is still active, the deposits are relatively small, and seem to be comparable to those in active, immature ridges. More data are needed to understand fully these areas.

(4) Deposits in highly-sedimented active ridge crest areas

Following the discovery of the metalliferous muds in the Red Sea, research attention was focussed on the Gulf of California, which appears to be a close geological analogue to the former area. The Gulf of California has several deep basins that are undergoing active sea-floor spreading. These basins are partially filled by sediment derived from the adjacent continent. They are displaced by active faulting and are cut by thin sills (Lonsdale et al., 1980). They are areas of anomalous heat flow (Williams et al., 1979), and are thus ideal for the development of metalliferous brines.

Lonsdale et al. (1980) reported the discovery of a site of hydrothermal mineralization in the "northern trough", an active ridge in the Guaymas Basin. They recovered a single sample containing talc and minor pyrrhotite. The sulphide portion of the sample contained 0.7% Cu, but no chalcopyrite was detected. Subsequent surveys have not revealed any active hydrothermal plumes in this trough.

Subsequent studies in the Guaymas Basin have determined the presence of approximately 100 sulphide mounds (Scott, 1985) in the "southern trough", an area approximately 12km², approximately 30km south of the area of initial discovery of the talc deposits (Lonsdale and Becker, 1985). The southern trough is an asymmetric fault-bounded rift valley. It has distinctive bounding faults, and several scarps adjacent to the bounding faults are buried beneath 10 to 50m of turbidites (Lonsdale and Becker, 1985). The strata are tilted along these faults. Within the rift valley, the sediments are domed above sills; in the central part of the valley, sediments are at least 400m thick. The sedimentary pile is intruded by mafic sills and plugs (Einsele, 1982), intersected by DSDP holes 477 and 477a (Curray et al., 1982). The sediments above these sills are uplifted into mounds. The DSDP cores and interstitial waters contain evidence of a large heat source, such as a major subvolcanic intrusion, at depth (Curray et al., 1982).

The sulphide deposits occur in clusters on a flat turbidite plain, near the area of small intra-rift hills and low fault scarps (Koski et al., in press). Some deposits lie along the eastern marginal faults. The sulphide mounds are typically 10 to 15m high and 10 to 100m in diameter. Koski et al. (in press) describe the sulphides as being pyrrhotite-rich, compared to deposits found in the sediment-poor axial ridge zones such as the 21°N area on the East Pacific Rise. They note that the deposits are poor in base metals, but relatively rich in calcite, barite and opaline silica. J. Peters (pers. comm., University of Toronto) substantiates the observations of Koski et al.; he observes that the average chimney contains 20.5% SiO₂, 0.235% Pb, whereas the average mound contains 39.0% SiO₂, 0.093% Cu, 0.322% Zn, and 0.093% Pb. A relatively metal-rich chimney has 32.5% SiO₂, 0.43%Cu, 3.78% Zn, and 2.13% Pb. The Guaymas sulphides are clearly much more lead-rich, compared to other ridge-crest deposits, and they fit compositionally into the zinc-lead-copper group of volcanic-associated massive sulphide deposits (Franklin et al., 1981).

Koski et al. (in press) and Scott (1985) both indicate that the hydrothermal system responsible for these deposits formed due to the interaction of evolved seawater with volcanic rocks deep in the rift, and also with the organic and carbonate-rich sediments nearer the seafloor. This suggestion fits with the observation of Franklin et al. (1981) that the more lead-rich deposits formed in environments where either felsic volcanic rocks or clastic sedimentary rocks are a significant component of the footwall stratigraphic sequence.

The sulphide deposits in actively sedimented ridge crest areas are potentially of more economic significance than those in the volcanic-dominated regimes because they seem to be moderately large (up to 1.5Mt, using the maximum dimensions reported by Koski et al., in press). Rapid deposition of covering sediments preserves the sulphides from destruction due to oxidation by the bottom waters. Metals may be obtained through leaching of the sedimentary detritus with relative ease compared to the processes involved in leaching metals from volcanic rocks (discussed below), thus enabling the development of larger metalliferous hydrothermal systems and larger deposits.

Genetic considerations

From the study of the active hydrothermal areas on the sea floor, it is possible to gain a better understanding of the processes of formation (precipitation) of a massive sulphide deposit. From the study of the composition of the fluids that are being expelled from these vent sites, together with data from experiments involving reactions between various rocks and seawater, we can gain some insight into the process of formation of a metalliferous hydrothermal brine. Conclusions drawn from these experiments and direct observations must explain both the alteration patterns observed below preserved deposits, as well as the characteristics of metal distribution within the deposits, if they are to have any value as components of a predictive model for use in exploration.

