

Metamorphism and Massive Sulphide Generation in Oceanic Crust

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Summary

Recent studies of oceanic crust have shown that downward, convective percolation of sea water through highly permeable igneous rock is a fundamental process in the submarine environment of spreading ridges. Sea-water penetration occurs to depths of at least three to five km, providing an efficient means of igneous cooling and resulting in pervasive low to medium grade hydration. Sub-sea floor fluid-circulation consists of three main stages: - a) slow convective percolation, b) collection in aquifers and c) vigorous discharge, focussed along faults and fracture systems. The latter stage is conducive to the generation of amphibolites, serpentinites and rodingites.

Sea water undergoes major chemical evolution during circulation and reaction with oceanic crust. Originally oxygenated, alkaline, Na-Mg-SO₄-Cl sea water, evolves into a reduced, slightly acid, dominantly Na-Ca-Cl brine and under these conditions is capable of transporting significant quantities of metals, as chloride complexes. The phenomena of metal leaching by the action of circulating sea water is a highly potential ore-forming process capable of generating metal concentrations equivalent in tonnage to known massive sulphide bodies. In the deep oceanic

environment magmatic-fumarolic activity is not likely to be a significant mechanism for transport of metals from depth to surface.

Massive sulphide deposition on the ocean floor will occur as a result of the reduction of ocean sulphate in the vicinity of hydrothermal discharge. This may take place by the reducing action of the solutions themselves or by biological mechanisms.

Introduction

It is only in recent years that geoscientists have established a rationale for understanding global distribution of ore deposits and the processes responsible for ore formation. The framework for this model, is linked to plate tectonic theory which has developed along with our rapidly increasing knowledge of modern oceanic crust and processes active at plate margins. The modern oceanic crust is a natural laboratory where, with the help of modern technology, geoscientists have been observing igneous, metamorphic and ore forming processes *in action*. This direction of research is not only fascinating from the academic point of view, in that it leads to an understanding of processes responsible for ancient ore-bearing rocks, but it is also invaluable in its contribution to our knowledge of the immense ore reserves already known to exist in the modern ocean crust. In the March-April (1974) issue of *Cooperation Canada* from the International Development Association (CIDA) we find the following statement: "Just think: enough copper to last us for 1,100 years, enough nickel for 23,000 years, enough cobalt for 260,000 years! It's all there under the ocean and it belongs to nobody or to everybody". This was of course in reference to the immense fields of manganese nodules and metal-rich muds which blanket large areas of the deep ocean floor. However, an intriguing and equally significant consideration (the main subject of this paper) is the almost certain existence of massive, base metal-sulphide ores, within the modern oceanic crust, generated by processes known to be active in the environment of divergent and convergent plate boundaries. Such potential reserves are impossible to estimate. In any case, there is little doubt that in the next few decades, oceanic

crust will become a major source of raw materials and perhaps even geothermal power. For this to be accomplished will require increasingly active international cooperation and advances in submarine technology. Despite the fact that much time and effort is being invested in exploring the ocean floors we still know very little about this complex environment and as Rona (1973), has observed, our sampling procedure has been analogous to "flying a balloon at an altitude of up to six miles and suspending a bucket at the end of a cable to scrape up loose rocks from the surface of the land".

Information concerning the geological environment of modern oceanic crust is derived through a combination of diverse methods. Direct observation has been accomplished by highly sophisticated techniques of photographing, dredging and drilling the deep ocean floor and more recently by the use of manned deep-sea submersibles. Direct measurement of structure and physical properties of oceanic crust has been accomplished by equally sophisticated techniques involving seismic refraction (Christensen and Salisbury, 1972, 1975) and paleomagnetism (Watkins and Paster, 1971; Scott *et al.*, 1974). The most useful indirect means of exploring the nature of modern oceanic crust involves the study of ophiolites which are recognized as uplifted segments of oceanic crust generated at ancient oceanic spreading centres (Fig. 1).

The Role of Sea Water

Recent studies of modern oceanic crust have clearly shown that downward convective circulation of sea water through igneous rock is a fundamental process with respect to igneous cooling and metamorphism in the sub-sea floor environment of spreading ridges. Interpretation of heat flow data measured from the modern ocean floors strongly suggest that cooling of oceanic crust as it proceeds away from ridge crests cannot take place by simple conduction alone, but must involve circulation of sea water to significant depth (Palmason, 1967; Deffeyes, 1970; Talwani *et al.*, 1971; Lister, 1972; Lowell, 1975). Lister (1974) has shown that the upper layers of oceanic crust are astonishingly permeable, (10⁻⁷ cm²), and predicts that sea-water penetration

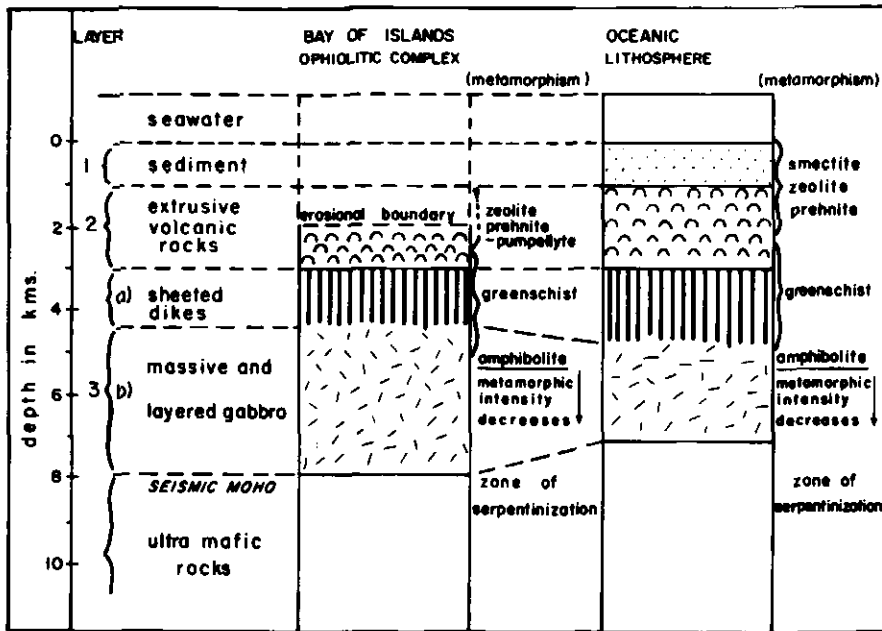


Figure 1
 Close correspondence of both structure and metamorphic distribution, between the Bay of Islands ophiolitic complex (L. Riccio, personal communication) and oceanic crust (Christensen and Salisbury, 1975).

will be a pervasive phenomenon to depths of at least three to five and probably up to seven kms. Williams *et al.* (1974), demonstrate that convective circulation of sea water accounts for approximately 80 per cent of geothermal heat released near ridge crests.

