International Seabed Authority

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ISA Technical Study: No. 2

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Polymetallic Massive Sulphide Deposits at the Modern Seafloor and their Resource Potential

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Since 1979, polymetallic massive sulphide deposits have been found at water depths up to 3,700 m in a variety of tectonic settings at the modern seafloor including mid-ocean ridges, back-arc rifts, and seamounts. Many of the sulphide deposits consist of a black smoker complex on top of a sulphide mound which commonly is underlain by a stockwork zone. It has been widely established that circulating seawater which is modified in a reaction zone close to a subaxial magma chamber is the principal carrier of metals and sulphur which are leached out of the oceanic basement. Precipitation of massive and stockwork sulphides at and beneath the seafloor takes place in response to mixing of the high-temperature (up to 400°C) metal-rich hydrothermal seawater fluid with ambient seawater. Polymetallic seafloor sulphide deposits can reach a considerable size (up to 100 million tonnes) and often carry high concentrations of copper (chalcopyrite), zinc (sphalerite), and lead (galena) in addition to gold and silver. Extremely high concentrations of gold have recently been found in a new type of seafloor mineral deposit previously only known as epithermal (magmatic) gold deposits on the continents. Due to the high concentration of base and precious metals, seafloor polymetallic sulphide deposits have recently attracted the interest of the international mining industry. The recovery of those deposits appears to be both economically and environmentally feasible due to certain advantages over land-based deposits and will likely become reality within this decade. For logistical and technical reasons, future mining operations will largely focus on deposits in national rather than international waters.

1. INTRODUCTION

The discovery of high-temperature black smokers, massive sulphides, and vent biota at the crest of the East Pacific Rise at 21°N in 1979[1,2] confirmed that the formation of new oceanic crust through seafloor spreading is intimately associated with the generation of metallic mineral deposits at the seafloor. It was documented that the 350°C hydrothermal fluids discharging from the black smoker chimneys at this site at a water depth of about 2,600 m continuously precipitate metal sulphides in response to mixing of the high-temperature hydrothermal fluids with ambient seawater. The metal sulphides including pyrite, sphalerite, and chalcopyrite eventually accumulate at and just below the seafloor and have the potential to form a massive sulphide deposit. It has also been documented that circulation of seawater through the oceanic crust is the principal process responsible for the formation of massive sulphide deposits in this environment. Seawater which deeply penetrates into the oceanic crust at seafloor spreading centres is being modified to a hydrothermal fluid with low pH, low Eh, and high temperature during water-rock interaction above a high-level magma chamber. This fluid is than capable of leaching and transporting metals and other elements which eventually precipitate as massive sulphides at the seafloor or as stockwork and replacement sulphides in the sub-seafloor. The resulting massive sulphide deposits can reach considerable size ranging from several thousand to about 100 million tonnes. High concentrations of base (copper, zinc, lead) and in particular precious metals (gold, silver) in some of these deposits have recently attracted the interest of the international mining industry.

In the two decades since the discovery of hydrothermal vents at the mid-ocean ridges, significant mineral deposits have been documented in more than a dozen different volcanic and tectonic settings around the world at water depths up to 3,700 m. Polymetallic sulphide deposits are found on fast-, intermediate-, and slow-spreading mid-ocean ridges, on axial and off-axis volcanoes and seamounts, in sedimented rifts adjacent to continental margins, and in subduction-related arc and back-arc environments (*Figs. 1 and 2*).

Land-based massive sulphide deposits and polymetallic sulphides at the seafloor are products of the same geological and geochemical processes and many analogies can be drawn between modern examples and base metal deposits currently being mined on land[3,4,5,6,7]. Detailed geological, mineralogical, and geochemical analyses of massive sulphides from back-arc spreading centres of the western and south-western Pacific have indicated that these subduction-related sites represent the closest modern analogues of the majority of the economically important land-based deposits which occur in felsic volcanic rocks instead of mid-ocean ridge basalts[8]. Modern seafloor hydrothermal systems are thus excellent natural laboratories for understanding the genesis of volcanic-hosted massive sulphide deposits, and this knowledge can be translated directly to the ancient geological record on land, where evidence for the origin and nature of mineral deposits is often obscured by millions of years of geological history.

2. GEOLOGIC SETTING

Following the discovery of black smokers at the East Pacific Rise, there was a rapid growth in the number of hydrothermal deposits found on fast-spreading mid-ocean ridges. So many deposits were found along fast-spreading segments of the East Pacific Rise, and virtually nowhere else, that it became widely accepted that slower-spreading ridges could not support productive hydrothermal activity.

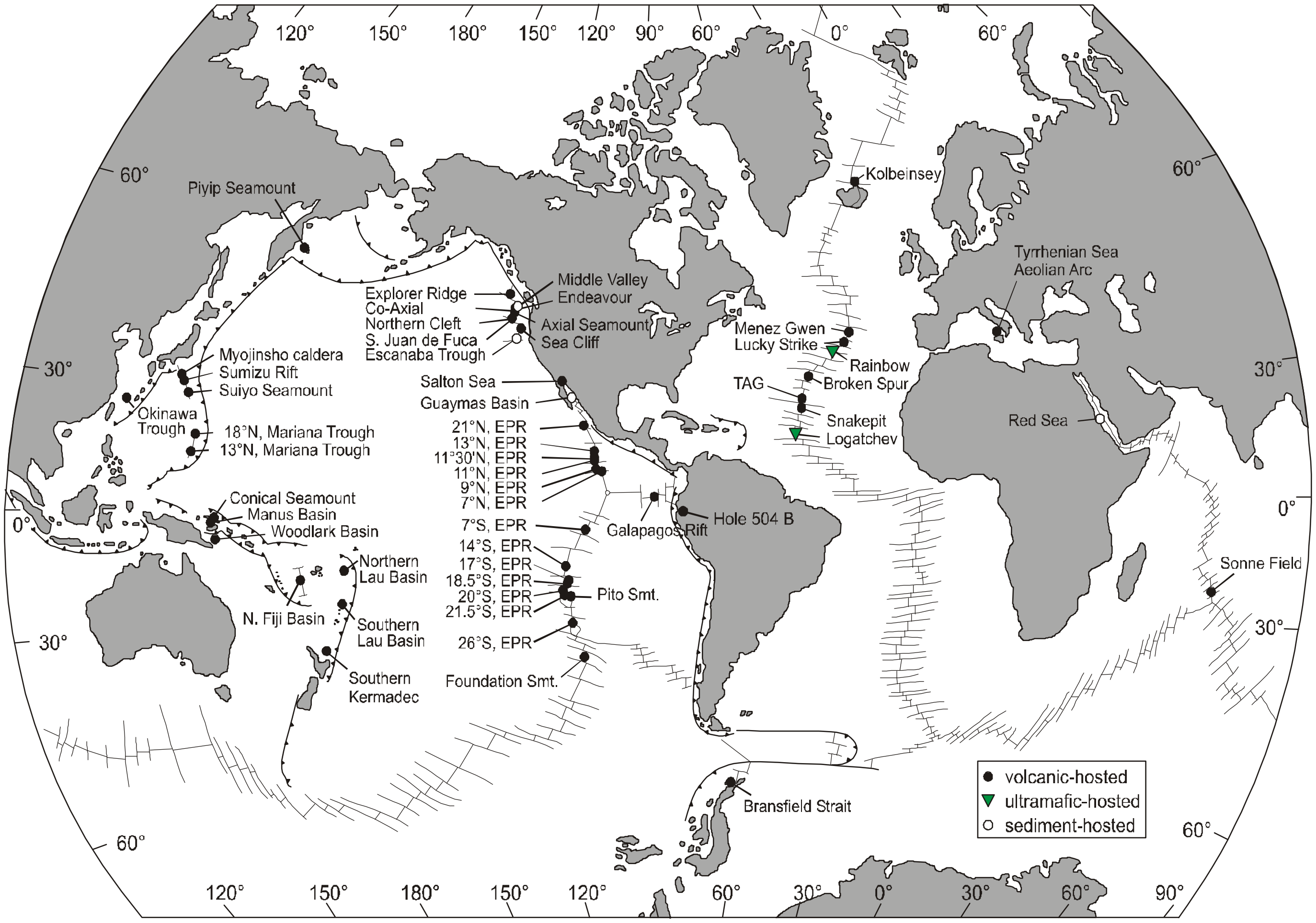

Figure 1. Location of hydrothermal systems and polymetallic massive sulphide deposits at the modern seafloor.

However, in 1985, the discovery of black smokers in the large TAG hydrothermal field at the Mid-Atlantic Ridge[9] offered compelling evidence that slow-spreading ridges may also be important settings for sulphide deposits. This idea has since been confirmed by the discovery of a number of further large sulphide occurrences along the Mid-Atlantic Ridge (Logatchev, Snakepit, Broken Spur, Lucky Strike, Menez Gwen[10,11,12,13]) and the Central Indian Ridge (Sonne Field[14,15,16]).

Shortly after the discovery at 21°N, large sulphide deposits were also discovered in sediment-filled basins in the Gulf of California (Guaymas Basin[17]). The idea that sedimented ridges might also be important sites for sulphide accumulation was confirmed in 1991 and 1996, when the Ocean Drilling Program intersected about 100 m of massive sulphides in the large Middle Valley deposit on the Juan de Fuca Ridge off-shore Canada[18,19].

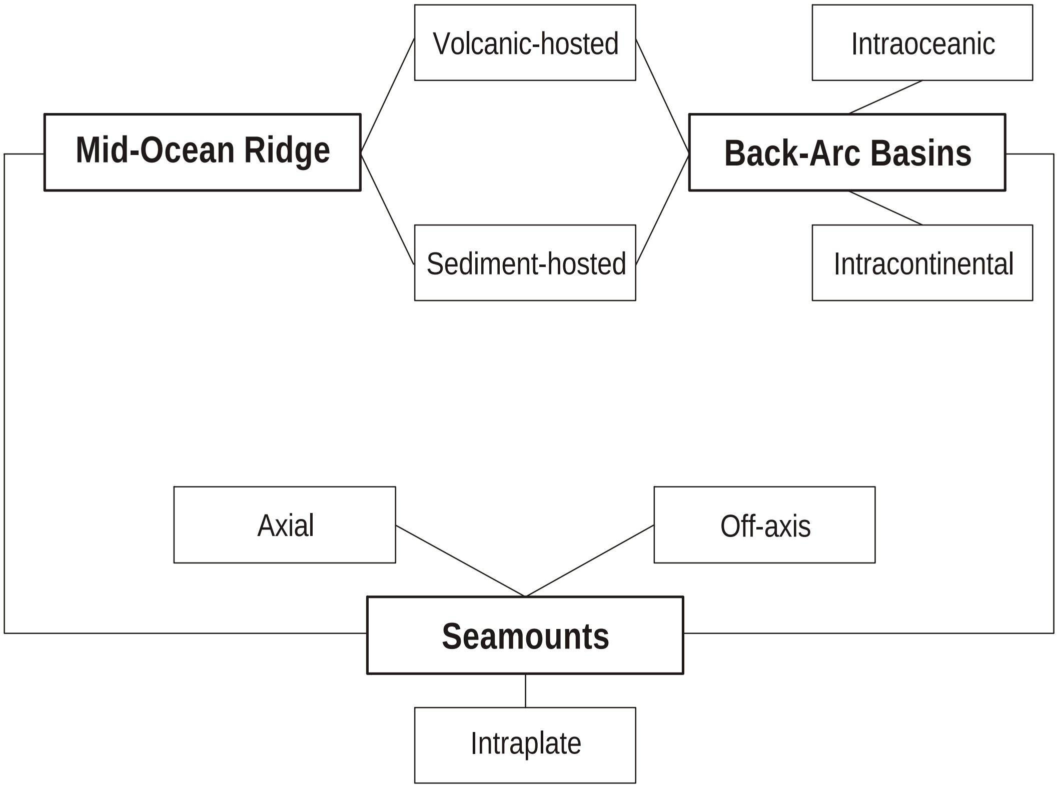

Figure 2. Simplified diagram showing the diverse geological environments for the occurrence of seafloor hydrothermal systems. Polymetallic massive sulphide deposits have been found in all settings except for intraplate seamounts.

The first sulphide deposits reported in back-arc spreading centres were found in the Central Manus Basin[20] and the Mariana Trough[21,22]. These discoveries led to extensive exploration of the marginal basins and the arc and back-arc systems of the western and southwestern Pacific in the late 1980s. The complex volcanic and tectonic settings of convergent margins in the Pacific suggested that a number of different deposit types might be present in this region. A wide range of mineral deposits have since been found in back-arc rifts at different stages of opening (immature versus mature), on volcanoes along the active volcanic fronts of the arcs, as well as in rifted fore-arc environments. Well-known examples of polymetallic massive sulphide deposits have been described from mature back-arc spreading centres such as the North Fiji Basin[23], along propagating back-arc rifts such as the Valu Fa Ridge in the southern Lau Basin[24], and in nascent back-arc rifts such as the Okinawa Trough[25]. In 1991, extensive sulphide deposits were found to be associated with felsic volcanism in the Eastern Manus Basin [26], and hydrothermal deposits have also been located in the western Woodlark Basin, where seafloor spreading propagates into the continental crust of Papua New Guinea[27]. Today, more than 100 sites of hydrothermal mineralisation are known at the modern seafloor[28,29,30] including at least 25 sites with high-temperature (350-400°C) black smoker venting.

The majority of sites so far have been located at the East Pacific Rise, the Southeast Pacific Rise, and the Northeast Pacific Rise, mainly because the first discovery of an active high-temperature hydrothermal system was made at 21°N at the East Pacific Rise off shore Baja California. Only one site has so far been located at the ridge system of the Indian Ocean, close to the Rodriguez Triple Junction[14,15,16]. The scarcity of sulphide deposits on the Mid-Atlantic Ridge and in the Indian Ocean is, at least to a large extent, a function of restricted exploration activity in these areas. It has been assumed that today only about 5% of the 60,000 km of oceanic ridges worldwide have been surveyed and investigated in some detail.

3. HYDROTHERMAL CONVECTION

At oceanic spreading centres, seawater penetrates deeply into the newly formed oceanic crust along cracks and fissures, which are a response to thermal contraction and seismic events typical for zones of active seafloor spreading. The seawater circulating through the oceanic crust at seafloor spreading centres is converted into an ore-forming hydrothermal fluid in a reaction zone which is situated close to the top of a subaxial magma chamber (*Fig. 3*). Major physical and chemical changes in the circulating seawater include (i) increasing temperature, (ii) decreasing pH, and (iii) decreasing Eh.

The increase in temperature from about 2°C to values >400°C[31,32] is a result of conductive heating of a small percentage of seawater close to the solidified top of a high-level magma chamber[33]. This drives the hydrothermal convection system and gives rise to black smokers at the seafloor. High-resolution seismic reflection studies have indicated that some of these magma reservoirs may occur only 1.5-3.5 km below the seafloor[34,35]. The crustal residence time of seawater in the convection system has been constrained to be 3 years or less[36]. Data from water/rock interaction experiments indicate that, with increasing temperatures, the Mg^{2+} dissolved in seawater (about 1,280 ppm) combines with OH-groups (which originate from the dissociation of seawater at higher temperatures) to form $Mg(OH)_2$, which is incorporated in secondary minerals such as smectite (<200°C) and chlorite (>200°C)[37,38,39,40]. The removal of OH-groups creates an excess of H^+ ions, which is the principal acid-generating reaction responsible for the drop in pH from seawater values (pH 7.8 at 2°C) to values as low as pH 2[41]. Exchange of H^+ for Ca^{2+} and K^+ in the rock releases these elements into the hydrothermal fluid.

The leaching of Ca^{2+} balances the continuous removal of Mg^{2+} from seawater. Endmember hydrothermal fluids are defined as presumed deep-seated high-temperature fluids computed by extrapolating compositions and physical parameters back to Mg=0 on the assumption of quantitative removal of Mg. At high temperatures, however, the formation of epidote (Ca fixation) also results in an excess of H^+ which further contributes to the acidity of the hydrothermal fluid. These reactions take place at water/rock ratios of less than five and commonly close to one[42]. The oxygen which is present in the circulating seawater in the form of sulphate is removed partly by precipitation of anhydrite and partly through conversion of igneous pyrrhotite to secondary pyrite and the oxidation of Fe^{2+} to Fe^{3+} forming Fe-oxyhydroxides and secondary magnetite in the basalt[40]. Partial reduction of seawater SO_4^{2-} contributes to the formation of H_2S, but most of the reduced S in the fluid is derived from the rock itself.

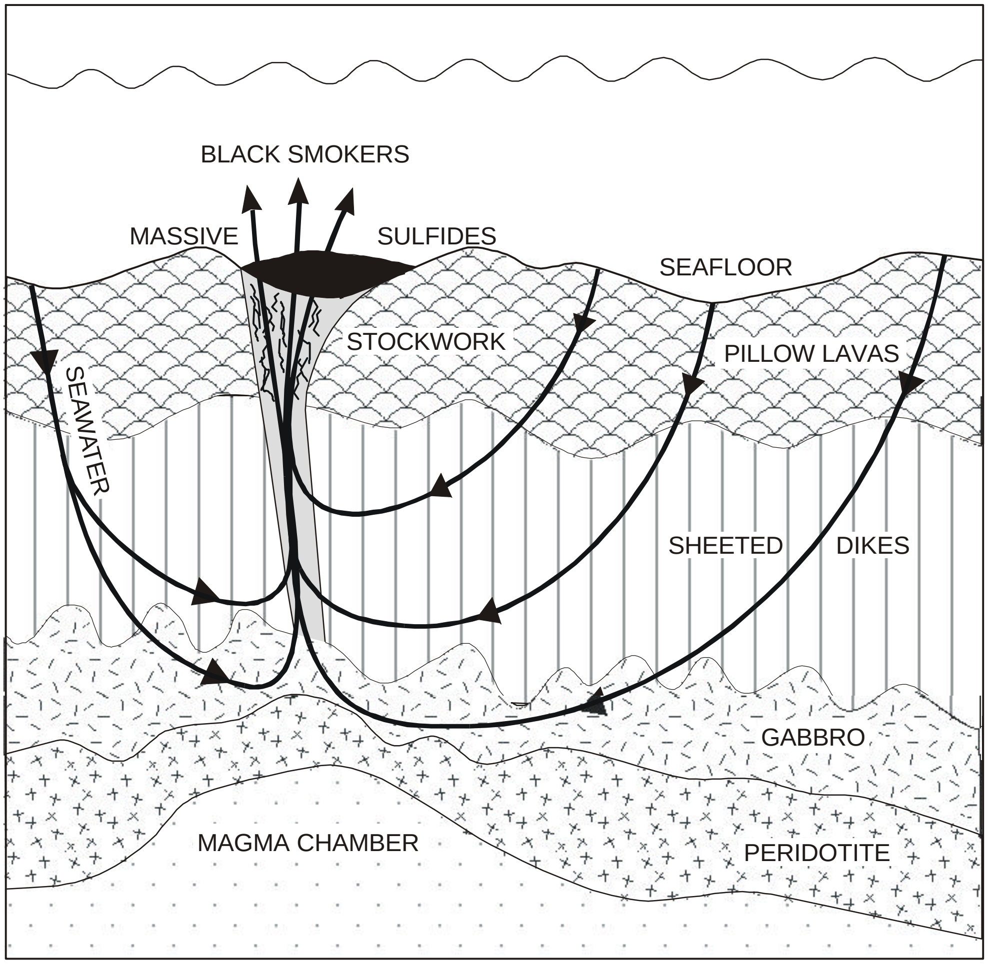

Figure 3. Model showing a seawater hydrothermal convection system above a subaxial magma chamber at an oceanic spreading centre. Radius of a typical convection cell is about 3-5 km. Depth of the magma chamber usually varies from 1.5-3.5 km.

This highly corrosive fluid is now capable of leaching elements such as Li, K, Rb, Ca, Ba, the transition metals Fe, Mn, Cu, Zn, together with Au, Ag and some Si from the oceanic basement[43]. Sulphide droplets in the basalt are considered to be the major source for metals and S[44]. The metals are mainly transported as chloride complexes at high temperatures and, in some cases, as bisulphide complexes (in particular Au) at lower temperatures.