(a) Formation of sulphide mounds

The extreme buoyancy of the high temperature hydrothermal fluids discharging on the sea floor results in them rising as much as 200m above the vent sites. The fine particulate matter in these plumes is probably rapidly oxidized, and forms a discrete horizontal layer in the water column that may be traced for at least hundreds of metres away from the plume sites (Lupton et al., 1984). Thus, almost none of the sulphide particulate material settles to the sea floor in the immediate area of the "black smoker" sites. The only obvious mechanism operating to form solid sulphides is that which forms the individual chimneys. That process, as described by Hekinian et al. (1984) and Haymon (1983), involves the initial precipitation of anhydrite from rapidly heated entrained seawater at the orifice, and subsequent overgrowth of the anhydrite by pyrite and by other sulphides. Anhydrite is precipitated due to its retrograde solubility; sulphides form in the chimney through nucleation and growth from the cooling of the high temperature fluid as it diffuses out through the anhydrite. Only the coating of isocubanite on the inner wall of the chimney is directly precipitated from the high temperature fluid. As pointed out in the descriptions of the sulphide distribution in the volcanic-dominated ridge crest areas, isolated chimneys do not coalesce to form mounds of dimensions greater than a few tens of metres. Various studies (Haymon and Kastner, 1981; Mottl, 1983) indicated that only a few percent of the sulphide-forming components are actually preserved at the vent site. In order to form larger accumulations of sulphides in modern oceans, the following stages and factors seem important:

(1) The area should be relatively tectonically stable, in order to permit fluids to vent at one location for a period of time sufficient to allow the construction of a mound. Depending on the efficiency of entrapment or containment of the precipitants, this might require several tens or hundreds of years. During the same period of time, a sufficiently sustained source of heat must be available at a shallow level within the oceanic crust (probably approximately 2km) in order to attain temperatures sufficient to dissolve metals into the hydrothermal fluid (discussed below). These two conditions appear to be met best by ridge-crest areas that are in a quiescent stage of propagation, as typified by part of the Endeavour Ridge. In the Endeavour area, Kappel and Ryan (in press) described intense faulting and fissuring, with the elongate summit depression of variable width and depth. They suggest that the collapse of the crestal ridge summit coincides with a period of inactive volcanism.

In the volcanically inactive or "mature" ridge-crest areas, heat is transferred primarily by hydrothermal venting, as volcanic activity is much less intense than in the more active areas such as the East Pacific Rise (13°N and 21°N) and the southern Juan de Fuca area (Normark et al., 1983). The fluids are vented along marginal faults in the "mature" areas, and due to the much reduced volcanic and tectonic activity, they are able to vent at one location for a longer time than in the "immature" ridge-crest areas. Ultimately, thissustained venting should enable the formation of larger deposits.

- (2) In order to form and preserve a large mound of massive sulphide, a substrate on which to form or trap the sulphides must be present. In the chimneys, this is anhydrite. Anhydrite could form along a venting fracture as a semicontinuous mat, but in the present seafloor vent areas, anhydrite forms over broad areas through infilling and replacement of the tube worm clusters. These clusters inhabit low temperature vents, but if subjected to periodic infusions of high temperature fluids, they die and are replaced by anhydrite. Continued expulsion of the high temperature fluid into these replaced tube worm areas results in the formation of an anhydrite mat. This mat can begin to trap some of the particulate material, and also can become the substrate on which the overgrowth sulphides can form.
- (3) The anhydrite mat forms a protective and everrenewing cap to a sulphide body; the sulphides thus can grow from below. High temperature fluids are trapped beneath the mat, and due to cooling and

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Element	Galapagos	21°N	Guaymas	13°N	Seawater	400°Exp	300°Exp
K	735	899-1 017	195	938	398	1 146	1 250
Ca	986-1 611	480-842	1 632	641	413	1 059-1 304	1 224-2 178
Sr	7.6	7.9		7.8	7.6	7.8	7.7
Ba	2.4-5.9	4.8-13			0.02	2.0-3.6	1.5-5
Mn	39-55	40-56	6.2-13.2	33.5	0.0011	37-55	2.2-7
Fe	45-134	38-139	1-1 004	101		103	2
Si	615	603	309-393	618	4.5		
SO4	0	0	0	0	2 696		
Zn	2.6-2.9	7.2	0.26	.0001	0.1	2.0	N.D.
Na		9 851-11 707	_	10 310		_	

Data from Mottl, 1983, and Michard, 1984; also see references in Mottl, 1983. Exp = experimental data.