Stable isotope studies of metamorphosed ophiolitic rocks (Wenner and Taylor, 1973; Spooner *et al.*, 1973; Spooner *et al.*, 1974), and altered rocks recovered from the modern ocean floor (Aumento and Loubat, 1971; Muehlenbachs and Clayton, 1971; Muehlenbachs and Clayton, 1972), strongly support the concept of downward, convective penetration of sea water as the main process of oceanic crust metamorphism.

Chemical interaction between sea water and oceanic crust must take place on a rather massive scale (on the basis of changes in Fe^{2+}/Fe^{3+} ratios, Spooner (pers. com.) provides evidence for water/rock ratios like 100:1 in the ore regions of Cyprus). The nature of this interaction will vary according to local conditions of permeability and heat flow, resulting in the generation of distinct types of alteration as follows: - (a) Low temperature weathering at the sea-floor

interface, as a result of prolonged exposure of rock to sea water; (b) Low intensity hydration, the result of slow, convective percolation of sea water under the influence of low to moderate geothermal gradients and a process which affects the bulk of oceanic crust; (c) Intense, hydrothermal alteration resulting from localized, episodic, vigorous discharge of heated sea water along faults and major fracture systems. Hydrothermal circulation of heated, chemically altered sea water through oceanic crust, in the intensely active magmatic-volcanic submarine environment of plate margins, provide all the necessary ingredients for highly efficient ore formation on the ocean floor. In order to comprehend the potential of such an environment, it is first necessary to understand the basic physical and chemical processes involved. With this objective in mind, we have developed the following general, but much simplified model of the sub-sea floor hydrothermal environment. This model is constructed primarily on the basis of observations from well-studied subaerial systems, accumulated knowledge of the submarine metamorphic environments, and recent experimental studies concerning hot water/rock interaction.

The Nature of Sub-Sea Floor Fluid Circulation

Physical Aspects. We envisage that circulation of sea water in the sub-sea floor environment will consist primarily of three stages: - a) slow convective percolation through oceanic crust with simultaneous heating, b) collection in aquifers, and c) localized, episodic vigorous discharge to the surface along discrete zones of high permeability, such as faults and fracture systems.

Subsurface storage of hot water within extensive aquifers is typical of most subaerial systems. These aquifers are usually multi-level, that is, they consist of numerous horizons at different stratigraphic levels, and they are always much greater in total volume than predictable from their surface activity. For example, the sub-surface volumes of the Waireki and Salton Sea hydrothermal systems are each at least 100 km³, whereas their total surface expression involves less than 10 kms² (Ellis, 1967; White, 1968). Underground hot water storage on a vast scale has been reported in central Asia (20,000 km²) and Western Siberia (3 million km²) (Ellis, 1967). It is well known that some of the most important aquifers for ground-water storage and movement are basalt piles such as those found in the Pacific Northwest of the U.S. Water storage of a similar nature undoubtedly occurs as a significant stage of sub-sea floor hydrothermal activity. Studies of the Reykjanes geothermal system in Iceland (Björnsson *et al.*, 1972) which involves circulation of heated sea water through tholeiitic basalt flows and hyaloclastites, reveal that most of the good aquifers occur within highly fractured lava flows and interbeds of the basalt formation. Such horizons, including highly permeable vesicular and scoriaceous flow tops, will serve as favorable sites for sea-water accumulation and the generation of extensive aquifers within the sub-sea floor environment.

As calculated by Spooner and Fyfe (1973), one km³ of basic magma, cooling from 1200°C to 300°C is capable of heating three km³ of sea water to 300°C. Intrusion into the vicinity of aquifers will result in vigorous heating of the waters and rapid build-up of fluid pressure. Release of heated waters will take place along specific zones of high permeability such as faults and fracture

systems which were previously present or newly formed as a result of the intrusion. Such concentrated discharge of hydrothermal fluid has been directly observed along present oceanic ridge systems (Muecke *et al.*, 1974; Scott *et al.*, 1974; Williams *et al.*, 1974), and is well known in the neovolcanic zone of Iceland (Bodvarsson, 1961), an integral part of the northern mid-Atlantic ridge system, and the presently active spreading axis of the Red Sea (Degens and Ross, 1970; Backer and Schoell, 1972). The characteristic location of amphibolites, serpentinites and rodingites on faults and major fracture systems along the present mid-ocean ridges (Melson *et al.*, 1968; Aumento and Loubat, 1971; Hekinian and Aumento, 1973; Williams *et al.*, 1974; Honnorez and Kirst, 1975), is also indicative of rapid introduction and focussed discharge of large volumes of hydrothermal fluids. If such metamorphic rocks are any indication of the conditions of massive flow, this phenomenon potentially involves temperatures of 200–500°C and water pressures in the order of 1000–3000 bars (Honnorez and Kirst, 1975).

As long as heat is supplied, continuation of hydrothermal discharge to the surface will depend on the preservation of permeability. Rock which is saturated with water in cracks and pore spaces is structurally weakened and in a tectonically active environment will experience almost continuous seismic activity, as is observed in the geothermal areas of Iceland (Ward and Björnsson, 1971). Under such conditions, fractures and microfaults will be continually generated and renewed, and permeability will remain high.

As noted by Elder (1965), submarine systems are characterized by a water/water-rock interface as opposed to the air/water-rock interface of subaerial systems. In this situation gravitational constraints on the mass movement of water from the system at the surface are drastically reduced, giving rise to the potential of very high rates of discharge and single pass as opposed to multipass systems will prevail.