Due to its increased buoyancy at high temperatures, the hydrothermal fluid rises rapidly from the deep-seated reaction zone to the surface along major faults and fractures within the rift valley or close to the flanks of the rift. In particular the intersections of faults running parallel and perpendicular to the ridge axis are the loci of high-velocity discharge black smokers and massive sulphide mounds. The sulphide precipitation within the upflow zone (stockwork) and at the seafloor (massive sulphides) is a consequence of changing physical and chemical conditions during mixing of high-temperature (250-400°C), metal-rich hydrothermal fluids with cold (about 2°C), oxygen-bearing seawater (*Fig. 4*).

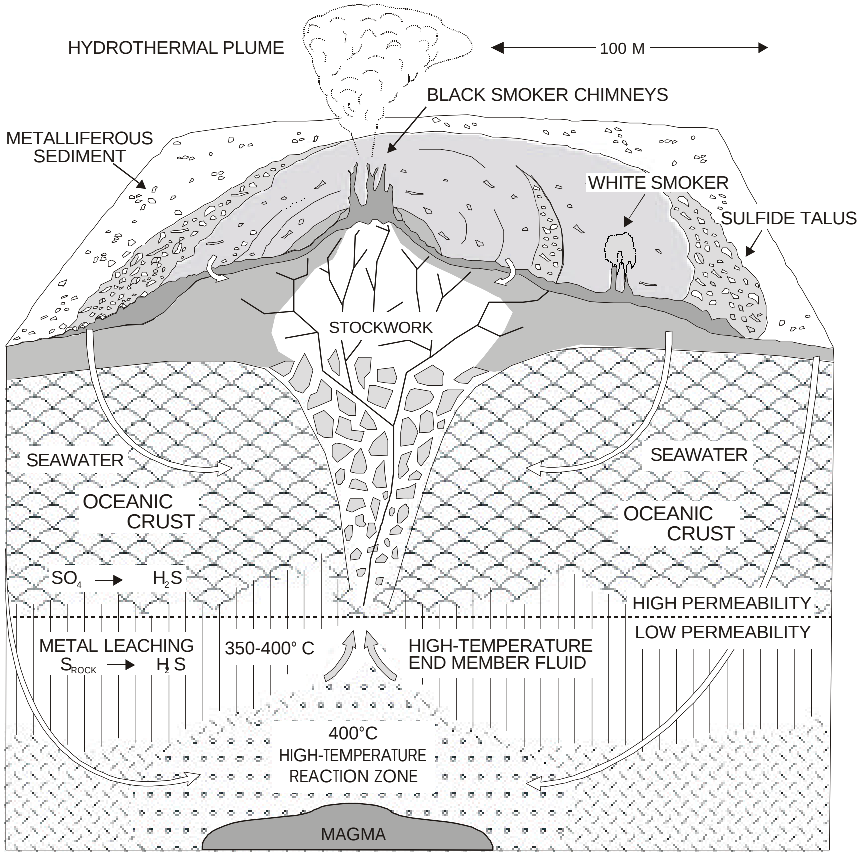

Figure 4. Cross-section showing the principal components of a seafloor hydrothermal system.

4. MINERALOGY

The mineralogy of seafloor sulphide deposits (*Table 1*) has been documented in a number of detailed studies of samples from various sites[22,45,46,47,48,49,50,51,52]. The mineral paragenesis of sulphide deposits at volcanic-dominated mid-ocean ridges usually includes assemblages that formed at temperatures ranging from about 300-400°C to less than 150°C. High-temperature fluid channels of black smokers and the interiors of sulphide mounds commonly consist of pyrite and chalcopyrite together with pyrrhotite, isocubanite, and locally bornite.

The outer portions of chimneys and mounds are commonly composed of lower temperature precipitates such as sphalerite/wurtzite, marcasite, and pyrite, which are also the principal sulphide minerals of low-temperature white smoker chimneys. Anhydrite is important in the high-temperature assemblages, but is typically replaced by later sulphides, amorphous silica, or barite at lower temperatures.

Sulphide mineralisation at back-arc spreading centres has some mineralogical characteristics that are similar to hydrothermal precipitates at volcanic-dominated mid-ocean ridges. Commonly, pyrite and sphalerite are the dominant sulphides. Chalcopyrite is common in the higher temperature assemblages, but pyrrhotite is rare. Barite and amorphous silica are the most abundant non-sulphides.

Many of the deposits forming in back-arc rifts are characterised by a variety of minor and trace minerals such as galena, tennantite, tetrahedrite, cinnabar, realgar, orpiment, and complex, non-stoichiometric Pb-As-Sb sulphosalts. The first examples of visible primary gold in seafloor sulphides were documented in samples of lower temperature (<300°C) white smoker chimneys from the southern Lau Basin[53,54] and occur as coarse-grained (18 microns) co-depositional inclusions in massive, Fe-poor sphalerite.

Table 1. Mineralogical Composition of Seafloor Polymetallic Sulphide Deposits

	Back-Arc Deposits	**Mid-Ocean Ridge Deposits**
Fe-sulphides	pyrite, marcasite, pyrrhotite	pyrite, marcasite, pyrrhotite
Zn-sulphides	sphalerite, wurtzite	sphalerite, wurtzite
Cu-sulphides	chalcopyrite, isocubanite	chalcopyrite, isocubanite
silicates	amorphous silica	amorphous silica
sulphates	anhydrite, barite	anhydrite, barite
Pb-sulphides	galena, sulphosalts	
As-sulphides	orpiment, realgar	
Cu-As-Sb-sulphides	tennantite, tetrahedrite	
native metals	gold	

5. METAL CONTENTS

Despite moderate tonnages in several seafloor deposits, recovered samples from about 50 deposits worldwide represent no more than a few hundred tonnes of material. Based on existing data and lacking information on the third dimension it is premature to comment on the economic significance of seafloor massive sulphides. Published analyses of sulphide samples, however, indicate that these deposits may contain important concentrations of metals that are comparable to those found in ores from massive sulphide mines on land. Estimated concentrations of base metals in seafloor massive sulphides tend to be higher, which in part may be due to a strong bias in sampling.

A large number of seafloor sulphides are recovered during submersible operations. A bias in the analytical data arises, because sulphide chimneys which are relatively easy to sample are often the focus of study. However, they are unlikely to be representative of the bulk composition of the deposits as a whole (e.g., 11 analysed samples from the Southern Juan de Fuca site have an average Zn content of greater than 34 wt.%) and little is known about the interiors of larger sulphide mounds and the underlying stockwork zones. Systematic sampling of both high- and low-temperature assemblages across the surfaces of some large active areas (e.g., TAG hydrothermal field, Explorer Ridge, Galapagos Rift) are more representative of the range of sulphide precipitates which comprise large deposits. Sufficient sampling, which has lead to potentially realistic estimates of metal concentrations, has been achieved at only a few sites (e.g., Middle Valley, Explorer Ridge, Galapagos Rift) while quantitative assessment of contained metals has been possible only for the Atlantis II Deep in the Red Sea. Adequate information about the continuity of base and precious metal concentrations in the interiors of the deposits can only be provided by drilling, as successfully demonstrated at the TAG mound (Ocean Drilling Program Leg 158[55]) and the Middle Valley site (Ocean Drilling Program Leg 139[18], Ocean Drilling Program Leg 169[56]).

Comparison of close to 1,300 chemical analyses of seafloor sulphides reveals systematic trends in bulk composition between deposits in different volcanic and tectonic settings (*Table 2*). The sediment-hosted massive sulphides (e.g., Escanaba Trough, Guaymas Basin), while being somewhat larger than deposits at the bare-rock mid-ocean ridges, appear to have lower concentrations and different proportions of base metals. Massive sulphides from these deposits average 4.7 wt.% Zn, 1.3 wt.% Cu, and 1.1 wt.% Pb (n=57). This reflects the influence of thick sequences of turbidite sediments on hydrothermal fluids ascending to the seafloor and the tendency for widespread precipitation of metals beneath the sediment-seawater interface. Calcite, anhydrite, barite, and silica are major components of the hydrothermal precipitates and may significantly dilute the base metals in sediment-hosted deposits. On basaltic, sediment-free mid-ocean ridges, sulphides are precipitated largely around the vent site, resulting in smaller deposits, but higher concentrations of metals. The largest deposits for which there are representative suites of samples (e.g., Explorer Ridge, Endeavour Ridge, Axial Seamount, Cleft Segment, East Pacific Rise, Galapagos Rift, TAG, Snakepit) have a narrow range of metal concentrations, and average 8.5 wt.% Zn and 4.8 wt.% Cu, but have only low concentrations (0.1 wt.%) of Pb (n=1,259, *Table 2*). Anhydrite, barite, and silica are important constituents of some chimneys, but on average they account for <20 % of the samples analysed.

Vent fluid compositions at all of the bare-rock mid-ocean ridge sites are remarkably similar, reflecting the high-temperature reaction of seawater with a uniform basaltic crust at greenschist facies conditions[57,58,59]. Therefore, large variations in base metal concentrations between deposits on the mid-ocean ridges likely reflect a sampling bias or differences in the conditions of formation of the deposits. For example, zinc-rich deposits at Axial Seamount and the Southern Juan de Fuca site appear to have formed at lower average temperatures (<300°C) than Cu-rich deposits (>300°C) elsewhere at the mid-ocean ridges.

Relative to samples from sediment-starved mid-ocean ridges, massive sulphides forming in basaltic to andesitic environments of intraoceanic back-arc spreading centres (e.g., Mariana Trough, Manus Basin, North Fiji Basin, Lau Basin) are characterised by elevated average concentrations of Zn (16.5 wt.%), Pb (0.4 wt.%), and Ba (12.6 wt.%), but low contents of Fe (13.0 wt.%, n=573, Table 2). Polymetallic sulphides in the Okinawa Trough, where rhyolites and dacites are a product of back-arc rifting in continental crust, have low Fe contents (6.2 wt.%) but are enriched in Zn (20.2 wt.%) and Pb (11.8 wt.%), and have high concentrations of Ag (2,304 ppm, maximum 1.1 wt.%), As (1.8 wt.%), and Sb (0.7 wt.%, n=40, *Table 2*). High Sb and As contents are accounted for by the presence of tetrahedrite, stibnite, and As-sulphides (i.e., realgar and orpiment) in these assemblages.

Table 2. Bulk Chemical Composition of Seafloor Polymetallic Sulphides

Element	Intraoceanic Back-Arc Ridges	Intracontinental Back-Arc Ridges	Mid-Ocean Ridges
Pb (wt.%)	0.4	11.8	0.1
Fe	13.0	6.2	26.4
Zn	16.5	20.2	8.5
Cu	4.0	3.3	4.8
Ba	12.6	7.2	1.8
As (ppm)	845	17,500	235
Sb	106	6,710	46
Ag	217	2,304	113
Au	4.5	3.1	1.2
(N)	573	40	1,259

The bulk composition of seafloor sulphide deposits in various tectonic settings is a consequence of the nature of the volcanic source rocks from which the metals are leached. Potential source rocks identified in the different tectonic environments range from MORB and clastic sediments at the mid-ocean ridges, to lavas of bimodal composition (andesite, basalt) in intraoceanic back-arcs and felsic volcanics (dacite, rhyolite) which are typical for young intracontinental back-arc rifts. These compositional variations are reflected by differences in the composition of the respective vent fluids. For example, chemical analyses of endmember fluids from the Vai Lili hydrothermal field which occurs in andesites of the Valu Fa Ridge in the southern Lau Basin indicate much higher concentrations of Zn, Pb, As and other elements compared to typical mid-ocean ridge fluids. Massive sulphides from the Okinawa Trough[25] are even more enriched in Pb than massive sulphides from the Lau Basin, which is likely a consequence of the high Pb contents of rhyolites and andesites in the source region and the characteristics of the hydrothermal fluids generated in this environment. High Pb and Ba contents of sediment-hosted seafloor sulphides simply reflect the elevated Pb and Ba contents of individual components in the sediment (e.g., feldspar). Similar trends in the bulk composition of massive sulphide deposits are widely recognised in ancient terrains[3,52,60].

6. SIZE AND TONNAGE

Considering that estimates of the continuity of sulphide outcrop are difficult, and that the thickness of the deposits is commonly poorly constrained, estimates for several deposits on the mid-ocean ridges suggest a size of 1-100 million tonnes, although the depth extend of mineralisation is difficult to assess. The by far largest deposits are found on failed and heavily sedimented but still hydrothermally active oceanic ridges. Drilling carried out by the Ocean Drilling Program during Legs 139 and 169 at the sediment-covered Middle Valley deposit on the northern Juan de Fuca Ridge has indicated about 8-9 million tonnes of sulphide ore[56] (*Table 3*). During both legs, about 100 m of massive sulphides and 100 m of stockwork were drilled at the Bent Hill site. The sub-seafloor stockwork zone is underlain by a stratiform Cu-rich horizon (“deep copper zone“) with copper grades ranging up to 17 wt.% Cu[56]. This significant discovery now represents an important new exploration target for the land-based mineral industry. The TAG hydrothermal mound located in 3,650 m water depth at the Mid-Atlantic Ridge 26°N was drilled during Ocean Drilling Program Leg 158 in 1994 to a total depth of 125 m[55,61]. It was estimated that the active TAG mound contains about 2.7 million tonnes of sulphide ore above the seafloor and approximately 1.2 million tonnes of sulphides in the sub-seafloor stockwork[62]. A comparison of the size of the modern deposits with some of the ancient ore bodies and ore districts indicates that extremely large deposits such as Kidd Creek in Canada (135 million tonnes) or Neves Corvo in Portugal (262 million tonnes) so far have not been discovered at the modern seafloor.

The largest known marine sulphide deposit is still the Atlantis II Deep in the Red Sea, which was discovered more than ten years before the first black smoker at the East Pacific Rise[63]. The Atlantis II Deep mineralisation largely consists of metalliferous muds, instead of massive sulphides, which is a consequence of the high salinity which the hydrothermal fluids acquire by circulation through thick Miocene evaporites at the flanks of the Red Sea rift. A detailed evaluation of the 40 km^2 deposit has indicated 94 million tonnes of dry ore with 2.0 wt.% Zn, 0.5 wt.% Cu, 39 ppm Ag, and 0.5 ppm Au[64,65,66] which results in a total precious metal content of roughly 4,000 tonnes of Ag and

50 tonnes of Au. A pilot mining test at 2,000 m depth has shown that this deposit can be successfully mined.

Estimates of sizes between 1-100 million tonnes for individual massive sulphide deposits on the seafloor thus are well within the range of typical volcanic-associated massive sulphide deposits on land. However, most occurrences of seafloor sulphides amount to less than a few thousand tonnes, and consist largely of scattered hydrothermal vents and mounds usually topped by a number of chimneys with one or more large accumulations of massive sulphide. More than 60 individual occurrences have been mapped along an 8 km segment of Southern Explorer Ridge, but most of the observed mineralisation occurs in two large deposits with dimensions of 250 m x 200 m[67]. The thicknesses of the deposits are difficult to determine unless their interiors have been exposed by local faulting. Typical black smokers are estimated to produce about 250 tonnes of massive sulphide per year. Thus, a local vent field with a few black smokers can easily account for a small size sulphide deposit, pending on the duration of activity. Reports of explored dimensions of deposits based on visual estimates from submersibles may be accurate to only +/-50% of the distances given and commonly include weakly mineralised areas between larger, discrete sulphide mounds (thereby over-estimating the continuity of sulphide outcrop). Reports based on transponder navigated camera tracks are probably accurate to +/-20%, but the extent of coverage is limited due to the slow tow-speeds and the narrow image. No geophysical tools currently provide a good basis for estimating the area of sulphide outcrop. High-resolution, deep-towed side-scan sonar may be refined to provide more accurate information over larger areas.

7. OCCURRENCE AND DISTRIBUTION OF GOLD

Gold grades are locally high in samples from a number of seafloor deposits at the mid-ocean ridges[50,68,69,70], and in particular in samples from the back-arc spreading centers[54]. Average gold contents for deposits at the mid-ocean ridges range from <0.2 ppm Au up to 2.6 ppm Au, with an overall average of 1.2 ppm Au (n=1,259, *Table 5*) In volcanic-dominated, sediment-free deposits, high-temperature (350°C) black smoker chimneys composed of Cu-Fe-sulphides typically contain <0.2 ppm Au. Here, much of the gold is lost to a diffuse hydrothermal plume. The gold content of massive sulphides from the interior of hydrothermal mounds is supposed to be similar to the gold content of the high-temperature chimney assemblages. Higher concentrations of primary gold occur in lower-temperature (<300°C), sphalerite-dominated assemblages with sulphosalts and late-stage barite and amorphous silica at Axial Seamount (6.7 ppm Au[68,70]). Comprehensive sampling of a few large, mature deposits at sediment-free ridges in the Northeast Pacific and Mid-Atlantic indicates typical average gold contents in the range of 1-2 ppm Au. Local enrichment of more than 40 ppm Au (TAG hydrothermal field[71]) is a consequence of remobilisation and reconcentration (hydrothermal reworking) of gold during sustained venting of hydrothermal fluids through the sulphide mounds (i.e., zone refining).

Table 3. Gold Grades in Polymetallic Massive Sulfides from the Modern Seafloor

	Au (ppm)		
	range	average	(N)
Conical Seamount (PNG) magmatic-epithermal system	0.01 – 230.0	26.0	40
Immature Back-Arc Ridges (intermediate to felsic volcanics)			
Lau Basin	0.01-28.7	2.8	103
Okinawa Trough	0.01-14.4	3.1	40
Central Manus Basin	0.01-52.5	30.0	10
Eastern Manus Basin	1.30-54.9	15.0	26
Woodlark Basin	3.80-21.1	13.1	6
Mature Back-Arc Ridges (MOR-type volcanics)			
Mariana Trough	0.14- 1.7	0.8	11
North Fiji Basin	0.01-15.0	2.9	42
Mid-Ocean Ridges (MORB)	0.01-6.7	1.2	1,259

The gold contents of sulphides from deposits in sedimented rifts (e.g., Guaymas Basin) are typically <0.2 ppm Au. Here, the interaction of hydrothermal fluids with organic-rich sediments causes strongly reducing conditions which limit the amount of gold that can be transported in hydrothermal solutions. However, Cu-rich sulphides from the Escanaba Trough are an exception as they contain up to 10 ppm Au with an average of 1.5 ppm Au. This is likely explained by an enriched source in the underlying sediments[72,73]. The metalliferous muds in the Atlantis II Deep have bulk gold contents of about 0.5 ppm Au[64], but sulphide-rich horizons have gold contents from <0.5 up to 4.6 ppm Au and average close to 2 ppm Au[66].

Polymetallic sulphides from a number of back-arc spreading centres have revealed particular high concentrations of gold averaging between 3-30 ppm Au[54]. Gold appears to be most abundant in sulphides associated with immature seafloor rifts in continental or island arc crusts. These settings are dominated by calc-alkaline volcanics including andesites, dacites, and rhyolites (e.g., Okinawa Trough, Lau Basin, Manus Basin). Polymetallic sulphides from the Valu Fa Ridge in the Lau back-arc have gold contents of up to 29 ppm Au with an average of 2.8 ppm Au (n=103, *Table 3*). These samples represent the first known examples of visible primary gold in polymetallic sulphides at active vents[53,54]. In the Okinawa Trough, gold-rich sulphide deposits with up to 14 ppm Au (average 3.1 ppm, n=40) occur in a back-arc rift within continental crust and resemble Kuroko-type massive sulphides[25,74,75]. Preliminary analyses of sulphides reported from the Central Manus Basin (Vienna Woods) indicate average gold contents of up to 30 ppm Au (n=10) and maximum concentrations of more than 50 ppm Au. The average gold content of massive sulphides in the Eastern Manus Basin (Pacmanus) is 15 ppm with a maximum of 54.9 ppm Au (n=26[76]) High gold contents up to 21 ppm Au have been found in barite chimneys in the Western Woodlark Basin, where seafloor spreading propagates into continental crust off Papua New Guinea[77,78].

The most gold-rich seafloor deposit found to date is located at Conical Seamount in the territorial waters of Papua New Guinea close to Lihir Island. Maximum gold concentrations in samples collected from the summit plateau of this seamount (2.8 km basal diameter at 1,600 m water depth, top at 1,050 m) range up to 230 ppm with an average of 26 ppm for 40 samples analysed[79,80].