Table 3. Composition (in ppm) of high temperature fluids from active hydrothermal vents and experimental studies.

mixing with infiltrating cold seawater, precipitation from this trapped fluid results in the formation of a mound of sulphides. As the mound grows, it becomes heated from below by the retarded fluids, and large thermal gradients within it control the dissolution and precipitation of various sulphide species. Chalcopyrite probably precipitates in the highest temperature portion of the mound, with sphalerite mobilized outwards to the flanking cooler zones. This replacement process probably leads to the strong metal zonation evident in many massive sulphide deposits, as demonstrated by Knuckey et al. (1982) for the Millenbach deposit.

The precipitation of sulphides within the mound, due to cooling of the high temperature fluid by mixing with cold seawater that is infiltrating into the mound, is probably a much more efficient mechanism for removing and trapping metals than has generally been appreciated. Although the precipitation mechanisms in the chimneys are very inefficient for preserving the bulk of the sulphide-forming elements, growth within the mound would enable the preservation of virtually all of the metallic constituents. The remaining cooled fluid probably diffuses out of the mounds as the "white smoke" that is so abundant in vent sites.

This sequence of events is consistent with the observations that have been made thus far on the sea floor mounds, and explains both the great variety of textures, including the apparent paragenetic relationships and the metal distribution within preserved deposits.

The appropriate physical setting, generated best in a period of relative tectonic quiescence, is necessary for large sulphide mounds to form. Two mechanisms may explain why many of the preserved deposits are much larger than those preserved in the volcanic-dominated ridge crests. Anoxic water may have been prevalent during the Archaean, and at the base of a stratified water column. Particulate sulphides which dissolve in the present oxidizing water column may have been preserved under anoxic conditions, and could have settled to form bedded sulphide deposits around black smoker sites. A second mechanism may be presently operating on the sea floor; sulphides may be protected from oxidative destruction in areas where the sedimentation rate is sufficiently high to form a protective blanket. Furthermore, sulphides may precipitate within the sedimentary mounds, such as those observed in Middle Valley of Endeavour Ridge. These mounds are growing, in part along active faults which bound the sedimentary basin, and are hydrothermally active (E. Davis, pers. comm., 1985). Sulphides are precipitating within them, but the size of the sulphide bodies is unknown. Such precipitation within sediments may have occurred in the Bathurst district for example.

(b) Formation of the metal-rich fluids

Considerable data are available on the composition of the fluids presently discharging from the hydrothermal vents; these are summarized in Table 3. The following are some of the observations pertinent to this study:

- (1) The fluids contain approximately 100ppm Fe and 5 to 7ppm Zn.
- (2) The sulphur is transported with the metals as H₂S.
- (3) Sulphur isotope data indicate that the sulphur is largely derived from a basaltic source, with only a small component, about 5%, formed due to inorganic reduction of seawater sulphate (Hekinian et al., 1980; Shanks et al., 1984). Shanks et al. indicate that this small amount of reduction takes place at the precipitation site. Thus no seawater sulphate is conserved or reduced in the hydrothermal system.
- (4) Strontium isotope data indicate that the fluid is dominated by basalt-derived strontium. Virtually all seawater strontium has been removed, possibly during precipitation of anhydrite in the recharge zone. This necessitates a very efficient mechanism for precipitation of strontium, as well as a low water/rock ratio in the leaching zone. Large volumes of water moving rapidly through such a hydrothermal system might not have lost their seawater strontium as effectively, and the basalt-derived strontium would be masked.
- (5) The fluids have virtually undetectable magnesium and sulphate contents.
- (6) The manganese content is high (20-60ppm) relative to normal seawater.
- (7) Potassium and calcium are typically two to three times more abundant in the hydrothermal fluids than in seawater. As much seawater calcium is lost due to the precipitation of anhydrite, the calcium in the hydrothermal fluid, as well as the potassium, must have come from basalt.