Chemical Aspects. During circulation through oceanic crust, sea water will experience a chemical evolution and the discharged fluid will be quite different in composition from the initial sea water. The main factors controlling the composition of the fluid will be: - a) temperature dependant solubility and ion exchange equilibria, b) the extent of reaction with the rock (a function of flow rate), and c) the rock/water ratio. As a result of recent experimental work (Mottle *et al.*, 1974; Bischoff and Dickson, 1975; Hajash, 1975), we are now beginning to appreciate some of the specifics of sea water-basalt interaction. Under the expected hydrothermal conditions (200–500°C; 500–2000 bars), sea water changes in composition from an originally oxygenated, slightly alkaline, Na-Mg-SO₄-Cl fluid, to a reduced, more acid, dominantly Na-Ca-Cl brine. Figure 3 is a simplified attempt to illustrate this process together with some of the physical aspects involved. Experimental data are in excellent agreement with the chemical evolution of sea water observed in natural systems (Tómasson and Kristmannsdóttir, 1972).

In order to understand the chemical changes we note that basalt contains the olivine-magnetite buffer system and therefore will experience oxidation during the initial stages of interaction (Fig. 2). Evidence for this is observed in the upper layers of ophiolites and modern oceanic crust (Gass and Smewing, 1973; Spooner and Fyfe, 1973; Spooner *et al.*, 1974; Andrews *et al.*, 1976), in the prolific generation of carbonate, hematite, epidote and ferric iron bearing clays (saponite, nontronite). Anhydrite, hematite and saponite-nontronite have also been observed as reaction products in sea water-basalt experimental studies (Bischoff and Dickson, 1975; Hajash, 1975).

As observed in experimental work (Bischoff and Dickson, 1975; Hajash, 1975) and also in the Reykjanes geothermal brines (Tómasson and Kristmannsdóttir, 1972), Mg²⁺ and SO₄²⁻ are almost completely removed from sea water during reaction with basalt. Magnesium is involved in the production of secondary phases such as montmorillonite and saponite. Precipitation of anhydrite and reactions involving the generation of sulphide are responsible for the depletion of SO₄²⁻. At

higher temperatures sea water becomes enriched in Ca, Si and K due to alteration of interstitial glass and silicate phases.

The pH lowering experienced by sea water during reaction with basalt (from about 8 to approx. 4–6 depending on temperature) is an observation based on measurements of quench pH under both natural and experimental hydrothermal conditions and the assumption that quench pH represents the actual conditions at elevated temperature. Unfortunately it is difficult to discuss pH controls in specific terms (that is, with respect to predicting specific reactions and their relative effects on the H⁺-OH⁻ balance of the system), due to the lack of accurate, high temperature thermochemical data and the complex nature of rock-fluid systems. The problem becomes even more difficult as temperature increases because simple electrolyte models become imperfect as inorganic solutions become dominantly molecular. In general, the pH change observed in the sea water-basalt system results from a complex interplay of: - a) secondary mineral reactions, and b) temperature dependent acid-base ionization equilibria (1. on Fig. 3), all of which participate in either increasing or decreasing the H⁺-OH⁻ ratio. Precipitation of calcite during initial sea water-basalt reaction undoubtedly contributes to pH lowering (2. on Fig. 3). Removal of SO₄⁻ by anhydrite precipitation (3. on Fig. 3) and the generation of smectites (saponites, nontronites) during alteration of glass and silicate phases such as olivine (4. on Fig. 3) may also be significant in this respect. In discussing pH maintenance of the oceans, Garrels (1965), pointed out the need for some mechanisms which would provide for release of H⁺ to sea water. If the immense volumes of sea water which are continuously circulating through oceanic crust are converted into neutral to slightly acid fluids, as the measurements imply, then this process must contribute significantly to the pH buffering of the oceans.

As a heated, reduced, Cl⁻ rich brine, sea water evolves into a solvent capable of transporting significant quantities of base metals (such as Fe, Mn, Cu, Pb, Zn, Ni, Au, Ag) in solution as chloride complexes. If sub-sea floor hydrothermal systems are visualized

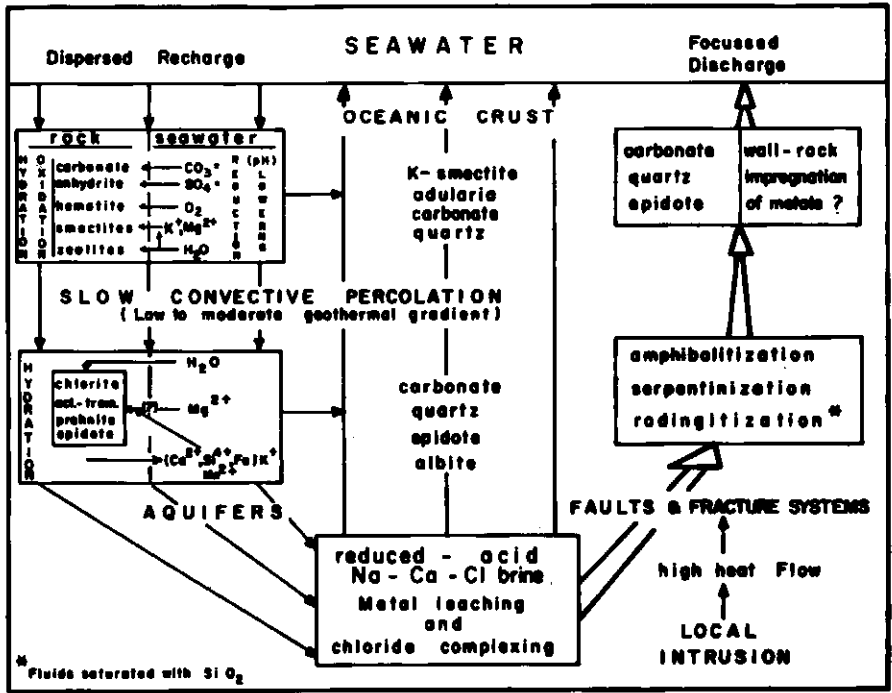


Figure 2
Some physical and chemical aspects of the convective movement of sea water through the upper layers of ocean crust.