8. RESOURCE POTENTIAL OF SEAFLOOR SULPHIDE DEPOSITS

Out of the more than 200 sites of hydrothermal mineralisation currently known at the modern seafloor, only about 10 deposits may have sufficient size and grade to be considered for future mining, although information on the thickness of most of those sulphide deposits is not yet available (*Table 4*). These potential mine sites include the Atlantis II Deep in the Red Sea, Middle Valley, Explorer Ridge, Galapagos Rift, and the East Pacific Rise 13°N in the Pacific Ocean, the TAG hydrothermal field in the Atlantic Ocean, as well as the Manus Basin, the Lau Basin, the Okinawa Trough, and the North Fiji Basin in the western and south-western Pacific. All of these sites except two (East Pacific Rise 13°N and TAG hydrothermal field) are located in the Exclusive Economic Zones of coastal states including Saudi Arabia, Sudan, Canada, Ecuador, Papua New Guinea, Tonga, Japan, and Fiji. Scientific drilling so far has been carried out by the Ocean Drilling Program to a depth of 125 m at the TAG hydrothermal field and to about 200 m at Middle Valley. Leg 193 of the Ocean Drilling Program is scheduled for December/January 2000/2001 to explore the third dimension of the Eastern Manus Basin (Pacmanus site). The Atlantis II Deep is still the only deposit that has been evaluated by a commercial company (Preussag, Germany) in the late 1970s based on standards usually applied by the minerals industry to land-based ore deposits. A pilot mining test has successfully demonstrated that the metalliferous muds occurring below the surface of a 60°C brine not only in the Atlantis II Deep can be continuously mined[81,82].

Table 4. Possible Sites for Mining of Seafloor Massive Sulphide Deposits

Deposit	Ocean Area	Water Depth	Jurisdiction	Country
Atlantis II Deep	Red Sea	2,000-2,200 m	EEZ	Saudi Arabia, Sudan
Middle Valley	Northeast Pacific	2,400-2,500 m	EEZ	Canada
Explorer Ridge	Northeast Pacific	1,750-2,600 m	EEZ	Canada
Lau Basin	Southwest Pacific	1,700-2,000 m	EEZ	Tonga
North Fiji Basin	Southwest Pacific	1,900-2,000 m	EEZ	Fiji
Eastern Manus Basin	Southwest Pacific	1,450-1,650 m	EEZ	Papua New Guinea
Central Manus Basin	Southwest Pacific	2,450-2,500 m	EEZ	Papua New Guinea
Conical Seamount	Southwest Pacific	1,050-1,650 m	EEZ	Papua New Guinea
Okinawa Trough	West Pacific	1,250-1,610 m	EEZ	Japan
Galapagos Rift	East Pacific	2,600-2,850 m	EEZ	Ecuador
EPR 13°N	East Pacific	2,500-2,600 m	International	
TAG	Central Atlantic	3,650-3,700 m	International	

Preussag has also performed active exploration for massive sulphide deposits in the Galapagos Spreading Centre 86°W in the mid 1980s during the GARIMAS project (Galapagos Rift Massive Sulphides), which consisted of three cruises with the German vessel SONNE. At that time it was concluded, that the Galapagos deposits are not sufficiently large and continuous to be economically mined.

It is also unlikely that deposits such as the TAG hydrothermal field, which is located in international waters at the Mid-Atlantic Ridge, the 13°N seamount at the East Pacific Rise or the Sonne hydrothermal field at the remote Rodriguez Triple Junction in the Southern Indian Ocean will become mining targets in the near future. This is also true for many of the sulphide deposits along the East, Northeast and Southeast Pacific Rises. However, in this decade, marine mining appears to be feasible under specific conditions ideally including:

(1) high gold and base metal grades,

(2) site location close to land, i.e., commonly within the territorial waters (200 nm Exclusive Economic Zone or even 12 nm zone) of a coastal state,

(3) shallow water depth not significantly exceeding 2,000 m (although the technology exists for mining in deeper water,).

Under those circumstances, massive sulphide mining can be economically attractive considering that the entire mining system is portable and can be moved from mine site to mine site. An investment into mining systems and ships is thus not tied to a certain location as is the case on land, where a typical mine development in a remote area including all infrastructure requires an initial investment of US$350-500 million.

Seafloor massive sulphide mining will likely focus on relatively small areas of the seafloor and largely be restricted to the surface (strip mining) and shallow subsurface (open cast mining) to recover sulphide mounds and chimney fields at and replacement ore bodies just below the seafloor. Environmental impact studies are yet to be carried out and will likely indicate that mining of seafloor massive sulphide deposits has only a relatively small environmental impact. For example, the high density of the sulphide particles (about 4 g/cm^3) will cause immediate redeposition of any sulphide debris produced by mining equipment such as large TV-controlled hydraulic grabs or continuous mining systems with cutter heads and airlift. Due to the large surface exposed to seawater, some of the liberated sulphide debris will oxidise in a way which is not different from the oxidation of inactive massive sulphides in many of the seafloor deposits described. Acid mine drainage, which usually causes significant environmental problems in land-based sulphide mines, will not have to be considered at the seafloor due to the diluting effect of the surrounding seawater.

Sediment which could be disturbed by mining and possibly be transported by bottom currents would potentially create a major hazard to the marine ecosystem[83]. Amos et al.[84] have pointed out that the greatest unknown and the greatest potential hazard with respect to manganese nodule mining is the behaviour and effect of sediment plumes at the seafloor, within the water column, and at the surface. While the bottom water will be directly affected by sediment disturbance due to mining equipment, the impact on the water column and the surface will be due to discharge of sediments which have been lifted along with the manganese nodules. However, a significant sediment cover is commonly not present at most seafloor sulphide deposits (except for Middle Valley and the Guaymas Basin) and thus has not to be taken into account. Consequently, mining of selected seafloor sulphide deposits, in particular those that are inactive and not inhabited by any kind of vent fauna, is feasible and does not create a larger environmental impact than the construction of a large harbour facility.

In December 1997, the Government of Papua New Guinea granted the first two marine exploration licences for seafloor sulphide deposits to an Australia-based mining company[85]. The licences cover an area of about 5,000 km^2 in the Manus back-arc basin and include the Vienna Woods (Central Manus Basin) and the Pacmanus (Eastern Manus Basin) sites, which are located on the west side of New Ireland. Mineralisation occurs at a water depth of 2,500 m (Vienna Woods) and 1,450-1,650 m (Pacmanus). Preliminary analyses of sulphides from both deposits indicate high average gold contents (see above) along with high concentrations of base metals. However, only a limited number of samples has been analysed so far and information about the depth extent of the mineralisation is still lacking.

A recent discovery of gold mineralisation at a seamount in a modern fore-arc environment of the Southwest Pacific suggests that a number of previously unexplored settings at the seafloor may be prospective for gold-rich hydrothermal systems. Mapping of largely uncharted waters in the Tabar-Feni island chain off Papua New Guinea revealed the position of several previously unknown volcanic cones about 10 km south of Lihir Island[86,87]. Conical Seamount, the largest of the seamounts south of Lihir (*Fig. 5* and *Fig. 6*), is host to a new type of marine mineral deposit, characterised by extremely high concentrations of gold and a style of mineralisation that indicates the participation of gold-rich magmatic fluids (as opposed to circulating seawater) in the formation of this deposit[71,87,88]. Samples of trachybasalt (1,200 kg) collected from the crater of Conical Seamount at a depth of 1,050 m contain up to 230 ppm Au (avg. 26 ppm, n=40, Table 5) with several dozen grains of native gold (up to 30 micron) identified as inclusions in sphalerite, galena, and amorphous silica. High concentrations of gold are uniformly associated with high concentrations of elements such as As, Sb, and Hg, known as the "epithermal suite" typical for the so-called epithermal (i.e., magmatic) gold deposits on land. The style of mineralisation is similar to that of the giant Ladolam gold deposit (1,300 tonnes Au content, daily production 60 kg Au) located on the neighbouring island of Lihir and it may be assumed that Conical Seamount represents a submarine analogue of this world-class terrestrial gold mine.

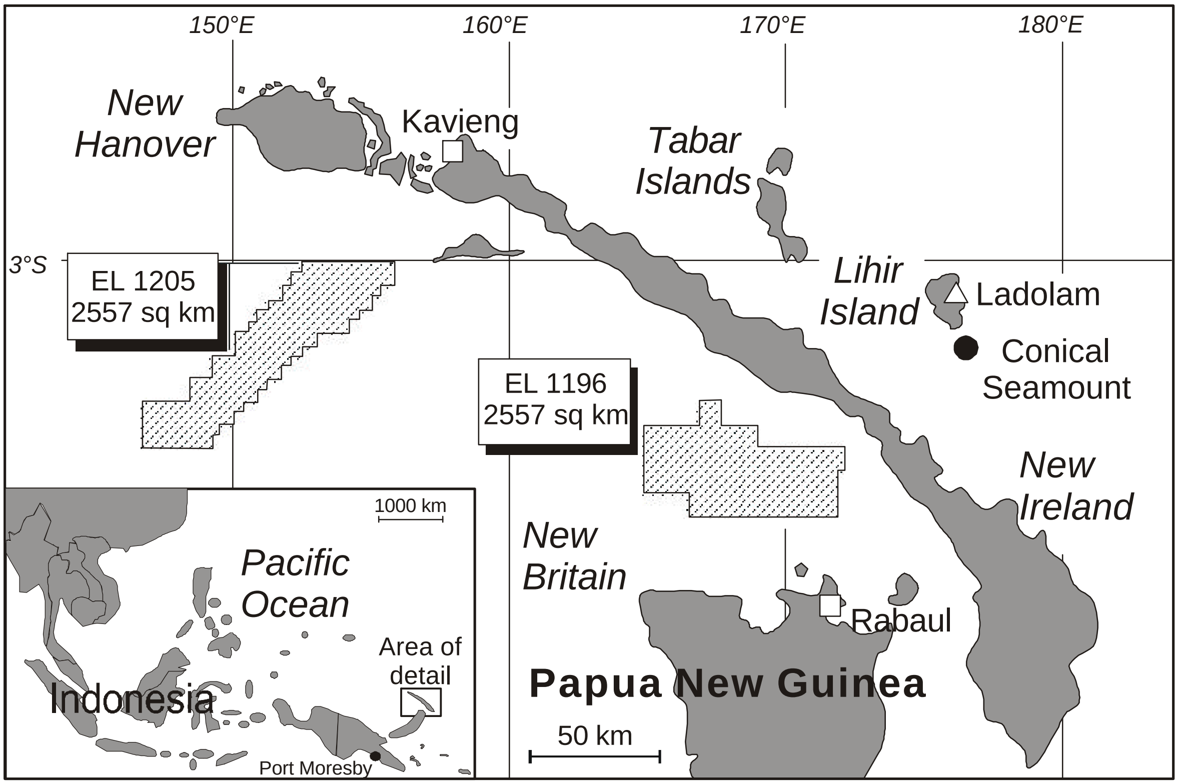

Figure 5. Map of the Manus Basin west of New Ireland showing the location of areas covered by an exploration licence granted to an Australia-based mining company by the Government of Papua New Guinea (after[85]). Notice the location of Conical Seamount south of Lihir Island and the Ladolam gold deposit on Lihir Island.

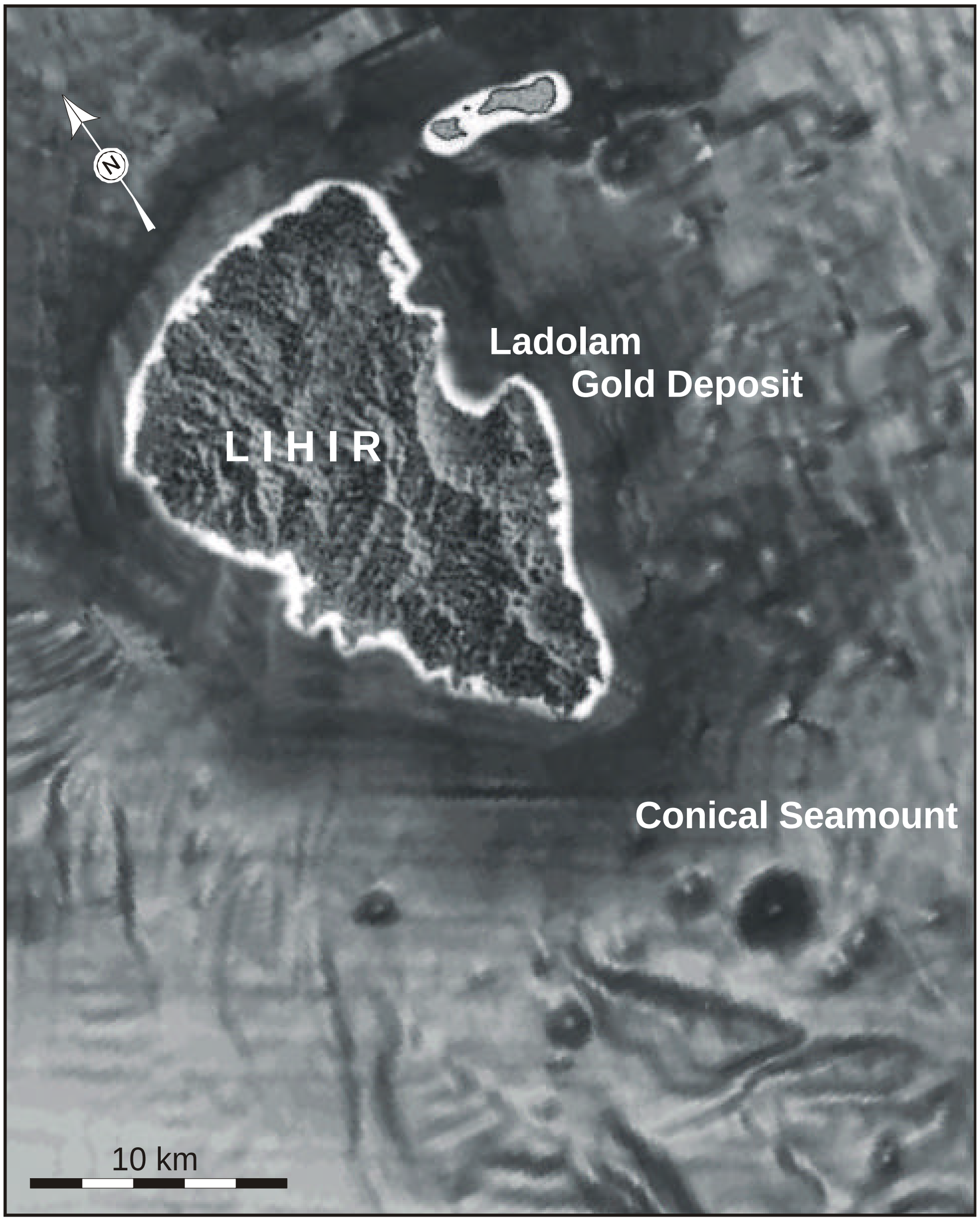

Figure 6. Bathymetry-based shaded relief of the Lihir Island group with the location of volcanic cones south of Lihir including Conical Seamount, which is host to a new type of submarine gold mineralisation.

9. PERSPECTIVE

If further exploration through drilling proves that high-grade gold mineralisation is widespread and abundant, Conical Seamount may become the first marine gold deposit to be mined. In addition to high concentrations of gold, the advantages of this site include shallow water depth (1,050 m) and the location within the 12 nm zone of Papua New Guinea. Furthermore, the deposit is inactive (no disturbance of fauna) and almost sediment-free (no plume development due to mining activities). Processing of the gold ore could take place in the 25 km distant Ladolam gold processing plant on Lihir. If this scenario becomes reality, it will have a very significant impact on the future development of seafloor mining for base and precious metals. Given the known distribution of potentially minable sulphide deposits on the seafloor, it is very likely that most future development of sulphide mining will take place in national rather than international waters.

Considering all critical factors, mining of seafloor polymetallic massive sulphide deposits is likely to take place in the current decade. In this context it should be remembered, that only about 35 years ago, the oil industry went off shore and there is no doubt that this was a very successful endeavour. Today, the international mining industry is about to follow …

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Cobalt-Rich Ferromanganese Crusts: Global Distribution, Composition, Origin and Research Activities

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Cobalt-rich Ferromanganese Crusts: Global distribution, composition, origin and research activities

Cobalt-rich ferromanganese crusts occur throughout the global ocean on seamounts, ridges, and plateaus where currents have kept the rocks swept clean of sediments for millions of years. Crusts precipitate out of cold ambient seawater onto hard-rock substrates forming pavements up to 250 mm thick. Crusts are important as a potential resource for primarily cobalt, but also for titanium, cerium, nickel, platinum, manganese, thallium, tellurium, and others. Crusts form at water depths of about 400-4000 m, with the thickest and most cobalt-rich crusts occurring at depths of about 800-2500 m, which may vary on a regional scale. Gravity processes, sediment cover, submerged and emergent reefs, and currents control the distribution and thickness of crusts. Crusts occur on a wide-variety of substrate rocks, which makes it difficult to distinguish the crusts from the substrate using remotely sensed data, such as geophysical measurements. However, crusts can be distinguished from the substrates by their much higher gamma radiation levels. The mean dry bulk density of crusts is 1.3 g/cm^3, the mean porosity is 60%, and the mean surface area is extremely high, 300 m^2/g. Crusts generally grow at rates of 1-6 millimetres per million years. Crust surfaces are botryoidal, which may be modified to a variety of forms by current erosion. In cross-section, crusts are generally layered, with individual layers displaying massive, botryoidal, laminated, columnar, or mottled textures; characteristic layering is persistent regionally. Crusts are composed of ferruginous vernadite (dMnO$_2$) and X-ray amorphous iron oxyhydroxide, with moderate amounts of carbonate fluorapatite (CFA) in thick crusts and minor amounts of quartz and feldspar in most crusts. Elements most commonly associated with the vernadite phase include manganese, cobalt, nickel, cadmium, and molybdenum, and with the iron oxyhydroxide, iron and arsenic. Detrital phases are represented by silicon, aluminium, potassium, titanium, chromium, magnesium, iron, and sodium; the CFA phase by calcium, phosphorus, strontium, yttrium, and carbon dioxide; and a residual biogenic phase by barium, strontium, cerium, copper, vanadium, calcium, and magnesium. Bulk crusts contain cobalt contents up to 1.7%, nickel to 1.1%, and platinum to 1.3 parts per million (ppm), with mean iron/manganese ratios of 0.4 to 1.2. Cobalt, nickel, titanium, and platinum decrease, whereas iron/manganese, silicon, and aluminium increase in continental margin crusts and in crusts with proximity to west Pacific volcanic arcs. Vernadite- and CFA-related elements decrease, whereas iron, copper, and detrital-related elements increase with increasing water depth of crust occurrence. Cobalt, cerium, thallium, and maybe also titanium, lead, tellurium, and platinum are strongly concentrated in crusts over other metals because they are incorporated by oxidation reactions. Total rare-earth elements (REEs) commonly vary between 0.1% and 0.3% and are derived from seawater along with other hydrogenetic elements, cobalt, manganese, nickel, etc. Platinum-group elements are also derived from seawater, except palladium, which is derived from detrital minerals. The older parts of thick crusts were phosphatised during at least two global phosphogenic events during the Tertiary, which mobilized and redistributed elements in those parts of the crusts. Silicon, iron, aluminium, thorium, titanium, cobalt, manganese, lead, and uranium are commonly depleted, whereas nickel, copper, zinc, yttrium, REEs, strontium, and platinum are commonly enriched in phosphatised layers compared to younger non-phosphatised layers. The dominant controls on the concentration of elements in crusts include the concentration of metals in seawater and their ratios, colloid surface charge, types of complexing agents, surface area, and growth rates. Seamounts obstruct the flow of oceanic water masses, thereby creating a wide array of seamount-generated currents of generally enhanced energy relative to flow away from the seamounts. The effects of these currents are strongest at the outer rim of the summit region of seamounts, the area where the thickest crusts are found. Those seamount-specific currents also enhance turbulent mixing and produce upwelling, which increases primary productivity. These physical processes also affect seamount biological communities, which vary from seamount to seamount. Seamount communities are characterized by relatively low density and low diversity where the Fe-Mn crusts are thickest and cobalt-rich. The make-up of the seamount communities, and population density and diversity, are determined by current patterns, topography, bottom sediment and rock types and coverage, seamount size, water depth, and size and magnitude of the oxygen-minimum zone. About 48 research cruises have been dedicated to the study of Co-rich crusts. Minimum expenditures were about US $40 million for ship and associated scientific operation related to filed work, and $50 million for shore-based research, for a total investment of about $90 million. Research and development on the technology of mining crusts are only in their infancy. Detailed maps of crust deposits and a better understanding of small-scale seamount topography are required to develop the most appropriate mining strategies. Based on grade, tonnage, and oceanographic conditions, the central-equatorial Pacific offers the best potential for crust mining, particularly the EEZ of Johnston Island (USA), the Marshall Islands, and international waters in the Mid-Pacific Mountains, although the EEZs of French Polynesia, Kiribati, and the Federated States of Micronesia must also be considered.