(8) Temperatures of "black smokers" range from 250°C to over 400°C (Merge Group, 1984). Temperatures of "white smokers", which are generally clear (no precipitation) or contain anhydrite, are commonly 15 to 30°C. However, substantial numbers of white smokers are much warmer; Speiss et al. (1980) measured white smoker temperatures of up to 330°C. These fluids have apparently either lost their sulphide-forming constituents within the mounds, as discussed above, or within the sub-seafloor zone. Although non-metal bearing fluids might have been generated, expulsion of both metalliferous and non-metalliferous fluids contemporaneously and at the same site, without mixing, seems impossible.

Experiments examining the reactions between seawater and basalt are summarized very well by Mottl (1983). These data illustrate the wide range of reactions that are possible, dependent on water/rock ratio and temperature. Data on experimentally-produced fluid compositions from Mottl (1983) are presented in Table 3 for comparison with naturally-occurring hydrothermal waters. Some of the principal discoveries are:

- (1) Virtually all the magnesium is stripped from seawater in a few days (at 300°C) or months (at lower temperatures) forming magnesium hydroxy-sulphate and smectite, chlorite, amphibole or talc. This removal occurs effectively at water/rock ratios of 50, and generates abundant H⁺.
- (2) Calcium is leached from the rock; some of this is reprecipitated as anhydrite, the remainder (approximately one-half) stays in solution. Sulphate is similarly effectively removed from seawater.
- (3) At low water/rock ratios, some sodium is removed from seawater to make secondary albite or analcime. At water/rock ratios greater than 10, however, sodium is leached from the rock.
- (4) At low (1-5) water/rock ratios, albite, actinolite epidote and chlorite all form as reaction products with basalt (at ca. 300°C). At high water/rock ratios (>10), only chlorite and quartz precipitate. Mottl (1983) notes that the magnesium content of chlorite increased at higher water/rock ratios.
- (5) Limited data (Table 3) on the base metal contents of solutions formed due to basalt-seawater reactions indicate that significant zinc was leached only by the highest temperature (400°C) experiments. More recently, Seyfried and Janecky (1983) and Seyfried (pers. comm., 1985) have completed experiments over longer periods than most of the previous work (summarized in Mottl, 1983), and at temperatures of up to 450°C. Seyfried has determined that the pH of the solution generated by reaction with basalt under low water/rock ratios and at temperatures below about 385°C is not consistently acid, and thus unlikely to be able to carry metals as stable chloride-ion complexes. Above 385°C, where actinolite becomes an important alteration product, the pH is continuously buffered to low values, and he observes that metal contents, as well as all other constituents of the resulting fluid, are essentially identical with those measured from actual vent fluids.

From the actual measurements as well as the experimental data, the following conclusions may be drawn regarding the conditions under which the metals go into solution:

- The temperature of the fluid must reach at least 385°C, and probably is at least a few degrees warmer than 400°C in the zone of leaching.
- (2) The water/rock ratio in this zone is probably about one; such conditions will ensure that the metal content of the fluid is not diluted, and that the rock will buffer the fluid composition.
- (3) The pressure in the metalliferous-brine generation zone may be as high as 700-750 bars (Mottl, 1983), although Bischoff and Rosenbauer (1984) suggest pressures of about 450-500 bars. At these pressures, the solution will contain from 1100 to 1300ppm SiO₂. These temperatures and pressures would place the zone of fluid generation at or near the upper zone of the magma chamber in an active rift, at a depth of from 2.0 to about 3.5km. (Morton and Sleep, 1983).
- (4) At 400°C and pressures of 450 to 600 bars, pure water has a specific gravity of approximately 0.56 to 0.60. Under the same conditions, a fluid with 1100ppm SiO₂ and 3.5 wt.percent NaCl would have a density of slightly less than 0.8 (extrapolated from Fournier et al., 1982); at the sea floor (2500m depth) the fluid density would be much less (0.16 for pure water, and probably not more than 0.4 for the aforementioned fluid). Thus the fluid could rise very quickly, provided that a suitable fluid pathway (synvolcanic fault) is available. The fluid probably rises adiabatically up a fault; according to Mottl (1983) adiabatic cooling will result in only a 10°C temperature drop.
- (5) Further cooling of the fluid will occur primarily by conductive heat exchange with cold seawater, and will likely occur primarily in the volcanic strata immediately below the sea floor. The water depth should exceed approximately 2175m in order to prevent boiling of a 400°C fluid. In areas such as Explorer Ridge (1850m) the rising hydrothermal fluid probably has been subject to separation of a vapour phase (boiling); the temperature of the remaining fluid is controlled by the two-phase boundary of seawater (Bischoff and Rosenbauer, 1984), and will cool to about 360°C prior to exiting.