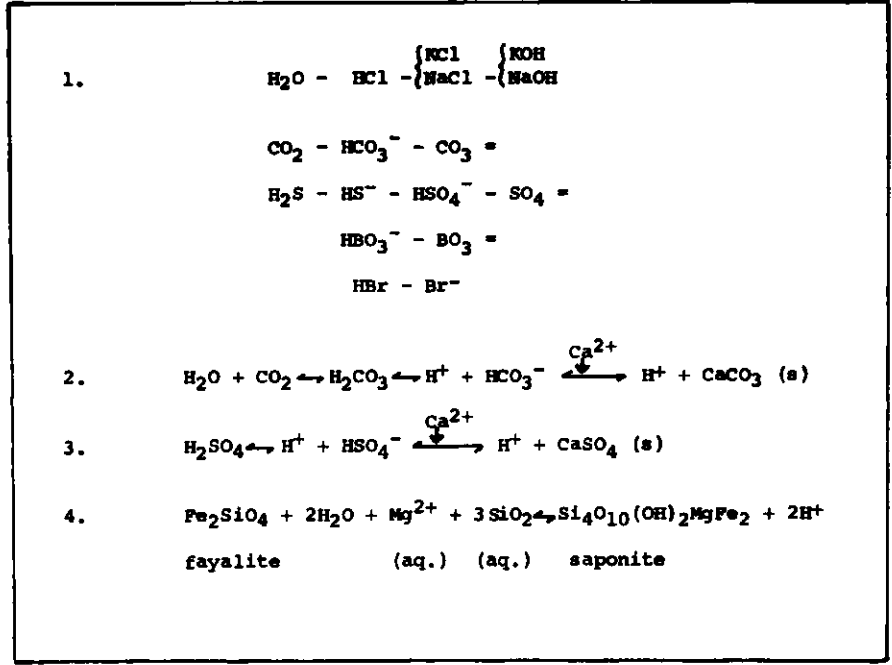


Figure 3
Equilibria possibly significant to the pH lowering experienced by sea water during reaction with basalt.

with respect to the physical model developed above (Fig. 2), the bulk of chemical reaction between sea water and ocean crust will occur during slow, convective percolation and flow through aquifers which will become storage areas for hot, chemically altered, possibly base-metal enriched waters.

As recognized by Spooner and Fyfe (1973), water in sub-sea floor hydrothermal systems may be supercritical due to the hydrostatic pressure of overlying sea water. In this situation boiling will not occur and solutions may discharge onto the sea floor at very high temperatures (given a depth of around 3000 metres, fluids could discharge at temperatures of 400°C). In subaerial systems, boiling not only acts as a constraint on the temperature of fluid discharge at the surface, but also results in drastic loss of dissolved gases such as CO₂. This process can cause sharp chemical changes in the fluid at depth. The absence of this phenomenon in submarine systems and high flow rates, will be conducive to the transport of high temperature fluids from depth to the surface chemically intact. As a result, any precipitation or concentration of dissolved constituents such as base metals will tend to take place at or near the sea-floor interface.

With a continuous supply of fresh, unaltered sea water, stable equilibrium between rock and fluid will be unlikely and transfer of various chemical species (such as base metals) from rock to fluid will not necessarily be controlled by solubility or saturation constraints, characteristic of closed systems. As long as the metals are available, a chemical gradient from rock to fluid will be continuously maintained and leaching capability enhanced.

Sub-Sea Floor Hydrothermal Activity and Ore Formation on the Ocean Floor

Divergent Boundaries. Some 90 massive sulphide deposits and prospects occur in the Troodos ophiolites of Cyprus (Johnson, 1972), a segment of a spreading centre which was probably active in the late Cretaceous (Moore and Vine, 1971). These deposits are stratiform bodies located primarily at the contact between basalt flows and are characteristically underlain by mineralized stockworks

(Fig. 4). Host rocks are intensely hydrothermally altered pillow lavas which grade upwards and outwards into zones of hematitization and silicification (Hutchinson and Searle, 1971; Johnson, 1972). The massive sulphide bodies themselves are commonly overlain by heavy metal enriched chemical sediments. Such features are common to many ophiolitic, massive sulphide occurrences (Sawkins, 1972; Sillitoe, 1972; Hutchinson, 1973; Strong, 1974) and strongly suggest formation as a consequence of hydrothermal discharge.

The Red Sea represents the earliest stage in the growth of a mid-oceanic spreading centre. In three small basins along the central spreading axis, metal-rich hydrothermal exhalations are presently depositing the richest submarine metallic (Au, Ag, Cu, Zn) sulphide deposit known. Bullard (1974) estimates that if the Cu and Zn alone, in just the upper 8.5 metres of hydrothermal sediment in the Atlantis II Deep, could be extracted, they would be worth, at January 1974 prices, over \$6 billion. There is substantial evidence to suggest that these metal-rich hydrothermal emanations result from the circulation of heated sea water through extensive aquifers (possibly up to 600 miles long) in sediments beneath the Red Sea (Craig, 1966; Degens and Ross, 1970). Metals originate from these sediments due to the leaching action of heated, chemically altered sea water (White, 1968).

Highly interesting occurrences of sulphide mineralization have been noted in the modern oceanic environment. As part of the JOIDES program, Hollister *et al.* (1972), report a 60 metre thickness of sediments in the western Atlantic, which very closely resembles the mineralized sediments of the Red Sea, containing zinc sulphide which in patches constitutes up to 50 per cent of the rock. Lower in the section, approximately 10 metres above basement basalt, they also discovered a thin vein of native copper. A similar observation is reported by Dmitriev *et al.* (1971), in their study of rocks recovered from the Carlsberg Ridge (Indian Ocean) and Mid-Atlantic Ridge. Sediments immediately overlying basement show well-defined horizons of metal enrichment, suggesting periodic hydrothermal introduction of metals onto the sea floor. High Cu values in