1. INTRODUCTION

Cobalt-rich iron-manganese (ferromanganese) oxyhydroxide crusts, hereafter called Fe-Mn crusts, are ubiquitous on hard-rock substrates throughout the ocean basins. They form at the seafloor on the flanks and summits of seamounts, ridges, plateaus, and abyssal hills where the rocks have been swept clean of sediments at least intermittently for millions of years. Crusts form pavements up to 250 mm thick on rock outcrops, or coat talus debris. Fe-Mn crusts form by precipitation from cold ambient bottom waters (hydrogenetic), or by a combination of hydrogenetic and hydrothermal precipitation in regions where hydrothermal venting occurs, such as near oceanic spreading axes, volcanic arcs, and hotspot volcanoes. Fe-Mn crusts contain sub-equal amounts of iron and manganese and are especially enriched in cobalt, manganese, lead, tellurium, bismuth, and platinum relative to their lithospheric and seawater concentrations (*Table 1*). There are two practical interests in Fe-Mn crusts, the first being their economic potential for cobalt, but also for manganese, nickel, and platinum, and possibly also titanium, rare earth elements (REEs), tellurium, thallium, phosphorus, and others. The second interest is the use of crusts as recorders of the past 60 million years (Ma) of oceanic and climatic history. Besides the high cobalt contents compared to abyssal Fe-Mn nodules, exploitation of crusts was viewed as advantageous because most high quality crusts occur within the Exclusive Economic Zone (EEZ; *Fig. 1*) of island nations and, therefore, are not subject to some of the perceived problems of recovery of mineral resources occurring in international waters.

1.1. Classification

Up until the late 1970s Fe-Mn crusts were usually not distinguished from abyssal Fe-Mn nodules. If a distinction was made, crusts were called seamount nodules. However, there are distinct differences between Fe-Mn nodules and crusts, other than just morphology (*Table 2*)[2]. Nodules nucleate on small bits of rock, bone, or old nodule fragments on the surface of sediments. Nodules commonly form by both diagenetic (components derived from sediment pore waters) and hydrogenetic precipitation and thus their composition reflects input from both seawater and sediments. However, some nodules form predominantly by either diagenetic or hydrogenetic processes. Nodules have sometimes been referred to as hydrogenous, regardless of their origin; consequently, we use the term hydrogenetic to avoid any confusion about a substrate contribution to crusts--a substrate contribution is not found in Fe-Mn crusts [3]. Generally, crusts and nodules have different mineralogical (vernadite versus todorokite and vernadite) and chemical compositions (for example high cobalt versus high copper) because of their genetic differences as well as differences in water depths of formation, although there is much overlap.

Table 1

Contents of manganese, iron, cobalt, nickel, platinum, cerium, copper, and tellurium (wt. %) in marine Fe-Mn crusts compared to contents in and enrichments over seawater and the Earth's crust (lithosphere)

	Seawater	Lithosphere	Fe-Mn Crusts
Fe/Mn	1.2	57	0.7
Manganese	5.0×10^{-9}	0.095	23
Mn/seawater	--	1.9×10^{7}	4.6×10^{9}
Mn/lithosphere	--	--	242
Iron	6.0×10^{-9}	5.4	17
Fe/seawater	--	9.0×10^{8}	2.8×10^{9}
Fe/lithosphere	--	--	3.1
Cobalt	1.0×10^{-10}	2.5×10^{-3}	0.70
Co/seawater	--	2.5×10^{6}	7.0×10^{8}
Co/lithosphere	--	--	280
Nickel	5.0×10^{-8}	8.0×10^{-3}	0.48
Ni/seawater	--	1.6×10^{5}	9.6×10^{6}
Ni/lithosphere	--	--	60
Platinum	2.4×10^{-11}	4.0×10^{-7}	5×10^{-5}
Pt/seawater	--	1.7×10^{4}	2.1×10^{6}
Pt/lithosphere	--	--	125
Cerium	2.8×10^{-10}	7.0×10^{-3}	0.18
Ce/seawater	--	2.5×10^{7}	6.4×10^{8}
Ce/lithosphere	--	--	26
Copper	2.5×10^{-8}	5.0×10^{-3}	0.09
Cu/seawater	--	2.0×10^{5}	3.6×10^{6}
Cu/lithosphere	--	--	18
Tellurium	1.66×10^{-11}	1.0×10^{-6}	0.005
Te/seawater		0.6×10^{-5}	3.0×10^{8}
Te/lithosphere			5000

Iron and manganese hydroxides and oxyhydroxides may also form by hydrothermal processes below the seafloor (*Table 2*). These deposits usually consist of stratabound layers or manganese-cemented volcaniclastic sediments and are distinctly different in texture and composition from hydrogenetic Fe-Mn crusts, especially with regard to the extreme fractionation of manganese and iron (*Table 1*) and low multiple-trace metal contents in the hydrothermal deposits [4]. In the hydrothermal deposits, iron/manganese varies from about 24,000 (up to 58% iron) for hydrothermal ironstones to 0.001 (up to 52% manganese) for hydrothermal stratabound manganese oxides. Many other minor types of iron and manganese mineralisation occur in the ocean basins (*Table 2*), but this paper is confined to cobalt-rich hydrogenetic Fe-Mn crusts.

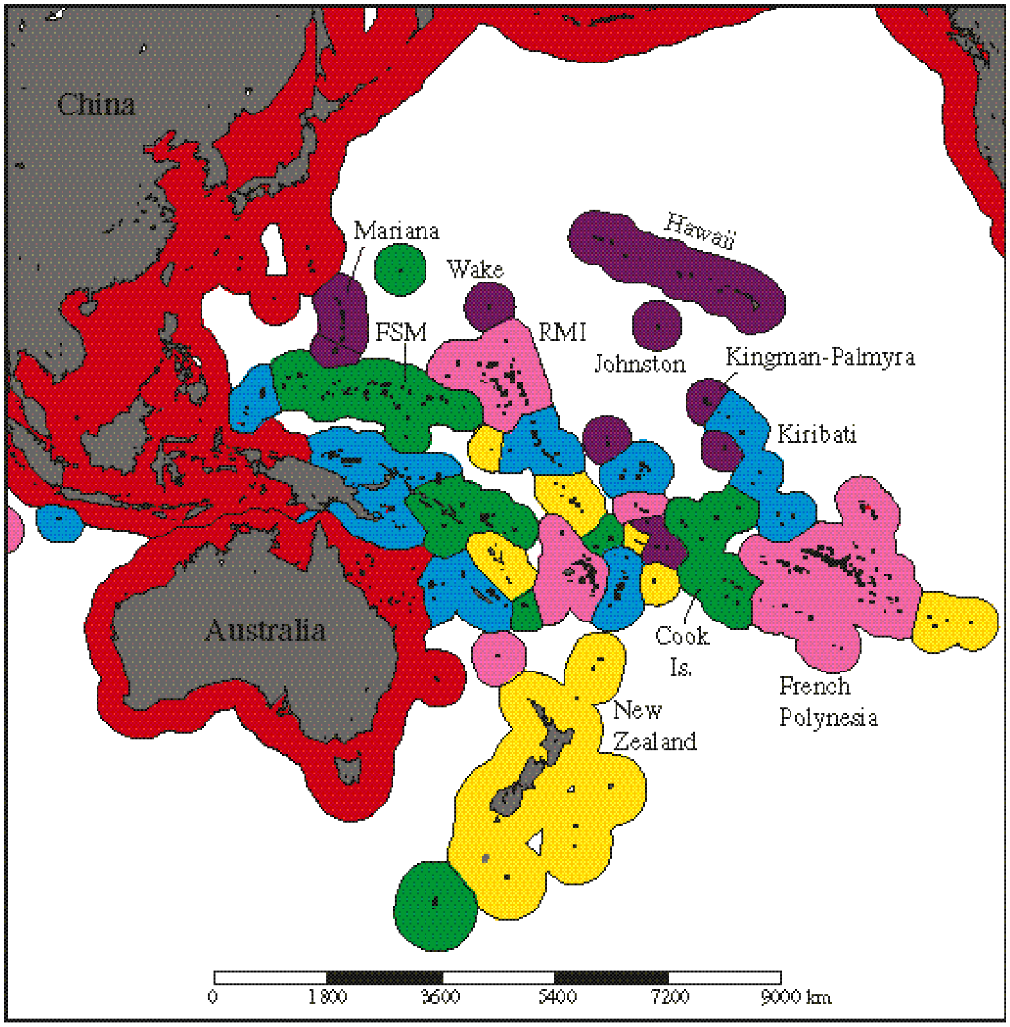

Figure 1. Exclusive Economic Zones (200 nautical mile limits) for island nations within the Pacific, only a few of which are named on this figure; those marked in purple are Territories, Possessions, and Commonwealths of United States, as well as the State of Hawaii; RMI = Republic of Marshall Islands; FSM = Federated States of Micronesia; most seamounts in the Pacific are associated with the islands that compose these nations and consequently much of the potential Fe-Mn crust resource occurs within these EEZs (taken and modified from the web side of SOPAC [www.sopac.org]).

Table 2
Classification of marine ferromanganese oxide deposits by form, processes of formation, and environment of formation; most common types in bold, from Hein et al. (1)

	Hydrogenetic	**Hydrothermal**	**Diagenetic**	**Hydrogenetic and Hydrothermal**	**Hydrogenetic and Diagenetic**	**Replacement**
Nodules	Abyssal plains, oceanic plateaus, seamounts[1]	Submerged calderas and fracture zones	Abyssal plains, oceanic plateaus	Submerged calderas	Abyssal plains, oceanic plateaus[1]	All areas (nodule nuclei)
Crusts	Midplate volcanic edifices[2]	Active spreading axes, volcanic arcs, fracture zones, midplate edifices	---	Active volcanic arcs, spreading axes, off axis seamounts, fracture zones	Abyssal hills	Midplate edifices (crust substrate rock)
Sediment-hosted stratabound layers and lenses	---	Active volcanic arcs, large midplate volcanic edifices, sediment-covered spreading axes	Continental margins[3]	---	---	Continental margins, volcanic arcs, midplate edifices
Cements	Midplate volcanic edifices[4]	Active volcanic arcs, large midplate volcanic edifices[5]	Midplate volcanic edifices[4]	---	Midplate volcanic edifices[4]	Volcanic arcs, midplate edifices
Mounds and Chimneys	---	Back-arc basins, spreading centers, volcanic arcs	---	---	---	---

[1] *Less common on ridges, continental slope and shelf;*
[2] *Includes seamounts, guyots, ridges, plateaus;*
[3] *Fe and Mn carbonate lenses and concretions;*
[4] *Mostly fracture and vein fill, cement for volcanic breccia;*
[5] *Mostly cement for breccia, sandstone and siltstone*

1.2. Distribution of Fe-Mn Crusts

Fe-Mn crusts have been recovered from seamounts and ridges as far north as the Aleutian Trench in the Pacific and Iceland in the Atlantic and as far south as the Circum-Antarctic Ridge in the Pacific, Atlantic, and Indian Oceans. However, the most detailed studies have concerned seamounts in the equatorial Pacific, mostly from the EEZ (200 nautical miles) of island nations including the Federated States of Micronesia, Marshall Islands, Kiribati, as well as in the EEZ of the USA (Hawaii, Johnston Island), but also from international waters in the Mid-Pacific Mountains. Compared to the estimated 50,000 or so seamounts that occur in the Pacific, the Atlantic and Indian oceans contain fewer seamounts and most Fe-Mn crusts are associated with the spreading ridges. Crusts associated with those spreading ridges usually have a hydrothermal component that may be large near active venting, but which is regionally generally a small (<30%) component of the crusts formed along most of the ridges[5]. Those types of hydrogenetic-hydrothermal crusts are also common along the active volcanic arcs in the west Pacific [6], the spreading ridges in back-arc basins of the west and southwest Pacific, spreading centres in the south and east Pacific, and active hotspots in the central (Hawaii) and south (Pitcairn) Pacific. Very few (<15%) of the approximate 50,000 seamounts in the Pacific have been mapped and sampled in detail, and none of the larger ones have been so studied, some of which are comparable in size to continental mountain ranges.

Fe-Mn crusts occur at water depths of about 400-4000 m, but most commonly occur at depths from about 1000-3000 m. The most cobalt-rich crusts occur at water depths from 800-2200 m, which mostly encompasses the oxygen minimum zone (OMZ; *Fig. 2*). In the Pacific, the thickest crusts occur at water depths of 1500-2500 m, which corresponds to the depths of the outer summit area and upper flanks of most Cretaceous seamounts. The water depths of thick high cobalt content crusts vary regionally and are generally shallower in the South Pacific where the OMZ is less well developed; there, the maximum cobalt contents and thickest crusts occur at about 1000-1500 m [7]. Crusts become thinner with increasing water depth because of mass movements and reworking of the deposits on the seamount flanks. Most Fe-Mn crusts on the middle and lower seamount flanks consist of encrusted talus rather than encrusted rock outcrop, the latter however typically having thicker crusts [8]. Many seamounts and ridges are capped by pelagic sediments and therefore do not support the growth of crusts on the summit. Other volcanic edifices are capped by limestone (drowned reefs), which commonly supports thinner crusts than underlying volcanic and volcaniclastic rocks[9] because of the younger age of the limestones and therefore shorter time for crust growth coupled with the instability and mass wasting of the limestone. Fe-Mn crusts are usually thin down to as much as 3000 m water depth on the submarine flanks of islands and atolls because of the large amounts of debris that are shed down the flanks by gravity processes[10]. Reworked crust fragments occur as clasts in breccia, which is one of the most common rock types on seamount flanks[11]. Regional mean crust thicknesses mostly fall between 5 and 40 mm. Only rarely are very thick crusts (>80 mm) found, most being from the central Pacific, for which initial growth may approach within 10-30 Ma the age of the Cretaceous substrate rock. Clearly, while most Pacific seamounts are 65-95 Ma old, most crusts collected on those seamounts represent less than 25 Ma of growth because of reworking and episodic sediment cover. Thick crusts are rarely found in the Atlantic and Indian Oceans, with the thickest (up to 125 mm) being recovered from the New England seamount chain (NW Atlantic), and a 72 mm-thick crust being recovered from a seamount in the Central Indian Basin[12].

The distribution of crusts on individual seamounts and ridges is poorly known. Seamounts generally have either a rugged summit with moderately thick to no sediment cover (0-150 m) or a flat summit (guyot) with thick to no sediment cover (0-500 m). The outer summit margin and the flanks may be terraced with shallowly dipping terraces headed by steep slopes meters to tens of meters high. Talus piles commonly accumulate at the base of the steep slopes and at the foot of the seamounts; thin sediment layers may blanket the terraces alternately covering and exhuming Fe-Mn crusts. Other seamount flanks may be uniformly steep up to 20°, but most seamount flanks average about 14°[13]. The thickest crusts occur on summit outer-rim terraces and on broad saddles on the summits. Estimates of sediment cover on various seamounts range from 15% to 75%, and likely averages about 50%. Crusts are commonly covered by a thin blanket of sediments in the summit region and on flank terraces. It is not known how much sediment can accumulate before crusts stop growing. Crusts have been recovered from under as much as 2 m of sediment without apparent dissolution[14]. Based on coring results, Yamazaki[15] estimated that there are 2-5 times more Fe-Mn crust deposits on seamounts than estimates based on exposed crust outcrops because of their coverage by a thin blanket of sediment. Those thinly veiled crusts would be within reach of mining operations.

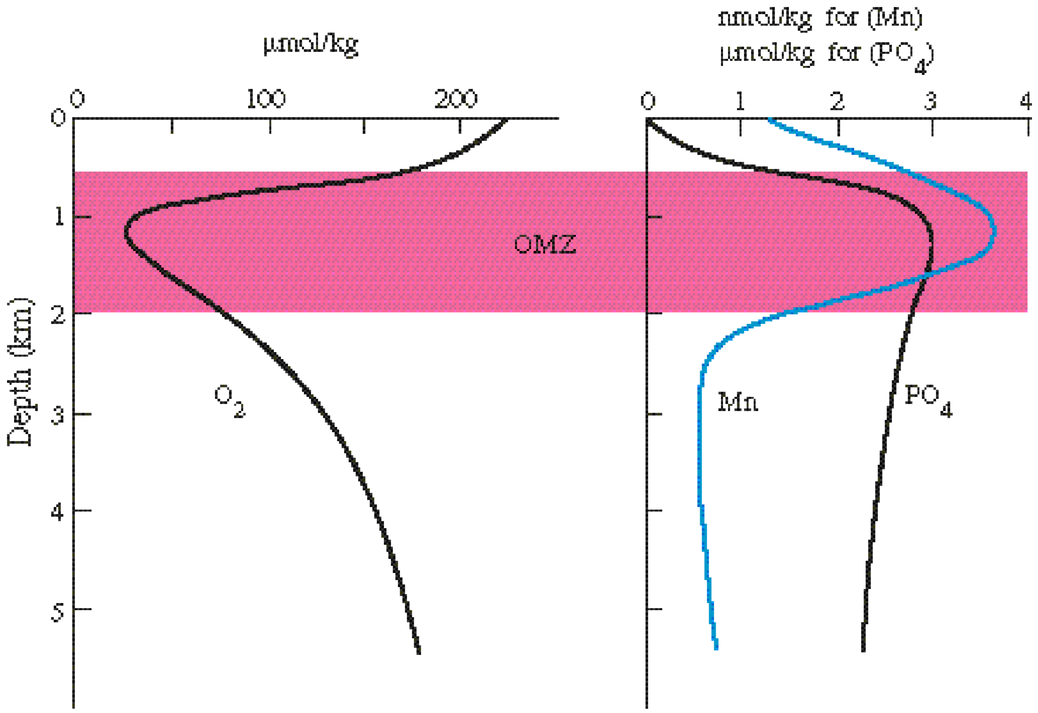

Figure 2. Profiles of dissolved manganese and phosphate compared to oxygen content of seawater over a seamount; low-oxygen seawater (the oxygen minimum zone, OMZ) is a reservoir for high manganese contents

1.3. Historical Background and Research Investment

The first major advance in the study of oceanic Fe-Mn deposits occurred with the discovery of deep-ocean nodules and crusts by the Challenger Expedition of 1873-6[16]. Dredge hauls collected black Fe-Mn nodules from abyssal depths (4500-6000 m) and coatings, layers, and crusts of iron-manganese oxides from depths as shallow as 370 m. Those samples contained significant minor concentrations of copper, nickel, cobalt, thorium, and thallium[17].

After World War II, it was established that metal scavenging on active catalytic surfaces concentrated metals in manganese oxides in the oceans[18]. Most nodules studied were from abyssal depths with 0.30% cobalt or less, whereas a few samples, from ocean spreading axes, had as little as 0.03% cobalt, and samples from seamounts had cobalt contents as high as 0.70%. During the escalation of interest in abyssal Fe-Mn nodules in the 1960s and 1970s, Mero[19] and others[20] noted that topographic highs (seamounts and ridges) in the central Pacific had deposits with the highest mean cobalt contents (1.2%) of any region of the global ocean. During that time, Cronan[21] showed that there is an inverse correlation between water depth and cobalt content of nodules (Fe-Mn crusts) recovered from seamounts. Fe-Mn crusts had begun to be distinguished from nodules in the 1970s[22] and their economic potential was recognized[23]. This economic recognition was punctuated by the fact that the price of cobalt had skyrocketed in 1978 (*Fig. 3*) as the result of the invasion of Zaire by insurgents from Angola and Zambia. Zaire has been the world's largest producer of cobalt, which is a by-product of copper mining in the West African copper belt.