Implications for alteration (1) Alteration pipes

The principal mineral constituent of alteration pipes associated with copper-zinc massive sulphide deposits is Mg-chlorite. Two models have been employed to explain this feature; Riverin and Hodgson (1980) suggested that the ore-forming fluid was alkaline, transporting metals as bi-sulphide complexes and also containing abundant magnesium; Roberts and Reardon (1978) suggested a two fluid model, with an ascending ore fluid, probably acidic, that mixed with, and was cooled by, a large volume of cold seawater immediately below the discharge point on the sea floor.

The fact that magnesium is essentially absent from even the highest temperature metalliferous vent fluids obtained at active sea floor vents indicates that a single fluid model as proposed by Riverin and Hodgson (1980) is probably incorrect. The chlorite pipes probably formed due to rapid heating of large volumes of cold, undepleted seawater that were drawn down in the immediate vent areas. Upon heating, the cold seawater lost its magnesium very rapidly

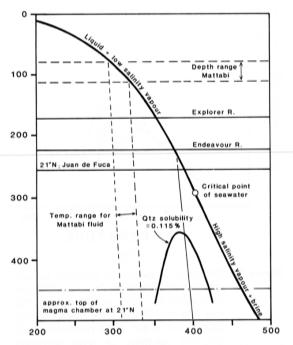


Figure 12. Pressure-temperature relationships of water (after Bischoff and Rosenbauer, 1984) showing water depths for four ridge crests, and top of magma chamber for 21°N. Note that 400°C fluid would not boil for the 21°N and Juan de Fuca fluids, it might boil immediately below the seafloor for the Endeavour fluids, and it definitely would boil at the Explorer Ridge. The Mattabi fluids probably underwent strong boiling, as the fluids could not exceed 320-340°C on the sea floor. Such extensive phase separation at Mattabi enabled the formation of a major amount of CO2-rich vapour, which formed the carbonatized stratiform alteration zone.

to form chlorite, smectite, talc or magnesium hydroxysulphate; this reaction produces H+ (Mottl, 1983), thus inhibiting the deposition of sulphides in the immediate subsurface. The size and vertical distribution of a chlorite pipe probably is a function of the primary permeability of the uppermost strata. Massive flows would probably inhibit the downflow of cold water, whereas pillowed or fragmental sequences would provide more adequate channelways. Highly fractured zones associated with major faults would also be more permeable. The rapid precipitation of chlorite and anhydrite from cold seawater in the immediate subsurface might cause the rapid sealing of these rocks, forcing the rising hydrothermal fluid to find (or make) new channelways. The vertical extent of chloritic alteration pipes may also be related to the velocity of the exiting fluid. The higher the exit velocity, the faster the draw-down of cold seawater in the area immediately surrounding the synvolcanic fracture or fault in which the hydrothermal fluids are rising. The exit velocity is controlled by the buoyancy of the fluid, which in turn is a function of the difference in fluid density between the bottom and top of the subsurface hydrothermal system. This difference is in part a function of the depth of water, as discussed below, and in part a function of the temperature of the base of the hydrothermal system.

The carbonate-rich pipes associated with the Pre-Cambrian deposits that formed in shallow water, relative to the Noranda and Mattagami Lake deposits, are more problematical. Carbonatization of the entire upper portion of the footwall sequence below the deposits at Sturgeon Lake occurred prior to the formation of the pipe (Franklin et al., 1975 and 1977). Apparently a CO2-rich phase diffused through the footwall sequence, and on reaching a zone of high water flux, identified by a broad stratiform area of sodium depletion, carbonate precipitated. The CO2-rich phase may have been generated by phase separation of seawater (Bischoff and Rosenbauer, 1984), heated to 400°C or more, at only moderate pressures (350 bars or slightly less). Such conditions may have been attained because (1) a major synvolcanic sill was present approximately 2 to 3km below the sea floor, and (2) the water depth at the time of formation of the deposits was probably not more than 1km (Groves, 1984). Should this phase separation have occurred, a volatile-rich phase, containing most of the CO2, would have separated quickly and moved upwards through the strata due to its very low density. The residual brine would be more dense and more chlorine-rich, with most of the metals contained in it. Due to its greater density, it would have risen more slowly, eventually cutting across the alteration which was formed slightly earlier by the CO2-rich vapour phase.