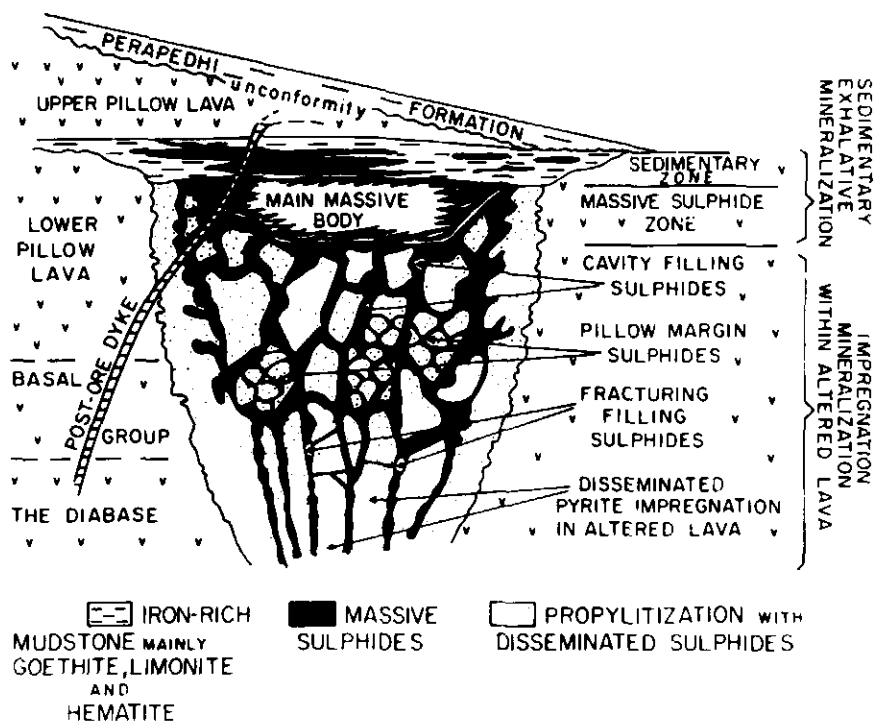


Figure 4

Diagrammatic section through a typical Cyprus sulphide deposit (Hutchinson and Searle, 1971).

greenschist basalt and very high Cu-Pb-Zn values in carbonate veins were recorded from igneous basement rocks. Bonatti (1975), reports sulphide mineralization in basalts from the equatorial Mid-Atlantic Ridge, occurring as "stockwork"-type veinlets and as disseminations of mainly pyrite and chalcopyrite; Fe and Cu-rich alteration minerals are also present. Andrews *et al.* (1976) discovered a native copper bearing vein in basalt core, recovered during the last DSDP, leg 37. This vein consists primarily of clastic carbonate and foraminiferal tests, so was obviously a channelway for circulating sea water. The native copper is associated almost exclusively with highly altered fragments of basalt, detached from the vein wall.

Convergent Boundaries. The Kuroko massive sulphide bodies of the Japanese Islands occur in an ancient island-arc environment of Miocene age and represent convincing evidence for the process of ore generation by hydrothermal circulation of sea water through oceanic crust (Fig. 5). These deposits have been the subject of intensive study of Japanese geologists and recent work has involved a

concerted effort to define the nature and origin of the Kuroko ore-forming fluids, primarily by the application of stable isotope techniques (Ohmoto, 1970; Kajiwara, 1971; Kajiwara, 1973; Sato, 1973; Sakai and Matsubaya, 1974). A review of the accumulated hydrogen and oxygen isotope data indicates that the Kuroko ore fluids were predominantly of sea-water origin (Ohmoto and Rye, 1974). Sulphur isotope studies indicate that the main source of ore-forming sulphur was sea-water sulphate (Kajiwara, 1971).

Leaching Source. Traditionally, magmatic-fumarolic activity was considered to be fundamental to hydrothermal ore generation but today the process of rock leaching by hydrothermal fluids has become increasingly emphasized. This evolution in thought stems primarily from direct observation of presently active ore forming systems. Helgeson (1964, 1969), developed a leaching/chloride complexing model to explain the metal rich, hydrothermal brines of the Salton Sea. Arnórsson (1969) and Arnórsson *et al.* (1967), considered a leaching phenomenon to explain distribution of

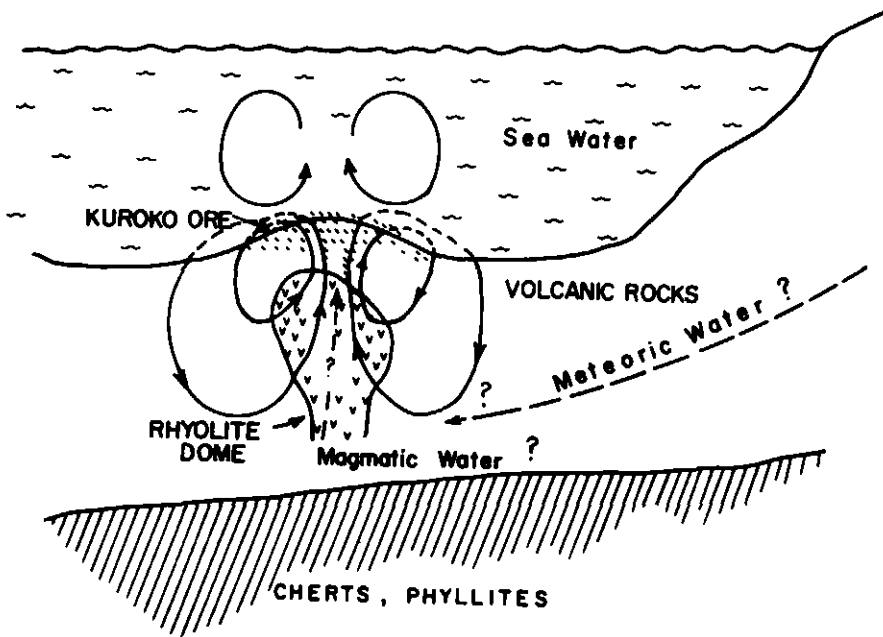


Figure 5
The formation of Kuroko massive sulphide ores, a model presented by Ohmoto and Rye (1974), based on stable isotope data.

transition metals in hydrothermally altered rocks and copper-rich springs associated with geothermal areas of Iceland. Degens and Ross (1970) conclude, primarily from isotopic evidence, that metal-rich hydrothermal emanations of the Red Sea result from leaching of sediments by circulating sea water and Lebedev (1972), explains the extremely metal-rich brines of the Chelekan Peninsula by a similar leaching mechanism. There is much evidence to suggest that rapid accumulation of heavy metals in sediments on the East Pacific Rise is a result of hydrothermal leaching of oceanic crust by heated, circulating sea water (Böstrom and Petersen, 1966; Bender *et al.*, 1971; Corliss, 1971; Dymond *et al.*, 1973; Piper, 1973; Piper *et al.*, 1975).