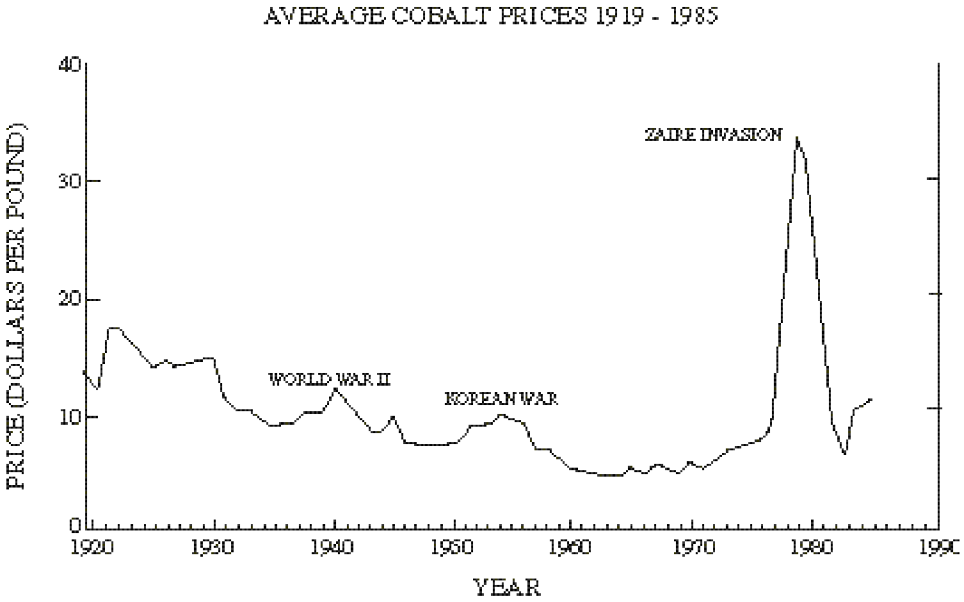

Figure 3. A 66-year record of average cobalt prices, from Manheim (24)

Table 3
Cruises (46) dedicated to the study of Co-rich Fe-Mn crusts, 1981-2002

Ship/Cruise	Year/month	Institution[1]	EEZ/Region
Sonne/SO18	1981/6-7	TUC	US: Johnston, Kingman, Palmyra Is; Kiribati: Line Is
S.P. Lee/L5-83-HW	1983/10-11	USGS	US: Hawaii, Johnston, Palmyra, Kingman Is
Sonne/SO33	1984/7-8	TUC	US: Hawaii, Johnston, Palmyra, Kingman Is
S.P. Lee/L9-84-CP	1984/8	USGS	Marshall Is
Kana Keoki/KK84-04-28-05	1984/6	UH	US: Hawaii
Kana Keoki/KK84-08-24-02	1984/8	UH	US: Hawaii
Sonne/SO37	1985/5-6	TUC	US: Howland, Baker, Johnston Is
Sonne/SO46	1986/11-12	TUC	US: Johnston I; Marshall Is
Sonne/SO46	1986/11-12	TUC	US: Johnston I; Marshall Is.
Farnella/F7-86-HW	1986/11-12	USGS/BOM	US: Johnston I

Jean Charcot/NODCO I	1986	IFREMER	French Polynesia
Tui/Tripartite II	1986	NZOI	Cook Is
Moana Wave/MW-86-02	1986/2-3	UH	Kiribati: Phoenix Is; Tuvalu
Moana Wave/MW-87-02	1987/2	UH	Cook Is; Kiribati: Line Is
?	1987	USSRAS	International: East Mariana basin
Hakurei Maru II/many	1980s-1990s	MMAJ	International waters between Hawaii and Japan
Hakurei Maru II/?	1987	MMAJ	Kiribati: Phoenix Is
Farnella/F7-87-SC	1987/12	USGS	US: California
Hakurei Maru II/?	1988	MMAJ	Tuvalu
Rapuhia	1988/1-2	NZOI	New Zealand
Akademik Nikolai Stakhov	~1988	USSRAS	International: northeast Atlantic
Hakurei Maru II/?	1989	MMAJ	Kiribati: Line Is
Farnell/F10-89-CP	1989/9-10	USGS/KORDI	Marshall Is
Sonne/SO 66	1990/1-2	TUC	Sonne/SO 66
Hakurei Maru II/?	1990	MMAJ	Samoa
Farnella/F11-90-CP	1990/10-11	USGS/KORDI	FSM
Farnella/F7-91-WP	1991/7-8	USGS/KORDI	FSM; Palau
Hakurei Maru II/?	1991	MMAJ	Kiribati: Gilbert Is
Vinogradov/91-AV-19/2	1991/6	RAS/USGS	US: Johnston I
Rig Seismic/BMR107	1992/2	AGSO	Australia: Christmas I.
Sonne/SO83	1992/12	FUB	International, NE Atlantic
Rig Seismic/147	1995	AGSO	Australia: Tasmania
Hakurei Maru II	1995	MMAJ	Tonga
Hakurei Maru II	1996	MMAJ	Marshall Is
Hakurei Maru II	1997	MMAJ	FSM
Haiyang 4/DY95-7	1997	CGS	West Pacific
Dayang 1/DY95-8	1997	CGS	Mid-Pacific Mountains
Onnuri/KODOS 97-4	1997/8-9	KORDI/USGS	Marshall Is
Hakurei Maru II	1998	MMAJ	FSM; Marshall Is
Haiyang 4/DY95-9	1998	CGS	West Pacific
Onnuri/KODOS 98-3	1998/8	KORDI/USGS	Marshall Is; FSM
Dayang 1/DY95-10	1999	CGS	Mid-Pacific
Onnuri/KODOS 99-1	1999/5-6	KORDI	Marshall Is.
Onnuri/KODOS 00-3	2000/6	KORDI	International: N of Marshall Is.
Onnuri/KOSDOS 01-2	2001/6	KORDI	International: N of Marshall Is.
Hakurei Maru II/SOPAC02	2002/6-7	MMAJ/JICA	Marshall Is.

[1] *TUC=Technical University of Clausthal, Germany; USGS=United States Geological Survey; UH=University of Hawaii; BOM=United States Bureau of Mines; IFREMER=L'Institut Français pour l'Exploitation de la MER, France; NZOI=New Zealand Oceanographic Institute; USSRAS=USSR Academy of Sciences; MMAJ=Metal Mining Agency of Japan; KORDI=Korean Ocean Research and Development Institute; RAS=Russian Academy of Sciences; AGSO-Australian Geological Survey Organization; FUB=Free University of Berlin; FSM=Federated States of Micronesia*

The first systematic investigation of Fe-Mn crusts was carried out in the Line Islands south of Hawaii during the 1981 German Midpac I cruise on the R.V. Sonne, headed by Peter Halbach of the Technical University, Clausthal-Zellerfeld (*Table 3*). That cruise made breakthrough discoveries using large dredges, seismic profiling, and bottom photography[25]. Subsequent German, U.S. Geological Survey (USGS), and University of Hawaii cruises (*Table 3; Fig. 4*) to submarine edifices in the central Pacific refined our knowledge of Fe-Mn crust distributions and chemical relationships. They showed that crusts were especially enriched in cobalt, iron, cerium, titanium, phosphorus, lead, arsenic, and especially platinum, but relatively lower in manganese, nickel, copper, and zinc compared to nodules[26].

USA activities in Fe-Mn crust studies accelerated as the result of the 1983 proclamation of President Reagan for a 200 nm EEZ, in which he made special mention of cobalt-rich Fe-Mn crust deposits. Subsequent USA research cruises (*Table 3*) revealed that the most promising Fe-Mn crust deposits occur within the EEZ of the Marshall Islands, Johnston Island (USA), Line Islands (USA and Kiribati), and on Blake Plateau (USA) in the Atlantic.

International complications partly linked to the location of abyssal Fe-Mn nodules in international waters contributed to the withdrawal of commercial consortia from active preparations for nodule mining in the late 1970s. The extensive occurrences of Fe-Mn crusts within the EEZ of coastal nations provided an incentive for mineral interests within areas of national jurisdiction[27]. This applied not only to Pacific seamount deposits, but also to Fe-Mn crusts along continental margins[28].

Other systematic iron-manganese minerals investigations during the 1970s, 1980s, and 1990s (*Table 3*) included a series of cruises by the Japanese Geological Survey, directed mainly toward abyssal nodule deposits (e.g.,[29]), crust studies centred in the Japanese EEZ (Izu-Bonin arc; see Usui and Someya[30] for compilation of data and references), and in international waters of the Mid-Pacific Mountains. Other Asian nations like Korea and China initiated Fe-Mn crust research with USA and other co-operators (e.g.,[31]), and, along with Japan and Russia, continue their field efforts in Fe-Mn crust studies today. Field studies by the USA, Germany, UK, and France have largely been discontinued.

A detailed database and review of the chemical composition of crusts based on data up to 1987 was published in 1989[32], and is also available on NOAA and MMS Marine Minerals CD-ROM, NGDC Data Set #0827, and web site *http://www.ngdc.noaa.gov/mgg/geology/ mmdb/*. A more recent compilation of mean chemical data was presented by Hein et al.[33] and those data are further updated here.

The list of 46 research cruises in *Table 3* is not comprehensive and data for a few cruises completed by the USSR (and later Russia) are not available to the author. However, based on an estimated 48 research cruises from 1981 through 2001, it is suggested that minimum expenditures were about US $40 million for ship and associated scientific operations related to field work, and $50 million for shore-based research, for a total investment of about $90 million.

2. Fe-Mn CRUST CHARACTERISTICS

2.1. Textures and Physical Properties

Crust surfaces exposed directly to the seafloor are botryoidal, with botryoids varying in size from microbotryoidal (millimetre size) to botryoidal (centimetre size). Fresh growth surfaces are characterized by a fractal distribution of botryoids with extreme surface area. Under conditions of high current flow, the botryoids are modified, either by smoothing or by accentuation of the relief by erosion around the margins of the botryoids, in places producing mushroom-shaped forms. With strong uni-directional flow, the botryoids become polished and fluted. Crusts on the sides of rocks are commonly more protected from current activity and grow at a slower rate thereby acquiring very high cobalt contents; textures of those side crusts are very porous and granular.

Crust profiles vary according to thickness and regional oceanographic conditions. Thin crusts (<40 mm) are usually black and massive, botryoidal, or laminated. Thicker crusts (40-80 mm) commonly have at least two distinct layers, a lower black, massive, dense layer that is phosphatised and an upper black to brown layer that is more porous, with laminated, mottled, botryoidal, and/or columnar textures. The thickest crusts (>80 mm) may have up to 8 distinct macroscopic layers, the lower several layers of which are commonly phosphatised. In polished thin sections, textures consist of alternating laminated, columnar, botryoidal, and mottled textures. Columns range in height from millimetres to 50 mm[34], with detrital grains separating columns and actually promoting columnar growth[35]. Mottled layers are the most porous and detritus-rich. The various textures probably reflect bottom-water conditions at the time of precipitation of the oxides. Mottled, columnar, botryoidal, and laminated textures likely represent progressively decreasing energy in the depositional environment[36].

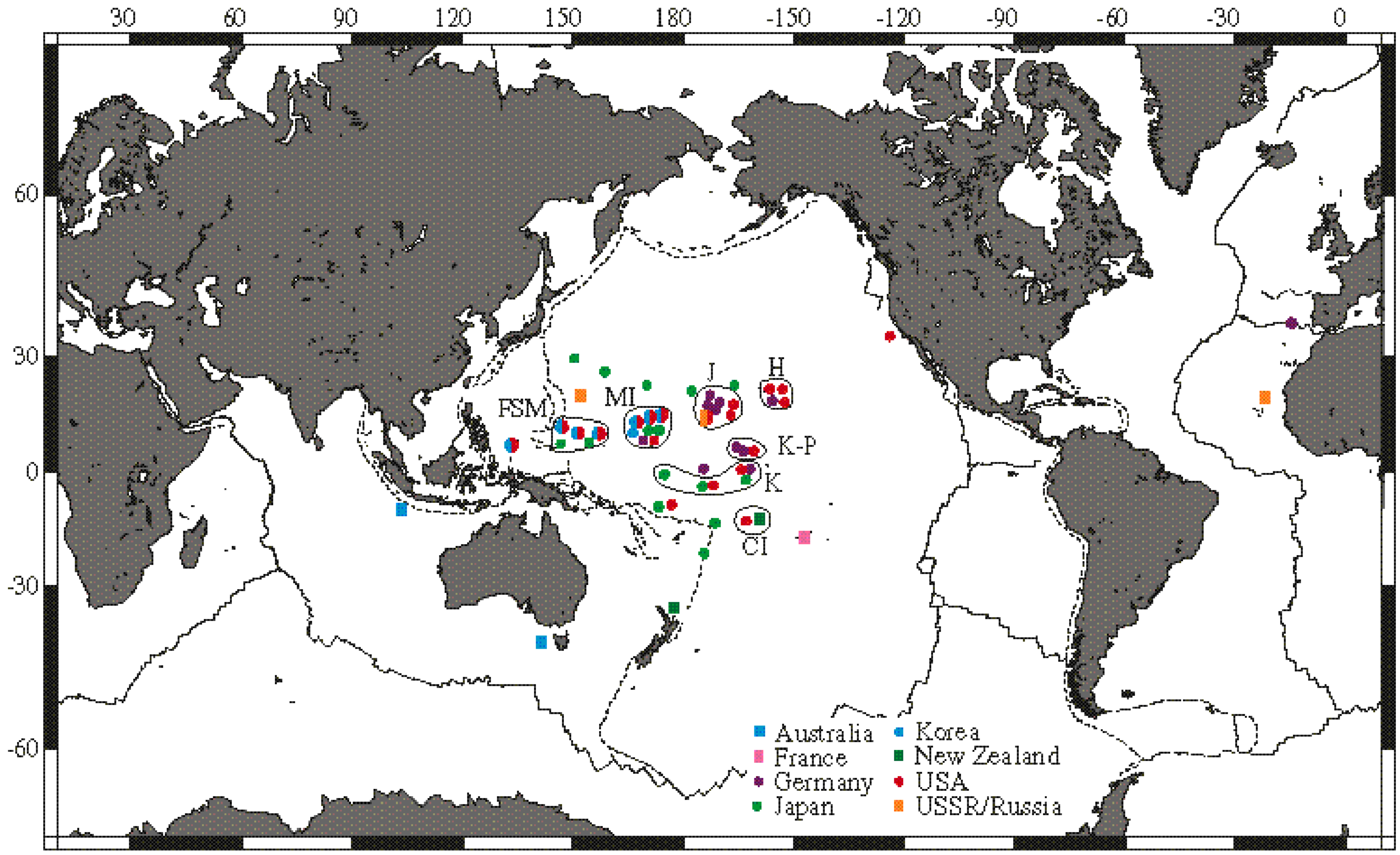

Figure 4. Distribution of research cruises dedicated to the study of cobalt-rich Fe-Mn crusts, 1981-1999 (listed in Table 3); CI = Cook Islands; FSM = Federated States of Micronesia; H = Hawaii; J = Johnston Island (USA); K = Kiribati; K-P = Kingman-Palmyra Islands (USA); MI = Marshall Islands.

An important consideration in the exploration and exploitation of potential crust resources is the contrast in physical properties between crusts and substrate rocks. Those comparisons are complicated by the fact that crusts grow on a wide variety of substrates including breccia, basalt, phosphorite, limestone, hyaloclastite, and mudstone in that order of abundance. Phosphorite and fresh basalt are strong, competent rocks and contrast significantly with crusts, which are weak, light-weight, and porous (*Table 4*); the other rock types, including altered basalt, may not contrast much in physical properties with Fe-Mn crusts. In general, crusts are much more porous (mean 60%) than most substrate rocks and have an extreme amount of specific surface area, which averages about 300 m^2/g (*Table 4*), similar to the surface area of silica gel. The surface area decreases by up to 20% when measured one month after collection of the crust and up to 40% after two months[45]. This clearly shows that many physical properties that are measured a long time after collection of the crusts may not closely approximate *in situ* crust properties. The mean wet bulk density of crusts is 1.90 g/cm^3 and the mean dry bulk density is 1.30 g/cm^3. The P-wave velocity of crusts may be less or more than that of sedimentary substrate rocks, but is generally less than that of basalt. This variable contrast will make it difficult to develop sonic devices for measuring *in situ* crust thicknesses. The most distinctive property of Fe-Mn crusts is their gamma radiation level, which averages 475 net counts/min in contrast to sedimentary rock substrates[101] and basalt substrates ([146]; *Table 4*). Gamma radiation may be a useful tool for crust exploration under thin-sediment cover and for measuring crust thicknesses *in situ*.

Table 4. Physical properties of Fe-Mn crusts and substrate rocks, from Hein et al. [37]

Physical Properties	**n**	**Fe-Mn Crusts**	**n**	**Sed. rock substrate**	**n**	**Basalt substrate**	**Ref.**
Porosity (volume %)							
Range	13	52-66	8	18-47	2	15-37	38
Mean	13	61	8	39	2	26	38
	-	41-74	-	7-69	-	7-67	39
	-	55	-	35	-	-	40
Wet bulk density (g/cm^3)							
Range	13	1.83-2.04	8	2.04-2.57	2	2.22-2.62	38
Mean	13	1.92	8	2.18	2	2.42	38
Range	18	1.90-2.44	7	1.59-2.68	23	2.06-2.66	41
Mean	18	2.00	7	1.90	23	2.34	41
Dry bulk density (g/cm^3)							
Range	13	1.18-1.48	8	1.56-2.38	2	1.84-2.46	38
Mean	13	1.29	8	1.78	2	2.15	38
	-	1.31	-	-	-	-	40

	-	1.04-2.17	-	1.44-2.92	-	0.78-2.74	39
Grain density (g/cm^3)							
Range	13	3.03-3.87	-	-	-	-	38
Mean	13	3.48	-	-	-	-	38
	-	2.70-3.44	-	2.54-2.81	-	2.32-2.95	42
Specific surface area (m^2/g)							
Range	15	250-381	-	-	-	-	43
Mean	15	323	-	-	-	-	43
Compressive strength (MPa)	-	8.36	-	3.66-32.6	-	-	40
	-	0.5-25.0	36	0.1-52.3	-	0.37-71.0	39
Seawater saturated	-	5.39-8.92	-	1.71-12.4	-	165-219	40
Tensile strength (MPa)	-	1.75	-	4.5	-	-	40
	-	0.1-2.3	-	0.1-4.5	-	0.1-18.9	39
Seawater saturated	-	0.45	-	0.23-0.48	-	11.9	40
Cohesive strength (MPa)	-	2.9	-	7.8	-	-	40
Seawater saturated	-	1.5	-	0.4-2.3	-	26.4	40
Shear strength (MPa)	-	1.26-2.5	-	-	-	-	44
Angle of internal friction	-	42°	-	52°	-	-	40
Seawater saturated	-	76°	-	61°-77°	-	76°	40
Young's modulus (GPa)	-	2.15	-	0.31-10.1	-	-	40
Seawater saturated	-	3.11-4.25	-	0.62-4.76	-	51.3-63.7	40
P-wave velocity (km/s)	-	2.09-3.39	-	1.76-5.86	-	-	39
Range, parallel to bedding	18	2.46-4.19	5	1.80-4.35	23	3.14-5.14	41
Mean, parallel to bedding	18	3.36	5	2.57	23	4.13	41
Range, perpendicular to layers	17	2.07-3.86	4	1.78-4.34	23	3.02-4.93	41
Mean, perpendicular to layers	17	3.16	4	2.56	23	3.99	41
	-	2.26	-	1.01-3.45	-	-	40
Seawater saturated	-	2.72-2.78	-	2.07-2.87	-	5.76-5.80	40
S-wave velocity-saturated (km/s)	-	1.35-1.83	-	1.15-1.67	-	3.46-3.57	40
Gamma radiation (net counts/min)							
Range	18	271-800	6	52-137	23	21-366	41
Mean	18	475	6	101	23	146	

dash means not reported

2.2. Mineralogy

The mineralogy of bulk crusts is relatively simple compared to hydrothermal and diagenetic iron and manganese deposits. The dominant crystalline phase is iron-rich d-MnO_2 (ferruginous vernadite[46]); with generally two X-ray reflections at about 1.4 Å and 2.4 Å that vary widely in sharpness as the result of crystallite size and manganese content. ?-MnO_2 generally makes up more than 95% of the X-ray crystalline phases, the remainder being detrital minerals such as quartz, plagioclase, potassium-feldspar, pyroxene, phillipsite, and authigenic carbonate fluorapatite (CFA; *Table 5*). The older parts of thick crusts are phosphatised and may contain up to 30% CFA in that part of the crust, but CFA is generally less than 10% of thick bulk crusts. Another major phase in crusts is X-ray amorphous iron oxyhydroxide (?-FeOOH, feroxyhyte;[47]), which is commonly epitaxially intergrown with ?-MnO_2[48]. In about 6% of 640 samples analysed, the feroxyhyte crystallizes as goethite in the older parts of thick crusts. In Pacific crusts, the quartz and part of the plagioclase are eolian, whereas the remainder of the plagioclase and the other volcanogenic minerals derive from local outcrops.