One poorly-understood aspect of the subsurface reactions involving CO_2 is the possibility that the hydrothermal fluid became immiscible with respect to CO_2 prior to its ascent, forming a very dense CO_2 -rich fluid at depth. The residual fluid would remain virtually unchanged with respect to its metal and other constituents, but would be very depleted in CO_2 . Should such a residual fluid eventually reach the phase separation boundary (Fig. 12) as proposed by Bischoff and Rosenbauer (1984), the resulting vapourrich phase would contain very little CO_2 .

Alteration pipes under the zinc-lead-copper deposits, typified by the Kuroko deposits, appear to be the products of conductive cooling of the hydrothermal fluid, with much less influence of local inflow of large volumes of cold fresh seawater. Magnesian chlorite, although present in the outer portions of the alteration pipes, is not as abundant as in the core zones of the pipes associated with copper-zinc deposits. The quartz which dominates the Kuroko-type pipes probably was deposited as a result of cooling of the ascending hydrothermal fluid. This process may have sealed the hydrothermal vent area from the influx of cold seawater, thus preventing the development of a magnesian core to the alteration pipe.

The volume of cold seawater that is drawn into the alteration pipe is a function of the permeability of the rocks immediately underlying the deposit, but is also related to the velocity of the escaping hydrothermal fluid and the size of the escapement orifice. The last mentioned is probably essentially constant for most vent areas. The escape velocity is a function of the pressure difference and the distance between the top of the reservoir and the sea floor, and the difference in specific gravity of the fluid between these two areas, according to Bernoulli's equation. The last difference is clearly the most important; for pure water at 400°C, the difference in specific gravity between 450 bars and 250 bars is approximately 0.3gm/cm3; the same differential between 350 and 150 bars is 0.13gm/cm3. As the velocity difference is proportional to the difference in specific gravity, the rate of escape of the fluids in the deeper-water environment should be greater. As the volume of fluid drawn down into the immediate subsurface varies with the rate of discharge of the upwelling hydrothermal fluid, more cold seawater should be drawn down in the higher velocity, deep water vent areas. This should cause these feeder zones to have more magnesian chlorite formed as an alteration phase.

The hydrothermal fluids in felsic or clastic sedimentary terrains may not have been as hot as those associated with deposits formed in basaltic terrains. In the former environments, clay minerals and feldspar are the dominant minerals that buffer the low water/rock ratio reactions. Fluids thus generated would have an acid pH regardless of temperature (Bischoff et al., 1981). Thus, substantial metal contents in the hydrothermal fluids could be attained in these environments at 250°C. Such fluids would have a density of over 0.8, and thus would not rise as quickly as those much less dense fluids formed in the higher temperature regimes associated with spreading ridges. Fluids which expelled less vigorously than the "black smokers" at ridgecrests would be less likely to have attendant drawdown zones immediately adjacent, thereby inhibiting the formation of magensium-enriched alteration zones.

(2) Lower semiconformable zones

Two types of stratabound alteration observed below massive sulphide deposits require explanation, the major zones of silicification beneath deposits which formed in relatively deep water and the similarly distributed zones of carbonatization beneath deposits formed in relatively shallow areas.

Silica solubility generally increases with temperature (Kennedy, 1950), but its solubility is dependent strongly on pressure and also on the dissolved NaCl content (Fournier and Potter, 1982; Fournier et al., 1982). Kennedy (1950) and Fournier (1983) noted that guartz has a solubility maximum that is pressure dependent, and extends over a region from about 340°C at the vapour pressure of the solution to above 500°C at 900 bars (Fig. 13). In this region, quartz solubility initially increases with temperature, but rapidly decreases as the boiling curve is approached. At NaCl contents close to those of modern seawater (3.2wt. percent, Bischoff and Rosenbauer, 1984) the solubility of quartz is slightly increased, although the topology of the system is quite close to that defined by Kennedy (1950) (Fig. 13). As seawater descends through the volcanic pile, its silica content probably is controlled by the vapourpressure curve, and the fluid is saturated with silica. Injection of a basaltic synvolcanic sill into a regime of this composition (probably at 400-500 bars) would effect local super-heating, and the fluid composition would move laterally in Figure 13, driving it past the solubility maximum, and causing rapid quartz precipitation. As noted by Fournier (1983), precipitation could also be induced by boiling of the reservoir fluid, as well as by exceeding the quartz solubility maxima. Rapid heating and possible boiling may explain the intense silicification noted by MacGeehan and MacLean (1980) adjacent to synvolcanic sills, beneath the deposits of the Mattagami Lake district.