Consideration of the metal leaching potential of a rock/fluid system must take into account: - a) the chemistry of fluids, b) distribution and therefore relative availability of metals in rock (that is, do the metals occur within silicates, oxides, sulphides or some other form), and c) the pervasiveness of alteration. Preliminary experimental investigations of the metal stripping and transporting capability of sea water has revealed that in a matter of weeks (a geologically

insignificant period of time), sea water experiences enrichment of up to two to three orders of magnitude in metals such as Fe, Mn, Cu and Ni (Bischoff and Dickson, 1975; Hajash, 1975). Ellis (1968), subjected andesite to NaCl solutions at 400 °C and after a few weeks, observed the almost complete removal of copper (70 ppm). Concentration in solution reached up to 4 ppm but this figure is probably low due to copper fixation onto the inner walls of the gold reaction capsules.

As yet there are few statistically reliable, quantitative data on the mineralogical distribution of metals in mafic rocks but it is significant that in the rock leaching experiments conducted by Ellis the almost complete removal of copper from andesite took place before any extensive alteration of the ferromagnesium or feldspar minerals. Alteration amounted to surface corrosion of pyroxene and the appearance of a few percent quartz and montmorillonite. Nesterenko *et al.* (1974) reported similar observations. It appears therefore, that Cu, and possibly other important transition metals such as Pb, Zn, Au and Ag, are held mainly on surfaces or in reactive interstitial material such as sulphide and are

readily available for solution into hydrothermal fluids (release of metals such as Co and Ni may require pervasive alteration of olivine and pyroxene). Hydrothermal alteration of basaltic glass to palagonite by the action of sea water during submarine eruption, may also contribute to local concentration of transition metals (Nayudu, 1974).

In the following, we attempt to evaluate the ore-forming potential of the sea water/basalt leaching process, by constructing simple models based on what little data is available, together with some reasonable estimates. For comparison, two models are considered which approach the problem from slightly different points of view. For both models we assume a sub-sea floor hydrothermal system active over a volume of 15 km³. This figure was chosen as a very conservative estimate, with respect to known systems of only moderate size, such as Waireki, which involves a volume on the order of 100 km³ (Ellis, 1967).

Model 1. We take the average Cu content of ocean floor tholeiite as 60 ppm and hence a total of about three million tons of copper available within our 15 km³ hydrothermal system. The volume of sea water/rock interaction within the system can be estimated by assuming a fracture frequency of 20 cm and an average crack width of 0.25 mm (recent studies by Lister, 1975, and others, indicate that fracture frequency in the upper layers of oceanic crust ranges between 2.4 cm and 30 cm). This figure is multiplied by 10 in order to account for actual volume of interaction (in studying deep sea basalts from the mid-Atlantic ridge, Andrews *et al.*, 1976, observed from oxidation halos that the actual volume of fluid/rock interaction is at least 10 to 15 times and up to 20 times the dimensions of associated cracks and veins). Assuming that 50 per cent of the Cu available in this volume of sea water/rock interaction, is actually taken into solution by hydrothermally circulating sea water (a reasonable assumption since this figure was almost 100 per cent in experiments conducted by Ellis, 1968, and Nesterenko *et al.*, 1974) a system of these dimensions would be capable of producing about 125,000 tons of Cu.

Model II. During experimental research on sea water/basalt interaction, Hajash (1975), measured Cu concentrations in solution of up to 0.3 ppm. In similar experiments, Ellis (1968), measured Cu concentrations in solution of up to four ppm. One km³ of basic magma, cooling from 1200°C to 300°C can heat three km³ of seawater to 300°C. On this basis each km³ of oceanic crust is capable of producing about 3X10¹² kg of hydrothermal sea water. During the life of our 15 km³ system this would be a total of 45X10¹² kg of hydrothermal sea water. If 0.3 ppm Cu were taken into solution, such a system could produce 15,000 tons of copper. With 4 ppm Cu in solution, the production would be about 200,000 tons. The tonnage estimated by model I approximates the average of the range indicated by model II. As illustrated on Table I, comparison of these figures to those of known deposits is reasonable.

Magmatic Source. At magmatic temperatures, volatility is important in the behavior of some of the common ore-forming metals and as indicated by Krauskopf (1964, 1967), considerable amounts must be present in magmatic gas at temperatures of around 600°C and higher. Vapour transport of metals in volcanic fumaroles will take place because: - a) metal compounds such as chlorides are highly volatile, and b) metal compounds may readily dissolve in highly compressed water vapour (Krauskopf, 1967). Both are subject to the condition that the H₂S content of the environment is not high. A recent analysis of sublimate from a lava fountain of Kilauea volcano, Hawaii (Table II), provides an illustration of such metal transport. Undoubtedly this is a potential ore forming process in subaerial and shallow water

Table II

Analysis of sublimate sampled directly from a lava fountain of Kilauea volcano, Hawaii. (Naughton et al., 1974).

Wt.% - moisture excluded		
Major cations %	Minor cations %	Anions and other %
Na 4.1	NH ₄ 0.22	SO ₄ 74.0
K 1.5	Ti 0.33	Cl 5.4
Ca 3.5	Zn 0.25	F 1.6
Mg 2.2	H 0.22	B 0.59
Al 2.8	Cu 0.12	SiO ₂ 0.39
Fe 2.6	Ni 0.04	

environments. In the submarine environment of a spreading ridge, basaltic magma, crystallizing under the combined load pressure of sea water and four to five kms of oceanic crust, will be undersaturated with respect to a water dominated gas phase. Under such conditions, water cannot generally form a separate phase with an independent physical behavior. Magmatic-fumarolic activity (in the conventional sense), is therefore an unlikely mechanism for transport of metals. On the other hand, it is well known that given the right structural setting, a shallow mafic intrusion can absorb significant amounts of water (up to 5%), available in the host environment as connate water, or ground water (Taylor, 1968). During crystallization approximately one per cent of this water will be fixed in hydrous phases such as amphibole, the remainder will be expelled as very high temperature hydrothermal fluid. These fluids will be the hottest and the most conducive for metal transport directly from magma, particularly if they originate from chloride-rich sea water. Such conditions are likely in the immediate vicinity of mid-oceanic ridge crests, where there is evidence to suggest that basaltic magma chambers exist at very shallow levels.