Table 5
Mineralogy of Pacific Fe-Mn crusts

Dominant	Common	Less Common	Uncommon or Uncertain
?-MnO_2 (iron-vernadite), Iron oxyhydroxide (feroxyhyte)	CFA, quartz, plagioclase, smectite	Phillipsite, goethite, todorokite, calcite, K-feldspar, pyroxene, opal-A, barite, amphibole, magnetite, amorphous aluminosilicates	Halite, illite, clinoptilolite, lepidocrocite, manjiroite, manganite, palygorskite, chlorite, dolomite, stevensite, kutnahorite, mordenite, natrojarosite, hematite, manganosite, maghemite, lithiophorite, analcite

CFA = carbonate fluorapatite

Todorokite, which is common in diagenetic Fe-Mn nodules and hydrothermal manganese deposits, is rare in hydrogenetic crusts. Of 640 X-ray diffraction analyses done by the USGS on Pacific crusts, only 5% (2% if offshore California samples are excluded) contain todorokite; 30% of crust samples from offshore California contain todorokite, which, because of very high biological productivity, may reflect the lower oxidation potential of seawater there compared to Pacific sites farther to the west. CFA occurs in 28% of the crust samples analysed, but not in any crusts from the east (offshore California) or far north Pacific; if those crusts are excluded, 34% of central and west Pacific samples contain CFA. Phosphatisation of Fe-Mn crusts generally occurred during two periods of time, about 34 Ma and 24 Ma ago[49]. Smaller percentages of Atlantic and Indian Ocean crusts contain CFA because those crusts are thinner and younger compared to Pacific crusts.

2.3. Ages and Growth Rates of Fe-Mn Crusts

Hydrogenetic Fe-Mn crusts grow at incredibly slow rates of <1 to about 11 mm/Ma, with the most common rates being from 1-6 mm/Ma (*Fig. 5*). These slow growth rates allow for the adsorption of large quantities of trace metals by the oxyhydroxides at the crust surface. Growth rates were first measured using either uranium-series or beryllium isotopes, which give reliable ages for the outermost 2 and 20 mm of crusts, respectively, or by radiometric or paleontological dating of the substrate rock and assuming that the substrate age is equivalent to the age of the base of the crust. With both methods, the growth rates and ages of the crusts are extrapolated and do not take into account changes in growth rates, growth hiatuses, or in the later method, the time between formation of the substrate rock and the beginning of growth of the crusts. For equatorial Pacific Cretaceous seamounts, the age of substrate rocks and crusts can vary by as much as 60 Ma, although in rare circumstances the ages of very thick crusts may approach those of the Cretaceous substrates. Beryllium isotope dating is the most reliable and widely used technique today. However, using beryllium isotope techniques requires that the age of the base of crusts thicker than about 20 mm be determined by extrapolation using the growth rate(s) determined for the outer 20 mm.

Ratios of osmium isotopes may provide a reliable dating tool for crusts as old as 65 Ma by comparing the ratios in various crust layers with ratios that define the Cenozoic seawater curve[52]. However, additional data are required on osmium isotopes in the oceans before that technique can be applied to age date crusts. Nannofossil biostratigraphy has been used to date crusts from impressions and molds of nannofossils left in crust layers after replacement of the carbonate by iron-manganese oxyhydroxides[53]. That technique, although reliable, is time consuming to perform and consequently has not been widely used. Recent nannofossil biostratigraphy confirms the crust ages determined from the extrapolation of beryllium isotope-determined growth rates (Puyaeva and Hein, unpublished data, 2000). Finally, empirical equations have been developed to date Fe-Mn crusts [54]. Those equations usually give minimum ages for the base of crusts and produce growth rates that are generally faster than those determined from isotopic techniques, although the Manheim and Lane-Bostwick[55] equation does generally produce rates more in line with those determined by isotopic methods[56]. It is clear that additional techniques are needed to accurately date thick crusts and the best opportunity may be development of osmium isotope stratigraphy, although argon isotopes, potassium-argon, and paleomagnetic reversal stratigraphy should also be studied. A significant problem with thick crusts is that the inner layers were phosphatised by a diagenetic process that promoted the mobilization of many elements[57]. However, the remobilisation of elements apparently did not affect neodymium and lead isotopic ratios[58] and also may not have affected osmium isotopic ratios. No correlation exists in this compiled data set between growth rates of the outermost layer of the crusts and water depth of occurrence.

2.4. Chemical Composition

All USGS chemical data in this report (*Table 6*) are normalized to zero percent hygroscopic water because that adsorbed water varies markedly depending on analytical conditions. Hygroscopic water can vary up to 30 weight percent (%) and thereby affects the contents of all other elements. Compositions normalized for hygroscopic water can be more meaningfully compared and also more closely represent the grade of the potential ore. Unfortunately, water contents are not provided in many published reports, so we were unable to correct compiled data listed in *Table 6*. Mean chemical compositions are provided for crusts that occur in the areas marked on Fig. 6, which correspond to the different columns in *Table 6*.

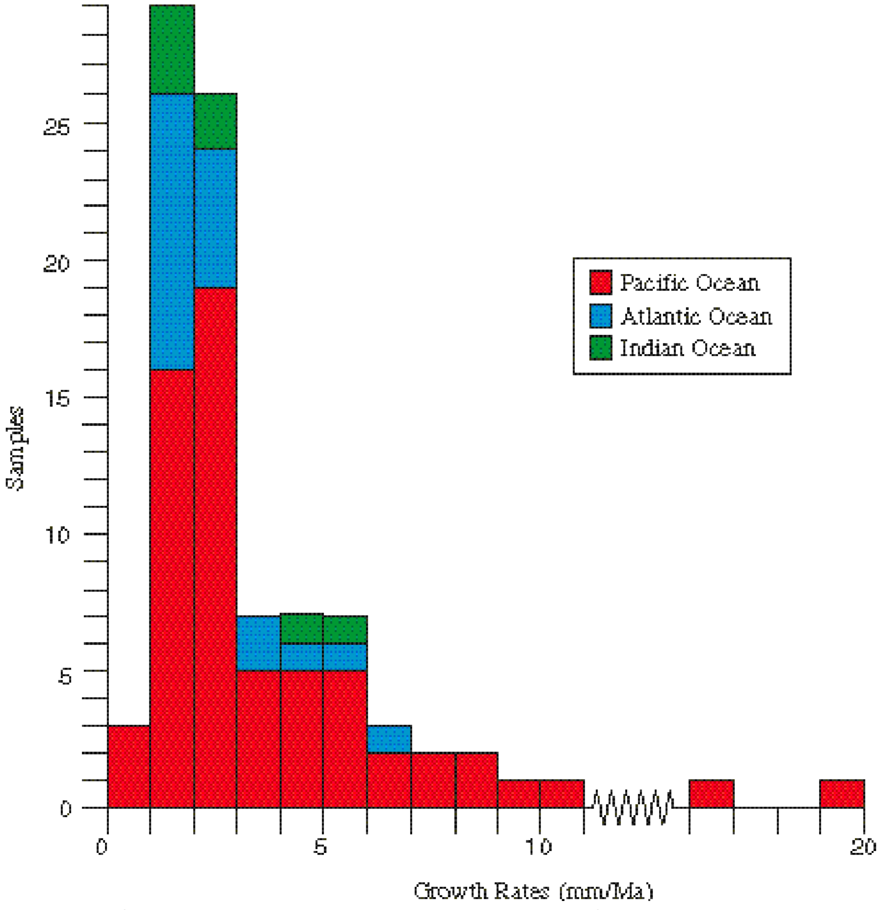

Figure 5. Range of isotopically determined growth rates of hydrogenetic Fe-Mn crusts. A hydrothermal component may exist in the two crusts with the fastest rates; updated (50) from Hein et al. (51)

Hydrogenetic Fe-Mn crusts generally have iron/manganese ratios between 0.4 and 1.2, most commonly 0.7 ± 0.2, whereas mixed hydrogenetic and hydrothermal crusts and continental margin hydrogenetic crusts have ratios between 1 and 3, mostly 1.3-1.8 (from data used to compile *Table 6*). Cobalt is the metal with the greatest economic potential in crusts and ranges from about 0.05-1.7% (500-17,000 parts per million, ppm) in individual bulk crusts and averages between 0.19% and 0.74% (1900-7400 ppm) for various parts of the global ocean (*Table 6*). Cobalt is also considered the element most characteristic of hydrogenetic precipitation in crusts[64] and is considered to maintain a constant flux from seawater to Fe-Mn crusts[65], regardless of water depth. Nickel and platinum are also considered of economic importance and range up to 1.1% and 1.3 ppm respectively for individual bulk crusts. Platinum ranges up to 3 ppm for individual crust layers[66]. Elements most strongly enriched over abyssal Fe-Mn nodules include iron, cobalt, platinum, lead, arsenic, bismuth, bromine, vanadium, phosphorus, calcium, titanium, strontium, tellurium, and REEs, whereas nodules are more enriched in copper, nickel, zinc, lithium, aluminium, potassium (only Pacific crusts), and cadmium. Fe-Mn crusts are enriched over seawater in all elements except bromine, chlorine, and sodium; enrichments over seawater between 10^8 and 10^{10} times include bismuth, cobalt, manganese, titanium, iron, tellurium, lead, and thorium, and between 10^6 and 10^8 times include tin, hafnium, zirconium, aluminium, yttrium, scandium, thallium, nickel, calcium, niobium, indium, copper, germanium, zinc, tungsten, and tantalum. Crusts are enriched over lithospheric concentrations about five thousand times for tellurium and a hundred to five hundred times for molybdenum, thallium, antimony, cobalt, manganese, bismuth, arsenic, selenium, and lead. Crusts may have an economic potential not only for cobalt, nickel, manganese, and platinum, but also for titanium, cerium, tellurium, thallium, zirconium, and phosphorus.

Elements in crusts have different origins and are associated with different crust mineral phases[67]. Generally elements are associated with five phases in crusts, d-MnO_2, iron oxyhydroxide, detrital (aluminosilicate), CFA, and residual biogenic phases. Manganese, cobalt, nickel, cadmium, and molybdenum are invariably associated with the ?-MnO_2 phase. In addition, in more than 40% of the regions studied, lead, vanadium, zinc, sodium, calcium, strontium, magnesium, and titanium are also associated with that phase. Iron and arsenic are most commonly the only elements associated with the iron oxyhydroxide phase, although less commonly vanadium, copper, lead, yttrium, phosphorus, chromium, beryllium, strontium, titanium, and cerium have also been reported to be associated with that phase. The detrital phase always includes silicon, aluminium, and potassium, and commonly also titanium, chromium, magnesium, iron, sodium, and copper. The CFA phase invariably includes calcium, phosphorus, and carbon dioxide, and also commonly strontium and yttrium; molybdenum, barium, cerium, and zinc may also be associated with the CFA phase in some regions. The residual biogenic phase includes barium, strontium, cerium, copper, vanadium, calcium, and magnesium, and in some regions also iron, arsenic, sodium, molybdenum, yttrium, phosphorus, carbon dioxide, lead, titanium, and nickel. Iron is the most widely distributed element and occurs intermixed in the ?-MnO_2 phase; is the main constituent in the iron oxyhydroxide phase; occurs in the detrital phase in minerals such as pyroxene, amphibole, smectite, magnetite, and spinels; and is in the residual biogenic phase. The strength of correlations between iron and other elements depends on the relative abundance of iron in the various phases[68]. The CFA phase only occurs in thick crusts because the inner layers of those crusts have been phosphatised. In thin crusts or the surface scrapes of thick crusts, calcium, phosphorus, and carbon dioxide are associated with the ?-MnO_2 and/or residual biogenic phases. CFA associated elements as well as platinum, rhodium, and iridium generally increase with increasing crust thickness. In contrast, cobalt and elements associated with the detrital phase usually decrease with increasing crust thickness [69].

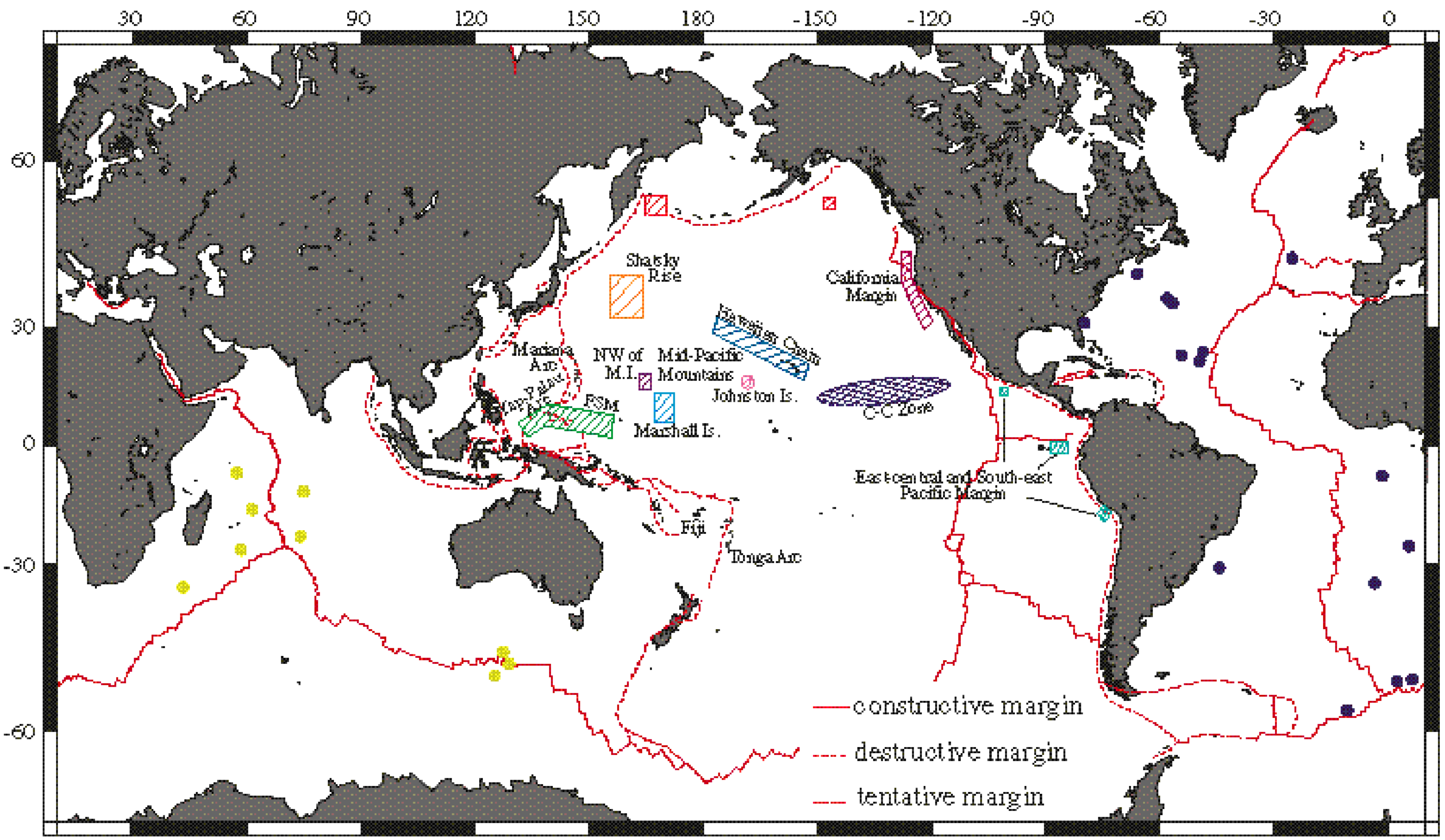

Figure 6. Lined boxes in the Pacific are regions with mean Fe-Mn crust compositional data listed in Table 6; far north Pacific data are from the two regions farthest north; the California margin includes the Oregon margin; the far south Pacific data cover areas mostly offshore New Zealand and southern Australia; the south Pacific data span most of the area between South America and the west Pacific arcs and between the equator and 25° south latitude; the crossed hatched oval region is the Clarion-Clipperton prime Fe-Mn nodule zone for comparison; data for all the stations in the Atlantic and Indian Oceans were averaged for each ocean for Table 6.

Table 6
Mean chemical composition of Fe-Mn crusts from the Pacific, Indian, and Atlantic Oceans compared with C-C and other abyssal Fe-Mn nodules; USGS data (columns 1-5, 8, 9, 10, 13, 14) normalized to 0% H_2O

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
	FSM-Palau	Marshall Is.	IW, NW of Marshall Is.	Johnston Is.	California Margin	Mostly IW, NW Pacific	Hawaii	IW, Far N Pacific	IW, Shatsky Rise	IW, EC-SE Pacific Margin	IW, S Pacific 0-25° Lat	IW, Far S Pacific >25° Lat	IW Atla
	n=35	n=116	n=43	n=103	n=71	n=1478	n=182	n=6	n=20	n=6	n=228	n=51	n=
Fe/Mn	1.00	0.67	0.76	0.71	1.24	0.68	0.85	0.95	0.93	1.07	0.98	1.14	1.54
Fe wt. %	20.2	15.7	16.6	17.4	19.5	15.1	17.8	20.3	22.5	25.9	21.2	19.0	21.6
Mn	20.1	23.3	21.7	24.4	15.7	22.1	21.0	21.4	24.3	24.1	21.6	16.7	14.0
Si	5.50	2.80	5.38	4.06	10.5	3.7	6.26	4.52	9.45	8.28	4.28	7.14	5.50
Na	2.14	1.57	1.70	1.67	1.81	1.6	1.71	2.04	1.92	1.85	1.76	0.88	2.16
Al	1.31	0.63	1.15	0.81	1.95	1.0	1.69	1.02	1.97	2.10	1.30	3.55	1.54
K	0.55	0.47	0.64	0.55	0.80	0.56	0.65	0.49	0.97	0.81	0.54	0.35	4.39
Mg	1.15	1.05	1.02	1.08	1.14	1.3	1.28	1.14	1.60	1.36	1.31	1.36	1.32
Ca	2.76	5.86	3.57	3.17	1.77	4.1	2.37	2.72	2.61	2.81	2.70	2.22	0.53
Ti	1.009	1.014	1.137	1.216	0.550	0.77	1.329	0.846	1.001	1.029	1.073	0.738	0.948
P	0.47	1.64	0.77	0.61	0.37	1.2	0.43	0.49	0.55	0.54	0.63	0.45	0.78
S	0.19	0.27	0.15	0.16	0.10	0.3	--	0.18	0.15	0.1	0.16	--	0.2
Cl	0.95	0.92	0.77	0.86	0.85	--	--	1.03	1.11	1.04	1.42	--	1.06
H_2O^+	9.2	7.6	8.4	8.5	9.21	--	6.98	--	--	--	10.2	--	28.3
H_2O^-	17.2	19.2	24.5	20.4	21.3	--	12.1	14.7	18.0	18.6	18.5	--	11.2
CO_2	0.70	1.1	0.65	0.64	0.37	--	0.45	--	--	--	0.83	--	--
LOI	36.9	37.2	49.0	41.8	27.6	--	29.3	31.2	20.3	19.6	37.3	14.6	--
Ag ppm	--	--	--	--	--	0.717	--	--	10.2	--	--	--	--
As	271	212	234	258	246	165	1050	259	210	246	254	544	289
B	238	179	177	162	315	115	--	278	326	381	336	--	257
Ba	1545	1987	2018	1865	3285	1695	1889	1844	2646	2150	1745	1298	1716
Be	6.9	6.0	4.9	7.5	5.6	--	--	4.9	6.9	8.0	6.9	--	8.4
Bi	17.5	41.0	59.1	64.3	9.5	--	--	30.7	33.3	12.7	25.4	--	15.3
Br	32	28	33	25	27	--	--	35	26	18	32	35	36
Cd	2.4	3.7	3.1	3.2	3.1	4.6	5.3	4.8	4.9	3.2	4.1	--	3.7