The silicification process that operated beneath the deposits at Noranda and Snow Lake may have been similar to that described above. Silica-saturated fluids may have been subjected to rapid heating by the periodic introduction of new melt into a subvolcanic intrusion. Rapidly increased temperature could have caused the fluid composition to move isobarically to the right in Figure 13, to a region of decreased silica solubility. At pressures below about 500 bars silica would either have become supersaturated, or would have been precipitated. A similar process might have occurred at the top of a hydrothermal reservoir, where

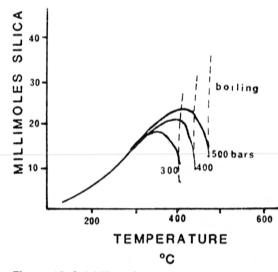


Figure 13. Solubility of quartz in aqueous sodium chloride solution (after Fournier, 1983 and Fournier et al., 1982), at 300, 400 and 500 bars pressure. Dotted lines indicate boiling boundaries at the three pressures. Note that the solubility of silica decreases rapidly at higher temperatures.

a pressure-decrease induced silica "blanket" may have formed. Such a blanket may have formed an impermeable cap or "seal" to the reservoir, thus preventing the hydrothermal fluids from escaping (Gibson et al., 1983). Fournier (1983) suggests that this process could have destroyed the permeability of some hydrothermal reservoirs, thus "selfsealing" a portion of this zone. Further heating may have induced boiling, and may possibly have caused the *in situ* brecciation of the upper part of the silicification zones at Noranda.

Alternatively, silica may have precipitated due to mixing and cooling of silica-saturated "reservoir" fluid with cold seawater at the top of the reservoir. This form of mixing might result in a less dramatic "dumping" of quartz, as, at lower temperature, silica solubility follows the vapourpressure curve, and the incremental loss of silica per degree of decrease of temperature is much less than the corresponding loss due to superheating at moderate pressures.

Carbonatization of the footwall strata may be related to the segregation of the mineralizing fluid into two phases. Above the critical point of water the fluid would boil, thus developing a low salinity, a CO2-rich vapour phase and a metal-chloride brine (Delaney and Cosens, 1982; Bischoff and Rosenbauer, 1984). Boiling would occur below the sea floor provided that the water depth is approimately 2.2km or less (for a fluid of approximately 400°C (Fig. 12). The vapour phase would have a very low density, and would separate from the brine phase very effectively, enabling the vapour to rise within the footwall strata, mixing with cold connate seawater. The reaction of a CO2-rich vapour with the cold seawater would cause carbonate precipitation. This would form a "blanket" of semi-conformable carbonate alteration that would seal the top of the reservoir. The remaining more dense metalliferous brine would subsequently move up as an ore-forming fluid; reaction of this fluid, which would have a high iron activity, with the preexisting carbonate deposited from the interaction of the vapour phase with the footwall strata, would form siderite.

The ability for a fluid to form the two phases and thus effect the carbonatization of the footwall strata is largely dependent on the depth of the sea floor.

Conclusions

1) In basaltic terrains, massive sulphide deposits formed primarily where a major mafic subvolcanic intrusion was situated approximately 2 to 3km beneath the sea floor. In back-arc areas, and in most of the Pre-Cambrian massive sulphide districts, these intrusions are commonly, but not exclusively, felsic.

2) In spreading ridge environments, sustained hydrothermal systems form best at the waning or inactive stages of volcanism, when fluid venting is confined to marginal faults in the ridge-crest area. At this time, the subvolcanic intrusion has cooled sufficiently to have a solid outer margin. This zone becomes highly fractured and permeable, enabling fluids to enter the upper regions of the intrusion and to become super-heated (Lister, 1974; Johnson, 1980; Mottl, 1983). Due to the passive nature of the ridge crest during this tectonic stage, the fluids are not easily vented to surface, and escape only along deep-penetrating active marginal faults. The faults are active during the collapse phase of the crestal ridge, coincident with volcanic inactivity and the formation of an elongate summit depression (Kappel and Ryan, in press).

3) The composition and extent of development of the alteration pipes may be indirectly related to the depth of water overlying the hot springs. Chloritic pipes formed in areas where the upwelling velocity was greatest, corresponding to the areas of greatest depth of seawater. In shallower areas, less cold seawater was drawn down into the immediately subjacent pipe areas; most of the alteration formed through precipitation from the cooling hydrothermal solution, leading to silicification rather than chloritization in the pipe.