Although there is no realistic method of evaluating the relative contribution of each of the above processes, it is perhaps reasonable to expect magmatic contributions to be most active at ridge crests, where magma chambers exist at very shallow depth, and the leaching phenomena to be relatively more significant on ridge flanks, where fracture penetration occurs to significant depth and sea-water circulation through oceanic crust becomes well established.

Metal Transport. The subject of metal transport by aqueous fluids is a major study in itself, details of which are discussed by Helgeson (1964); Barnes and Czamanske (1967); Burnham (1967) and Helgeson (1969). Experimental research together with field observation have led to the conclusion that hydrothermal solutions capable of dissolving and transporting significant quantities of transition metals will do so primarily by one of two ways: - a) by metal complexing with a sulphide species (such as S²⁻, HS⁻, S₂O₃²⁻) in a Cl⁻ poor environment, or b) by metal complexing with Cl⁻ in a sulphide poor environment. A solution containing significant quantities of both chloride and sulphide appears to be less

Table I

Copper contents of some known massive sulphide deposits in comparison with calculations based on simple theoretical models involving metal leaching of oceanic crust by sea water.

Deposit	Location	Host Rocks	Estimated Copper Tonnage	Reference
Skouriotissa	Cyprus	ophiolitic volcanics	135,000	Rona, 1973
York Harbour	Newfoundland	ophiolitic volcanics	5,640	Duke & Hutchinson, 1973
Lake Dufault	Ontario	Archean volcanics	92,000	Hutchinson, 1973
Metal leaching of oceanic crust by seawater		MODEL I	125,000	this report
		MODEL II	15,000-200,000	this report

conductive to metal transport since complex activity influences may reduce the activity of key species in the transport process (Barnes and Czamanske, 1967, p. 355). There are of course, a number of other chemical species such as hydroxide, carbonate, bicarbonate and sulphate which, under certain circumstances, could be important metal-complexing agents (Helgeson, 1964) but the data available suggests that processes of metal transport in the quantities required for extensive ore deposition will most likely involve either sulphide or chloride species.

The pervasive occurrence of sea water within the upper levels of oceanic crust represents the largest and most accessible reservoir of sulphur (as SO_4^{2-}) and Cl^- in this environment. As discussed above, the almost quantitative removal of SO_4^{2-} from sea water during initial interaction with oceanic crustal rocks, has been demonstrated experimentally (Bischoff and Dickson, 1975; Hajash, 1975) and observed in natural systems (Tómasson and Kristmansdóttir, 1972). The initial chloride concentration of sea water is relatively high (about 20,000 ppm) and if anything, will become more concentrated with time due to loss of H_2O during hydration and solution of chloride from wallrock (Ellis, 1967). We suggest, therefore, that metal transport of any significant quantity by hydrothermally circulating sea water, will involve chloride rather than sulphide complexing. Magmatic contribution of sulphide to circulating sea water undoubtedly occurs, but will be insignificant relative to chloride concentration. It is significant that most metal-rich hydrothermal emanations active today, such as those observed in the Salton Sea, the Red Sea and the Chelekan Peninsula, are chloride-rich - sulphide-poor in accord with Helgeson's (1964, 1969) conclusions.

The importance of chloride concentrations with respect to the ability of a fluid to transport metals in solution, is qualitatively illustrated on Figure 6. This figure plots Cl^- (vs) $\text{Cu}+\text{Pb}+\text{Zn}$ concentration in some of the presently active systems of the world. Although our use of this data is qualitative, a significant relationship is still apparent. The range indicating the metal transporting capability of sea water, with

respect to its normal chloride content, is in good agreement with experimental data.

Ore Deposition on the Ocean Floor

The deposition of metal sulphides in ore proportions is controlled by changes in the stabilities of metal complexes in solution. The conditions causing dissociation of metal complexes and localization of precipitating sulphides will involve a complex interplay of many

factors such as adiabatic expansion of the solution, changes in temperature and Eh-pH conditions as a result of dilution, mixing and hydrothermal rock alteration (Helgeson, 1964; Barnes and Czamanske, 1967; and Toulmin and Clark, 1967).

The behavior of ore fluids and the actual mechanism of ore formation in the submarine environment of the ocean floor, will be significantly affected by the following: - (a) the density of ore fluids