Table 6 continued

	1	2	3	4	5	6	7	8	9	10	11	12	13
Co	3991	6410	5019	7441	2746	6372	6904	4349	2713	1918	5508	3878	3574
Cr	31	24	17	8	31	22.4	118	31	33	67	35	34	31
Cu	876	963	1310	1059	679	1075	760	298	1270	558	1100	761	774
Ga	30	19	--	11	16	--	--	11	13	27	18	--	16
Hf	7	10	7	7	7	7.4	--	7	5	8	7	8	14
Li	5	3	4	2	12	63	--	5	12	6	4	--	35
Mo	402	504	420	482	329	455	374	794	530	471	470	--	429
Nb	54	51	70	48	32	--	--	34	43	40	62	--	54
Ni	3487	4626	3927	4398	2926	5403	3651	3393	3241	2654	4237	3385	2685
Pb	1327	1505	1713	1723	1207	1777	1715	1746	1740	833	1207	1531	1108
Rb	25	16	--	20	15	--	--	21	19	20	9	--	17
Sb	43.3	38.7	49.0	45.1	44.4	24.4	--	48.5	43.0	30.4	40.3	28.5	57.2
Sc	9.4	6.4	9.8	7.9	10.0	6.4	--	9.1	11.7	8.4	8.1	7.8	17.3
Se ppm	--	--	--	15	--	0.40	--	10	16	11	15	--	--

Sn	5	10	--	12	--	--	--	12	3	5	6	--	13
Sr	1502	1614	1531	1624	1241	1212	864	1619	1539	1399	1521	--	1341
Te	31.0	60.8	46.8	51.0	8.7	--	--	19.6	25.5	20.9	35.2	--	39.1
Tl	107	150	226	193	54.0	--	--	127.7	80.0	76.6	190	--	94.5
Th	11.4	11.2	15.9	13.5	31.1	33.	--	37.2	55.0	19.4	14.9	24.8	51.9
U	12.5	12.3	13.7	13.6	10.9	9.6	--	15.6	10.8	14.1	13.3	7.4	10.2
V	655	650	638	639	556	515	626	768	549	702	710	--	825
W	102	88	135	72	69	93.3	--	120	56	65	110	43	77
Y	196	251	225	204	159	166	178	200	178	195	205	--	184
Zn	658	719	646	697	620	680	531	535	674	597	688	822	598
Zr	586	538	678	682	605	172	--	544	602	570	610	--	564
La	365	293	438	345	294	202	361	323	266	184	256	180	277
Ce	831	1130	1635	1282	985	--	2354	1570	1742	594	894	868	1430
Pr	66.3	49.5	81.0	65.5	67.7	106	87.1	58.7	55.5	35.3	56.6	--	74.6
Nd	288	219	319	263	270	162	371	298	256	164	237	173	251
Sm	57.5	42.9	64.9	54.5	60.1	41.6	74.4	59.3	56.2	33.0	49.5	29.5	61.4
Eu	14.5	10.0	16.1	14.0	21.4	9.90	18.3	13.0	13.2	8.3	11.4	39.4	10.4
Gd	67.5	47.7	69.3	61.9	57.6	26	69.2	68.0	63.4	40.3	64.1	--	62.4
Tb	10.4	7.2	11.3	9.7	9.3	7.53	12.7	9.4	8.6	6.2	8.4	5.2	10.0
Dy	61.0	44.2	98.9	59.6	53.6	57.8	62.4	54.9	50.0	38.5	54.6	--	52.9

Table 6 continued

	1	2	3	4	5	6	7	8	9	10	11	12	13
Ho	12.5	9.3	13.5	12.4	10.1	6.6	11.4	9.8	8.8	8.2	11.8	--	9.3
Er	34.6	27.2	37.2	34.8	27.3	31.9	30.1	31.1	26.5	26.1	33.9	--	31.0
Tm	4.8	3.9	5.4	5.6	4.1	4.3	4.0	4.3	3.5	3.5	4.93	--	3.6
Yb	31.6	25.2	32.7	33.8	26.1	17.7	26.0	27.9	23.4	24.8	27.2	18.5	23.8
Lu	4.62	4.04	--	4.75	3.61	3.3	3.57	4.28	3.35	4.03	4.03	2.90	4.3
Hg ppb	15	9	11	10	39	--	--	1448	38	91	27	--	141
Au	--	107	--	57	26	--	--	30	25	17	30	36	6
Ir	5	16	8	--	2	--	4	3	6	3	2	--	5
Pd	2	4	3	3	4	--	--	5	8	7	8	--	6
Pt	217	489	510	206	69	777	155	157	259	117	286	--	567
Rh	15	24	24	19	9	--	10	10	15	10	20	--	37
Ru	19	16	21	--	6	--	12	13	12	12	15	--	18

Columns correspond to areas outlined in Fig. 5; IW=international waters; dash=not analysed; NW Pacific data from [59]; Hawaii from [60]; South Pacific [61]; Far South Pacific from [62]; C-C Zone (Clarion-Clipperton) & other abyssal nodule data from(63). Number of samples (n) that differ from those in the heading are: column 1, n=29-34 Al, H_2O^+, CO_2, As, Cr; n=2-16 S, Cl, B, Be, Bi, Br, Ga, Hf, Li, Nb, Rb, Sb, Sc, Sn, Te, Tl, Th, U, W, Zr, REEs, Hg, PGEs; column 2, n=75-106 H_2O^+, LOI, Cd, Cr, Y; n=26-45 S, Cl, B, Be, Bi, Br, Ga, Hf, Li, Nb, Rb, Sb, Sc, Te, Tl, Th, U, W, Zr, REEs, PGEs; n-2-10 Hg, Au; column 3, n=17-18 REEs, PGEs; n=1 Cl, H_2O^+, B, Be, Bi, Br, Hf, Li, Nb, Sb, Sc, Te, Tl, Th, U, W, Zr, Hg; column 4, n= 36 LOI; n=24 PGEs, n=15 REEs; n=2 Cl, H_2O^+, B, Be, Bi, Br, Ga, Li, Nb, Sb, Sc, Te, Tl, Th, U, W, Zr, Hg, Au; column 5, n=14-15 REEs, PGEs; n=1-8 Cl, H_2O^+, LOI, B, Be, Bi, Br, Ga, Li, Nb, Sb, Sc, Te, Tl, Th, U, W, Zr, Hg, Au; column 6, n=1418-1440 Co, Cu, Ni; n=100-370 Si, Na, Al, K, Mg, Ca, Ti, P, As, Ba, Mo, Pb, V, Y, Zn, Pt; n=2-67 Ag, B, Cd, Cr, Hf, Li, Sb, Sc, Se, Th, U, W, REEs; column 7, n=83-165 Si, Na, Al, K, Mg, Ca, Ti, P, H_2O^+, H_2O-, As, Ba, Cd, Cr, Mo, Pb, Sr, V, Y, Zn; n=32-35 REEs, n=2-3 PGEs, Tm; column 8, n=1-5 for S, Cl, B, Bi, Br, Cd, Cr, Hf, Nb, Rb, Sb, Se, Sn, Te, Tl, U, W, Zr, REEs, Hg, Au, PGEs; column 9, n=15-19 Cd, Hf, Se, Au; n=1-9 Ag, Sn, PGEs; column 10, n=1-5 Br, Cd, Li, Se, Sn, W, REEs, Hg, Au, PGEs; column 11, n=115-214 Fe, Si, Al, Mg, Ca, Ti, P, Ni, V, Zn; n=46-93 K, Ba, Pb; n=1-37 all other elements except Mn; column 12, n=12-34 Si, Na, K, As, Ba, Br, Hf, Pb, Sb, Sc, Th, W, Zn, REEs; n=1-9 Al, Mg, Ti, LOI, Cr, U, Au; column 13, n=20-24 As, Bi, Cr, Ga, Te, Tl, Th, Zr, REEs, Hg; n=10-19Cl, H_2O^+, B, Br, Cd, Hf, Sb, Sn, U, W; n=1-9 Rb, Au, PGEs; column 14, n=8-13 S, Cl, As, B, Bi, Cd, Cr, Hf, Li, Rb, Sn, Te, Tl, Th, U, W, Zr, REEs, Hg; n=1-6 Br, Sb, Se, Au, PGEs; columns 15-16, n=100-1000 Si, Na, Al, K, Mg, Ca, Ti, Ba, Mo, Sr, V, Cr, Cd, As, P, Ce, Y; n=1000-2000 Zn, Pb; n=2000-4000 Fe, Mn, Ni, Cu, Co; A means for the entire Pacific. A key to the chemical symbols is in Appendix 3.

REE and yttrium contents in Fe-Mn crusts are very high; 100s of ppm for yttrium and 1000s of ppm for total REE contents (cerium in one bulk crust sample from the Hawaii EEZ is very high, 1.1%--11,000 ppm). Concentrations of the trivalent REEs (includes all REEs except cerium) appear to increase in crusts with increasing water depth of occurrence[70]. Irrespective of their specific compositions, Fe-Mn crusts from the major oceans show remarkably similar REE patterns on normalize plots. Shale-normalized REE patterns generally show enrichment of the heavy REEs and commonly show positive anomalies of lanthanum, cerium, europium, and gadolinium, and a negative yttrium anomaly (*Fig. 7*). The REEs in crusts are derived from seawater, which in turn is supplied with REEs from fluvial and eolian input from continental sources. Except for oxidation-reduction (redox)-sensitive cerium, yttrium and REE distributions in Fe-Mn crusts represent the exchange equilibrium between yttrium and REEs dissolved in seawater and yttrium and REEs sorbed on the surface of iron-manganese oxyhydroxide particles. Cerium is the only REE that in near-surface environments may occur as a tetravalent ion, and the contrasting charge and size of cerium (IV) leads to its decoupling from the other REEs. In the marine environment, cerium uptake by manganese and iron oxyhydroxides is accompanied by cerium oxidation, which is mediated by microbial processes and/or a surface catalysis, a reaction that would otherwise be very sluggish (e.g., [73]).

Platinum Group Elements (PGEs: platinum, palladium, rhodium, ruthenium, iridium) are highly enriched in Fe-Mn crusts over their abundances in the Earth's crust (with the exception of palladium) and over concentrations in Fe-Mn nodules (*Table 6*). Platinum has been considered a potential by-product of cobalt mining of crusts and has mean values for different areas of up to 0.8 ppm and individual sample values of up to 3 ppm[74]. Rhodium, ruthenium, and iridium contents are up to 124, 32, and 54 parts per billion (ppb), respectively, whereas palladium contents (1-16 ppb) are usually at or just above its mean content in the Earth's crust. Most PGEs have a positive correlation with crust thickness and are concentrated in the inner part of thick crusts. Most PGEs commonly correlate inversely with water depth of occurrence of the crusts [75].

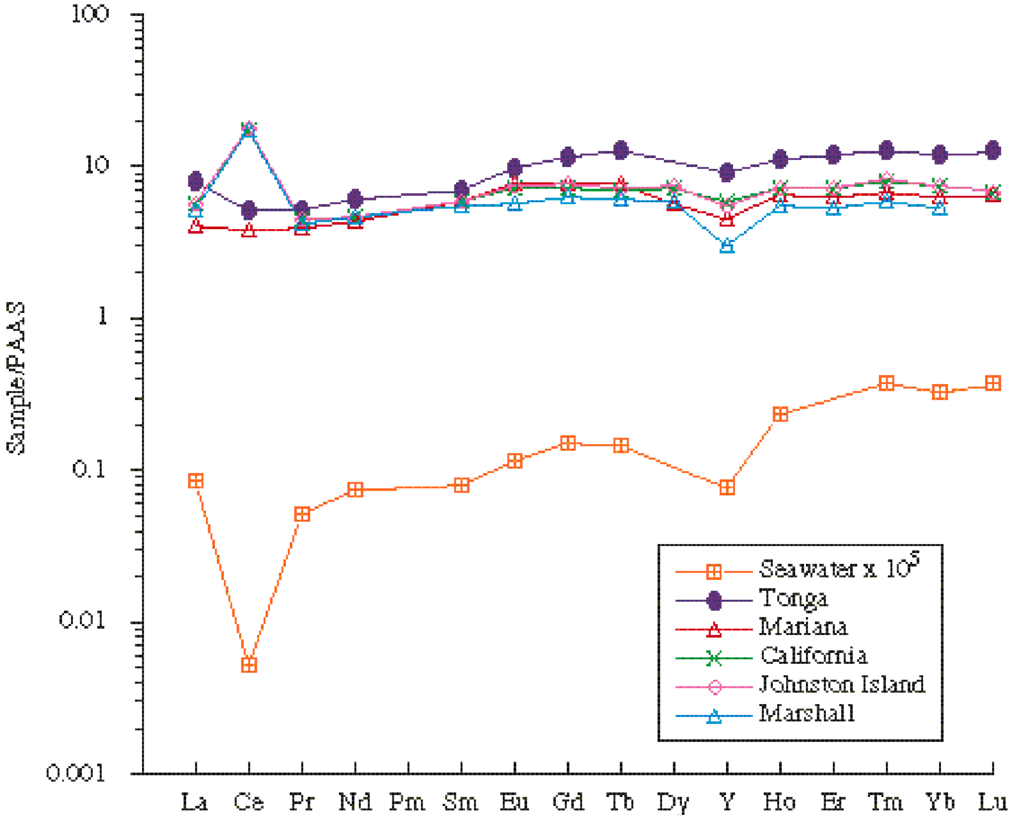

Figure 7. Shale (PAAS, Post-Archean Australian shales; (143)) REE patterns of typical hydrogenetic crusts (Johnston Island, California borderland, and Marshall Islands) and mixed hydrogenetic-hydrothermal crusts (Tonga Arc and mariana Arc) from the Pacific, compared to the seawater pattern at 1,250 m water depth (146).

Fe-Mn crusts from the Marshall Islands EEZ, areas in international waters to the north and northwest of the Marshall Islands, and the south Atlantic (*Fig. 6*) contain the highest PGE contents; crusts from French Polynesia also have high PGE contents. Platinum contents increase markedly in crusts from the west Pacific compared to the central and east Pacific: East Pacific (mean 72 ppb), central Pacific (mean 200 ppb), and west Pacific (mean 600 ppb); then platinum contents decrease again adjacent to the west Pacific arcs (*Table 6*)[76]. Platinum, rhodium, iridium, and in some regions, ruthenium comprise part of the δ-MnO$_2$ phase, whereas palladium is commonly part of the detrital phase[77]. Part of the ruthenium may also be part of the detrital phase and both iridium and ruthenium occur with the residual biogenic phase in some regions. Platinum, iridium, and rhodium are derived predominantly from seawater, whereas palladium and much of the ruthenium are derived from clastic debris, the remainder of the ruthenium being derived from seawater [78]. The extraterrestrial component (meteorite debris) in bulk crusts is small. Platinum is a redox-sensitive element and its varying concentration probably reflects changing seawater redox conditions, and diagenesis (maturation of oxide phases and phosphatisation) within the older generation of crusts where it is concentrated [79].

2.5. Phosphatisation of Fe-Mn Crusts

Most thick hydrogenetic Fe-Mn crusts that formed in the open Pacific consist of two growth generations: A phosphatised older generation and a younger non-phosphatised generation. Phosphatisation of older crust layers was widespread and is found in crusts from many locations in the central and south Pacific[80]. Crusts from relatively deep water (>2800 m), such as from the Teahitia-Mehetia region[81] and from the Tasman Rise[82], show only minor or no phosphatisation, which is also demonstrated by a decrease in CFA-associated elements with increasing water depth of crust occurrence (see next section). Phosphatised crusts are also not found in most continental-margin environments, such as in the EEZ off western North America.

Precipitation of the old crust generation began for most crusts between about 55 and 25 Ma ago (e.g., [83]) and was interrupted by several Cenozoic phosphogenic events[84]. Phosphogenesis entailed CFA impregnation of the older crust and formation of phosphorite partings within and at the top of the older generation of some crusts. Phosphatisation took place by CFA replacement of calcite infiltered into crust pore spaces, by direct precipitation of CFA in pore space, and by replacement of other crust phases, most commonly iron oxyhydroxide. The thickness of the phosphatised layer can be as large as 12 cm, and calcium and phosphorus concentrations can increase up to 15 wt.% and 5 wt.%, respectively. Growth of the younger crust generation started during the Miocene and continued to the present without interruption by further phosphogenic events.

According to Hein et al.[85], two major and possibly several minor Cenozoic episodes of phosphogenesis were responsible for formation of phosphorite on equatorial Pacific seamounts. Those same phosphogenic events also phosphatised the older generation of Fe-Mn crusts. Crust ages would allow for the major phosphogenic events centred on the Eocene-Oligocene (~34 Ma) and Oligocene-Miocene boundaries (~24 Ma), as well as the minor middle Miocene event at about 15 Ma, to have affected growth of Pacific Fe-Mn crusts. Extraction and dating of the CFA from older crust generations support the coeval phosphatisation of substrate rocks and crusts (Chan, Hein, Koschinsky unpublished data).

Phosphatisation of the older Fe-Mn crust layers caused changes in their chemistry and mineralogy [86]. Besides dilution of the primary crust contents by CFA, certain elements were added and others removed. Depletion of elements in the phosphatised crust generation compared to non-phosphatized crust layers occurred in the approximate order silicon>iron= aluminum=thorium> titanium= cobalt>manganese=lead=uranium; in contrast, nickel, copper, zinc, yttrium, REEs, strontium, platinum, and commonly barium are enriched in phosphatised crusts [87].

2.6. Local and Regional Variations in Composition

The iron/manganese ratios are lowest in crusts from the central and west-central Pacific and highest for crusts collected in the north Atlantic, Indian, south Atlantic, and near continental margins and volcanic arcs in decreasing magnitude of the ratio. The detrital-associated element (silicon, aluminium) contents increase in crusts with proximity to continental margins (off western North America, far South Pacific) and volcanic arcs in the west Pacific, which have contents equivalent to those found in most crusts from the Atlantic and Indian Oceans (*Table 6; Fig. 8A*). Within the central Pacific region, detrital-related elements are most abundant in the eastern part, along the Hawaiian and Line Islands. In contrast, cobalt, nickel, and platinum contents are generally highest in crusts from the central and northwest Pacific and lowest in crusts from along the spreading centres in the southeast Pacific, the continental margins, and along the volcanic arcs of the west Pacific (*Table 6; Fig. 8B, C*)[89]. Cobalt contents are low and nickel contents are the lowest for crusts from the Atlantic and Indian Oceans compared to crusts from other regions (*Fig. 8B, C*). Copper contents generally follow the trend for cobalt, nickel, and platinum, except for the Indian Ocean, where a high mean value (1254 ppm) is found. The reason for those high values is the much greater mean water depth for crusts collected from the Indian Ocean. Shatsky Rise crusts, mid-latitudes of the north Pacific, have a surprisingly high mean copper content, as well as the highest copper value measured in a single bulk crust, 0.4% (4000 ppm). Mean barium content is much higher in northeast Pacific crusts than anywhere else in the global oceans. Those high barium contents are the result of intense upwelling and high bioproductivity in that region[90], Hein et al., unpublished data). Trends for mean titanium contents do not follow those of aluminium and silicon, but rather follow those of cobalt, nickel, and platinum, which supports the idea that much of the titanium in crusts is a hydrogenetic phase[91]. Another interesting distribution is seen with phosphorus because it is not most enriched in areas where upwelling and bioproductivity are greatest (east Pacific, east equatorial Pacific), but rather is highest in crusts from the Marshall Islands and the northwest Pacific (*Fig. 8A*; see also Hein et al.[92]). It is not clear why phosphorus does not reflect the high bioproductivity in the east Pacific as does barium, or why CFA does not occur in crusts from that region. Phosphorus is relatively high in north Atlantic crusts, where bioproductivity is also high. Cerium is generally lower in south Pacific crusts than it is in north Pacific crusts and has moderate contents in Atlantic and Indian

Ocean crusts. Elements concentrated in crusts by oxidation reactions (cobalt, cerium, thallium, and also predicted for lead, titanium, tellurium, and platinum) should be highest in the west Pacific where seawater oxygen contents are the highest. However, that relationship is only clearly defined for platinum and the cerium anomaly (from REE plots), probably because regional patterns are somewhat masked by local conditions where upwelling around seamounts mixes various water layers[93].