4) Silicification in the lower semiconformable alteration zones probably occurred due to the rapid heating of silicasaturated seawater by recharge into the subvolcanic magma chamber. This would drive the fluid composition past the silica solubility maximum (Kennedy, 1950; Fournier, 1983) and cause rapid precipitation of quartz. Subsequent brecciation of the silicified rocks may have occurred through continued heating of the fluid to the boiling point, where the trapped vapour would escape by autobrecciation of the sealed rocks.

Carbonatization occurred where the interpore metalliferous fluid boiled under relatively low pressure (<220 bars), permitted only where the water depth was relatively shallow. The vapour phase would be very CO₂-rich, and would rise through the overlying strata until it mixed with unmodified seawater, where carbonate precipitation occurred.

5) Sulphide mounds formed through precipitation from within the mound, rather than by settling of particulate matter ejected from "black smokers". Particulate settling could only have occurred where the seafloor is anoxic. The mound initiated by the formation of an anhydrite cap around warm-water vents; the cap may have formed on a bacterial mat or a tube worm cluster. Sulphides were initially trapped by this mat, and also formed by overgrowth of it. Continued influx of new hydrothermal fluid from below, mixed with cold seawater infiltrating through the anhydrite cap, caused precipitation of more sulphides, and the mound grew. Thermal gradients within such a mound would have been very large. Thus various metals would precipitate in response to their solubility in a high thermal gradient, and effect distinctive metal zoning within the mound through a continuum of replacement processes. These processes probably were responsible for forming the copper core and more zinc-rich outer zones evident in many deposits.

6) Application of the aforementioned mechanism for formation of sulphide mounds in Pre-Cambrian terrains is somewhat speculative. Anoxic conditions during the Archean would provide an excellent environment for preservation of sulphides, but during the Proterozoic, some analogue of the anhydrite cap must have been present. Bacterial mats flourished throughout this time, and perhaps some primitive sulphur-consuming bacteria formed around Proterozoic hydrothermal vents, thus permitting the mechanism described above, (5), to operate. The immediate hangingwall strata of these deposits should be examined for evidence of these bacteria.

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Discussion

J. E. CHRISTOFFERSEN (Amax Exploration of UK Inc) asked:

1. In view of the rapid appearance and disappearance of sulphur species in "black smokers", what are the implications *re* the validity of paragenetic sequences in massive sulphide deposits? 2. Why did a massive sulphide deposit form at all at Sturgeon Lake if the submarine depositional environment was as shallow as indicated by volcanic litholo-

gies? i.e. why didn't the hydrothermal fluids boil in a subvolcanic environment?

REPLY:

1. Observations of paragenetic sequences are valid only at the scale at which they are observed. Due to the complex nature of dissolution, reprecipitation and recrystallization in the sulphide mounds, minerals that are forming in one part of the mound may be being dissolved in another part of the mound simultaneously. Minerals may be in chemical equilibrium on the local (few centimetres) scale, but as temperatures and the degree of oxidation vary very widely within the mound (due to the variable degree of mixing of the hot metalliferous brine with cool seawater) isotopic equilibrium attained in one part of the mound may not reflect the conditions in another part. Paragenetic sequences established to represent the overall sequence of events in a preserved deposit probably are gross oversimplificatons and should not be taken seriously.

2. Two points should be emphasized. (i) The Sturgeon Lake deposits formed under approximately 500-1 000m of water. Fluids at about 300°C would not boil in this depth interval and these fluids could carry much metal and dissolved H_2S . The problem lies with generating a high metal content in such a fluid, as the experimental evidence of Seyfried and others (Seyfried and Janecky, 1983) indicates that, in a basaltic domain, temperatures must be about 380°C in order to leach metals from the rock. Thus, at Sturgeon Lake, the fluid probably started out at 380°C or more, and cooled to about 300°C before emerging on the seafloor.

(ii) The process that cooled the fluid was probably phase separation (i.e. boiling) of the fluid within the pile, with accompanying separation of a CO_2 -rich vapour. Separation of this vapour would cool the fluid very effectively (see Bischoff and Pitzer, 1985, for discussion of this), thus forming a cooler residual metalliferous brine that continued upwards to form the deposit. At very shallow depths the cooling would be so effective as to cause precipitation of sulphides, thus forming a vein-type deposit below the seafloor. As this did not happen at Sturgeon Lake, the water depth must have been sufficient to permit only a modest amount of phase segregation.

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