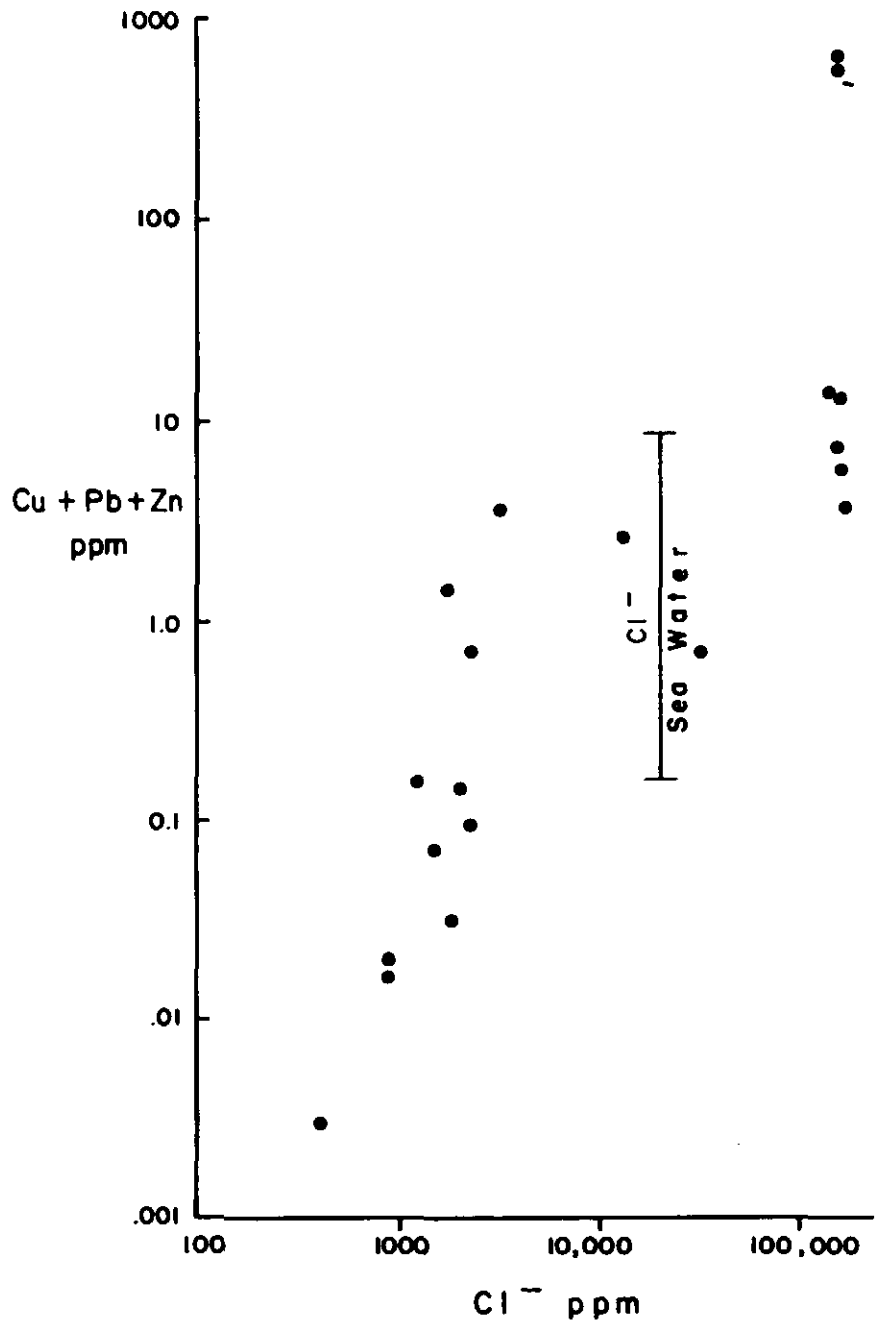


Figure 6
Cl (vs) Cu+Pb+Zn concentrations of presently active hydrothermal systems

(White, 1967; Ellis, 1967; White, 1968; Lebedev and Nikitina, 1968; Ellis, 1968; Browne, 1971; Ferguson and Lambert, 1972).

relative to that of sea water, (b) organic activity in the immediate environment, (c) local topography and current motions, (d) the chemistry of sea water.

As pointed out by Sato (1972), the physical behavior of the ascending ore-fluid in sea water will be dependent on its temperature-salinity conditions, that is, its density relative to sea water. If the solution is less dense than sea water, it will float upwards and eventually experience infinite dilution. If by some mechanism metals are released during this process they may accumulate as a colloidal suspension, eventually to settle out in the vicinity of the discharge area, or in the presence of bottom currents, they may be dispersed over a wide area of the ocean floor. The latter situation could very easily result in the generation of metal-enriched pelagic sediments, such as found in the vicinity of the East Pacific Rise. If the density is greater than sea water, the ore fluid will collect in topographic lows.

Upon discharge into the ocean the chloride-rich, sulphide-poor ore fluids will gain immediate access to an infinitely large reservoir of oxidized sulphur. On this basis, it is reasonable to assume that massive sulphide deposition on the ocean floor involves the reduction of sea water sulphate to sulphide, by the action of inorganic and/or organic processes in the immediate environment of hydrothermal discharge.

Inorganic Reduction. Detailed structural studies of some massive sulphide bodies suggest that under certain conditions, hydrothermal solutions discharging onto the ocean floor are able to produce their own reducing environment. This process is best demonstrated by considering some of the stratigraphic features exhibited by the Kuroko massive sulphide ores of Japan. These deposits characteristically exhibit the following sequence from the base up: - 1) gypsum-anhydrite beds, 2) massive sulphide ore, 3) barite beds, 4) ferruginous quartz beds (hematite + quartz) (Ohmoto and Rye, 1974; Lambert and Sato, 1974). In order to explain this sequence, we envisage the advance of hot, metal rich, hydrothermal fluids into a topographically restricted area of the ocean floor, where bottom-current activity is at a minimum. The

solubility of CaSO_4 decreases with increasing temperature so that initial heating of sea water in the immediate vicinity of discharge, results in precipitation of anhydrite directly from sea water (anhydrite precipitation will be greatly enhanced if discharging hydrothermal fluids are rich in Ca^{2+}). Continued discharge of the reduced, hydrothermal fluid results in a flushing out of most of the oxidizing species and the gradual establishment of a reducing environment. Reduction of sea water SO_4^{2-} to H_2S results in the precipitation of metal sulphides, which accumulate stratigraphically above and/or in the immediate vicinity of the anhydrite. The subsequent barite and ferruginous quartz deposition accompanies receding flow of the reducing ore solutions and the re-establishment of oxidizing conditions.

Organic Reduction. Production of significant quantities of H_2S could occur in interstitial sea water trapped in ocean floor sediments, as a result of the presence of sulphate-reducing bacteria and/or reactions involving oxidation of organic matter. Impregnation of these sediments by metal-bearing hydrothermal fluids would result in the precipitation of significant quantities of metal sulphide. This mechanism appears to explain the copper-bearing Nonesuch shales of Michigan (White, 1968). If sulphate-reducing bacteria are abundant in sea water immediately above the discharging fluids, it is conceivable that sufficient sulphide could be produced in this area to precipitate metals in significant quantities, which would slowly settle and accumulate on the sea floor below. There is substantial evidence to suggest that this type of mechanism is responsible for sulphide precipitation in brine pools of the Red Sea (White, 1968; Bischoff, 1969). It would also explain the large quantities of carbon in deposits such as Kidd Creek, Timmins.

Concluding Statement

There can be no doubt, that recent observations and experimental studies have produced reasonable models for sea-floor ore formation. The processes are complex and many variables contribute to the economically successful accident. On account of the vast sampling problems involved, it seems clear that developments in submarine geophysical and geochemical prospecting methods will be needed to locate the deposits that must certainly exist.

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