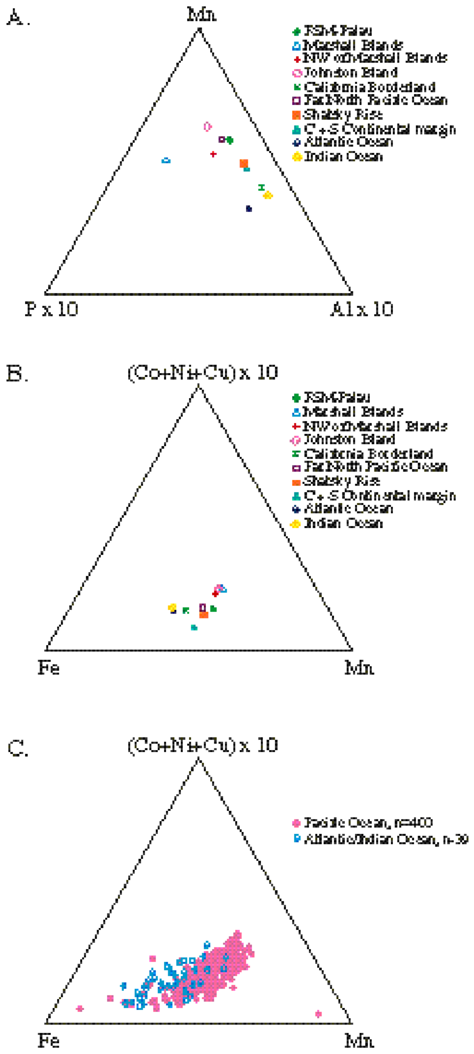

Figure 8. *(A)*-Mn-Px10-Alx10 ternary diagram for mean compositions of USGS data listed in Table 7; note that crusts from all areas except the Marshall Islands have about the same relative amounts of P, but highly variable relative amounts of A1 and Mn depending on proximity to continental margins for A1 and to the equatorial Pacific for Mn; *(B)* Mn-Fe-(Co+Ni+Cu)x10 ternary diagram after Bonatti et al. (146) for data as in (A); Note that crusts in

proximity to continental margins and volcanic arcs are relatively enriched in Fe and depleted in trace metals, whereas central Pacific crusts are relatively enriched in Mn and trace metals, with the Johnston Island and Marshall Islands crusts showing the greatest enrichments; *(C)* Complete data set used in the means in B.

Manganese, manganophile elements (e.g. cobalt, nickel, cadmium, molybdenum), and the iron oxyhydroxide phase generally decrease, whereas detrital phase-related elements (silicon, aluminium, iron, yttrium) increase with increasing latitude[94]. The intensification of the OMZ in the equatorial zone of high bioproductivity allows for greater amounts of manganese to remain in solution in seawater and slower growth rates of crusts. The increase in iron, silicon, aluminium, and yttrium to the north is partly due to increased supply of detritus by the trade winds. The same trends in manganese and manganophile elements should occur with longitude (increasing to the east) in the equatorial region because regional bioproductivity increases in that direction. However, a paucity of seamounts exists between Hawaii and North America, so that trend cannot be confirmed Pacific-wide; regardless, the trend is generally poorly developed regionally (e.g.,[95]). Contents of manganophile elements in California continental margin crusts are diluted by detrital and biogenic inputs, which ameliorates the increased d-MnO$_2$-related elements expected to occur there. The residual biogenic phase elements generally increase with proximity to the equatorial zone of high bioproductivity and in the eastern Pacific, where productivity is yet higher[96].

Manganese, manganophile elements, and CFA-related elements decrease, whereas iron, copper, and detrital-related elements increase with increasing water depth of occurrence of crusts[97]. Cobalt and other manganophile elements are enriched more than manganese is in shallow water[98]. Those relationships have been explained by the increased dissolved manganese in the OMZ (about 300-1500 m water depths; *Fig. 2*) and an increased supply of detrital phases at greater water depths, which contributed iron, aluminium, and silicon.

3. IRON-MANGANESE CRUST FORMATION

Even though Fe-Mn crusts form by hydrogenetic precipitation, the exact mechanisms of metal enrichments in the water column and at the crust surface are poorly understood. The ultimate sources of metals to the oceans are river and eolian input, hydrothermal input, weathering of ocean-floor basalts, release of metals from sediments, and extraterrestrial input. Elements in seawater may occur in their elemental form or as inorganic and organic complexes. Those complexes may in turn form colloids that interact with each other and with other dissolved metals (e.g.,[99]). Thermodynamic, surface-chemical, and colloidal-chemical models show that most hydrogenetic elements in crusts occur as inorganic complexes in seawater[100]. Hydrated cations (cobalt, nickel, zinc, lead, cadmium, thallium, etc.) are attracted to the negatively charged surface of manganese oxyhydroxides, whereas anions and elements that form large complexes with low charge-density (vanadium, arsenic, phosphorus, zirconium, hafnium, etc.) are attracted to the slightly positive charge of iron hydroxide surfaces.

Mixed iron and manganese colloids with adsorbed metals precipitate onto hard-rock surfaces as poorly crystalline or amorphous oxyhydroxides, probably through bacterially mediated catalytic processes. Continued crust accretion after precipitation of that first molecular layer is autocatalytic, but is probably enhanced to some degree by bacterial processes[101]. Additional metals are incorporated into the deposits either by co-precipitation, or by diffusion of the adsorbed ions into the manganese and iron oxyhydroxide crystal lattices. Cobalt is strongly enriched in hydrogenetic crusts because it is oxidized from cobalt to the less soluble cobalt at the crust surface, possibly through a disproportionation reaction[102]. Lead, titanium, tellurium, and thallium, as well as cerium are also highly enriched in hydrogenetic deposits, probably by a similar oxidation mechanism[103].

Concentrations of elements in seawater are generally reflected in their concentrations in crusts, although there are many complicating factors. For example, copper, nickel, and zinc occur in comparable concentrations in seawater[104], yet nickel is much more enriched in crusts than either copper or zinc. Copper contents may be relatively low in hydrogenetic crusts because it occurs mostly in an organically bound form in deep seawater, which is not readily incorporated into iron and manganese metal oxyhydroxides[105]. Zinc contents may be relatively low in crusts compared to nickel because little zinc may be adsorbed onto crusts after precipitation of the oxyhydroxides, which follows the order of nickel>cobalt>zinc>copper[106]. In contrast, comparable proportions of manganese:iron:cobalt exist in deep seawater (0.5-1.0:1:0.02-0.05;[107]) as exist in Fe-Mn crusts (0.6-1.6:1:0.02-0.05; *Tables 1, 6*;[108]).

The dominant controls on the concentration of elements in hydrogenetic crusts are the concentration of each element in seawater; element-particle reactivity; element residence times in seawater; the absolute and relative amounts of iron and manganese in the crusts, which in turn are related to their abundance and ratio in colloidal flocs in seawater[109]; the colloid surface charge and types of complexing agents, which will determine the amount of scavenging within the water column[110]; the degree of oxidation of MnO_2 (oxygen/manganese)--the greater the degree of oxidation the greater the adsorption capacity--which in turn depends on the oxygen content and pH of seawater [111]; the amount of surface area available for accretion, which at the surface of growing crusts is extremely large (mean 300 m^2/g), but which decreases with maturation of crusts[112]; the amount of dilution by detrital minerals and diagenetic phases; and growth rates. Elements that form carbonate complexes in seawater behave independently from those that form hydroxide complexes, which indicates their different modes of removal from seawater onto crust surfaces[113]. Very slow growth rates promote enrichment of minor elements by allowing time for extensive scavenging by the major oxyhydroxides. Accretion of oxyhydroxides will be slower where the OMZ intersects the seafloor than it will be above and below that zone, because manganese is more soluble in low-oxygen seawater (*Fig. 2*). Crusts exposed at the seafloor may not necessarily be actively accreting oxyhydroxides [114] because of mechanical erosion or, less commonly in the contemporary oceans, because of seawater oxygen contents that are insufficient to permit oxidation of the major metals.

4. BIOLOGICAL COMMUNITIES AND CURRENTS ON SEAMOUNTS

It is essential to understand the nature of biological communities that inhabit seamounts so that that information can be incorporated into environmental impact recommendations. It is also essential to understand the movement of water masses around seamounts so that appropriate mining equipment and techniques can be developed and dispersal routes of resuspended particles and wastes can be determined. Very few studies have addressed seamount currents and biology, especially the latter. Fe-Mn crusts occur on many different kinds of topographic features throughout the global ocean, but in this section, we concentrate on seamounts of the type that occur in the equatorial Pacific, where the most economically promising Fe-Mn crust deposits occur.

Seamounts obstruct the flow of oceanic water masses, thereby creating a wide array of seamount-generated currents of generally enhanced energy relative to flow away from the seamounts. Seamounts interact simultaneously with large-scale currents, mesoscale jets and eddies, and tidal flows[115], the combined effect of which produces seamount-specific currents. Those seamount-generated currents can include anticyclonic currents (Taylor column), internal waves, trapped waves, vertically propagating vortex-trapped waves, Taylor caps (regions of closed circulation or stagnant water above a seamount), attached counter-rotating mesoscale eddies, and others (e.g.,[116]). The effects of these currents are strongest at the outer rim of the summit region of seamounts, the area where the thickest crusts are found. However, the seamount-generated currents can be traced for at least several hundred meters above the summit of seamounts. Other water column features produced by the interaction of seamounts and currents are density inversions, isotherm displacement, enhanced turbulent mixing, and upwelling; the latter process moves cold, nutrient-rich waters to shallower depths. Upwelling increases primary productivity, which in turn increases the size and magnitude of the OMZ, and makes seamounts ideal fishing grounds. Seamount-generated currents also cause erosion of the seamounts (and Fe-Mn crusts) and move surface sediments, which produces sand waves and ripples.

Seamount height, summit size, types of ambient currents, and energy of the tidal currents determine which seamount-specific currents will be generated and their longevity. It is clear that some seamounts in the equatorial Pacific have been swept clean of sediment for most of 60 Ma, because that is the duration of crust growth in those areas, whereas other seamounts may be capped by as much as 500 m of carbonate sediment and therefore lack development of Fe-Mn crusts on the summit.

These physical processes also affect seamount biology. Seamount communities vary from seamount to seamount, even communities from the same water depths on adjacent seamounts. This is partly the result of the varying physical processes in the water column. Most studies of seamount biology have concentrated on seamounts with a sediment cap and on the biological communities living on (epifauna) and in (infauna) that sediment (e.g.,[117]). Fewer studies have addressed communities dwelling on the rock outcrops, which consist of mostly attached (sessile) organisms. A few studies have looked at the types of organisms that live on the surface of Fe-Mn crusts, which consist predominantly of agglutinated foraminifera (e.g.,[118]). The bacterial or microbiological processes that may mediate the growth of Fe-Mn crusts and the concentration of trace metals, have not been studied.

Seamount biological communities are characterized by relatively low density and low diversity where the Fe-Mn crusts are thickest and cobalt-rich. This occurs because the low oxygen contents in the OMZ decrease the abundance of consumer populations, excludes most tolerant species from seafloor habitats, and can produce steep gradients in seafloor communities[119]. Above and below the OMZ, the populations may be greater and more diverse. Levin and Thomas[120] found lower biological activity at the high-energy summit margin (covered by both rock and sediment) of the central-Pacific Horizon Guyot than at sediment-covered summit sites. In contrast, Genin et al.[121] found that antipatharian and gorgonian corals are more abundant in areas of seamount summits where flow acceleration is prominent. Thus, the make-up of the seamount communities and population density and diversity are determined by current patterns, topography, bottom sediment and rock types and coverage, seamount size, water depth, and size and magnitude of the OMZ, which in turn is related to primary productivity.

5. RESOURCE, TECHNOLOGY, AND ECONOMIC CONSIDERATIONS

During the initial stages of exploration for cobalt-rich crusts, the main objectives are to find a really extensive, thick, high-grade deposits. Later stages of exploration are dedicated to mapping the precise range of minable crusts. Consequently, a continuing refinement of detail is obtained for each seamount by successive iterations of sampling and surveying.

Field operations used for exploration include continuous mapping of seamounts using multibeam echosounder, side-scan sonar, and single- or multi-channel seismic systems; systematic sampling using dredges and corers; bottom video and photography; water column sampling; and laboratory analysis of crusts and substrates for composition and physical properties. Complimentary operations include gravity and magnetic surveys of the seamounts. Operations may also include collecting biological and ecological information that can be used in future environmental impact studies. The typical methodology has been to produce SeaBeam bathymetric maps and derivative backscatter and slope-angle maps, along with seismic profiles, which are used together to select sampling sites; and run geophysical surveys. For reconnaissance work, 15-20 dredge hauls and cores are taken per seamount. Then, video-camera surveys delineate crust, rock, and sediment types and distributions, as well as crust thicknesses if possible. These exploration activities require use of a large, well-equipped research vessel because of the large number of bottom acoustic beacons, large towed equipment, and volume of samples collected. During advanced stages of exploration and site-specific surveys, it is suggested to use deep-towed side-scan sonar including swath bathymetry, and tethered remotely operated vehicles (ROVs) for mapping and delineation of small-scale topography. Extensive sampling of deposits will be required by dredging, coring, ROVs, and a device to take close-spaced samples that has not yet been developed. Gamma-radiation surveys will delineate crust thicknesses and the existence of crusts under thin blankets of sediments. Current-meter moorings will be required to understand the seamount environment and biological sampling and surveys will be necessary.

Based on data collected during the first six years of Fe-Mn crust studies, Hein et al. [122], developed criteria for the exploration for and exploitation of Fe-Mn crusts, which was later expanded[123] to include 12 criteria.

<u>Regional Criteria</u>:

(1) large volcanic edifices shallower than 1000-1500 m;
(2) volcanic edifices older than 20 Ma;
(3) volcanic structures not capped by large atolls or reefs;

(4) areas of strong and persistent bottom currents;
(5) a shallow and well-developed OMZ; and
(6) areas isolated from input of abundant fluvial and eolian debris.

<u>Site-Specific Criteria</u>:
(7) subdued small-scale topography;
(8) summit terraces, saddles, and passes;
(9) slope stability;
(10) absence of local volcanism;
(11) average cobalt contents =0.8%; and
(12) average crust thicknesses =40 mm. Depending on the mining systems used, crust thickness may turn out to be more important than grade; if true, then the crust thickness criterion would increase and grade criterion would decrease. That relationship is inevitable because cobalt grade decreases with increasing crust thickness.

5.1. Mining Systems

Crust mining is technologically much more difficult than Fe-Mn nodule mining. Nodule mining concepts developed by mining consortia in the last decades consist of a hydraulic dredge and a slurry lift system[124]. Recovery of nodules is relatively easy because they sit on a soft-sediment substrate. In contrast, Fe-Mn crusts are weakly to strongly attached to substrate rock. For successful crust mining, it is essential to recover Fe-Mn crusts without collecting substrate rock, which would significantly dilute the ore grade. Five possible Fe-Mn crust mining operations include fragmentation, crushing, lifting, pick-up, and separation[125]. The proposed method of Fe-Mn crust recovery[126] consists of a bottom-crawling vehicle attached to a surface mining vessel by means of a hydraulic pipe lift system and an electrical umbilical. The mining machine provides its own propulsion and travels at a speed of about 20 cm/s. The miner has articulated cutters that would allow Fe-Mn crusts to be fragmented while minimizing the amount of substrate rock collected (*Fig.* 9). Hydraulic suction dredges are similar to trailing suction dredge heads commonly used with hopper dredges for sand and gravel mining. About 95% of the fragmented material would be picked up and processed through a gravity separator prior to lifting. Material throughput for the base-case mining scenario[128] is 1,000,000 t/y. That scenario allows 80% fragmentation efficiency and 25% dilution of crust with substrate during fragmentation as reasonable miner capabilities. The net recovery of crusts depends on fragmentation efficiency, pickup efficiency, and separation losses. Fragmentation efficiencies depend on small-scale topography and depth of the cut. Pickup efficiencies also depend on seafloor roughness, but to a lesser extent than fragmentation efficiency, and on the size of fragmented particles and type of pickup device[129].

The Japan Resource Association[130] studied the applicability of a continuous line bucket (CLB) system as a method of crust mining. The CLB could be competitive in an area where crusts are easily separated from substrate rock, or where the substrate is soft enough to be removed by washing[131]. While there is some merit in the CLB's simplicity, the most likely commercial crust mining systems will probably use hydraulic lift together with a mechanical fragmentation system attached to a self-propelled collector. That type of system has a better likelihood of efficient crust recovery and substrate separation[132]. Some new and innovative systems that have been suggested for Fe-Mn crust mining include water-jet stripping of crusts from the substrate, and *in situ* leaching techniques. Both suggestions offer promise and need to be further developed.

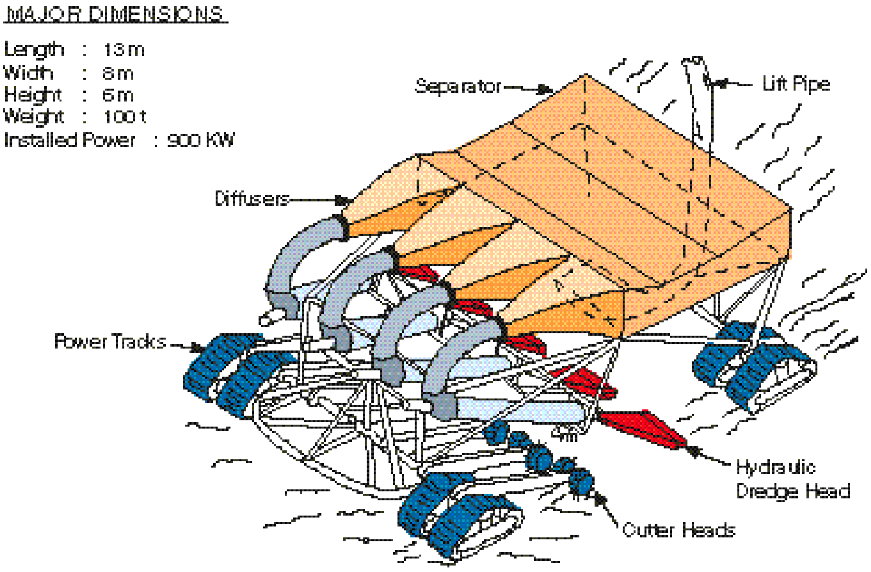

Figure 9. Schematic representation of a deep-sea mining vehicle for Fe-Mn crusts (from DO1-MMS (127); designed by J.E. Halkyard, OTC Corporation)

5.2. Economics

The importance of metals contained in Fe-Mn crusts to the world economy is reflected in their patterns of consumption[133]. The primary uses of manganese, cobalt, and nickel are in the manufacture of steel to which they provide unique characteristics. Cobalt is also used in the electrical, communications, aerospace, and engine and tool manufacturing industries, as well as its radioisotope in medicine. Nickel is also used in chemical plants, petroleum refineries, electrical appliances, and motor vehicles. Supplies of these metals and other rare metals found in crusts are essential for maintaining the efficiency of modern industrial societies and in improving the standard of living in the 21st century.

Most mineral industry analysts agree that the supply of cobalt is more uncertain than the supply of the other crust metals because most cobalt production comes from politically unstable Zaire (57%) and Zambia (11%) and cobalt is produced as a by-product of copper mining. Consequently, the supply of cobalt is tied to the demand for copper. This is also true for tellurium, which is produced as a by-product of both copper and gold mining. This uncertainty in supply has caused industry to look for alternatives to cobalt and tellurium, resulting in only a modest growth in their markets over the past decade, and consequently relatively low prices. If substantial alternative sources of cobalt and tellurium supply are developed, there should be a greater incentive to reintroduce them back into products and expansion of the markets (e.g.,[134]).

A preliminary estimate of the economics of crust mining and processing operations for the State of Hawaii[135] indicated that they were not economical, under the circumstances at that time (*Table 7*). The minimum required return on the investment of US $750 million in mining and processing is on the order of US $100 million per year. Neither pyrometallurgical or hydrometallurgical processing options would be commercially viable under the scenario of 700,000 dry t/y of crust production [137].

Table 7. Fe-Mn crust mining and processing, estimated annual revenues and costs

Commodity	**Output (t)**	**Prices (1985 dollars)**	**Amount ($ x 10^6)**
Pyrometallurgical Process Revenues			
Cobalt	5,710	11.70	133.6
Nickel	2,990	3.29	19.7
Copper	120	0.65	0.2
Fe-Mn	195,000	0.30	117.0
Total Revenues	-	-	207.5
Costs	-	-	-291.0
Net Revenues	-	-	-20.5
Hydrometallurgical Process Revenues			
Cobalt	5,365	11.70	125.5
Nickel	2,900	3.29	19.1
Copper	420	0.65	0.5
Total Revenues	-	-	145.1
Costs	-	-	-204.0
Net Revenues	-	-	-58.9

From DOI-MMS [136]

Table 8. Value of metals in one metric ton of Fe-Mn crust from the central-equatorial Pacific

	Mean price of metal (1999 $/Kg)	Mean Content in Crusts (ppm)*	Value per Metric Ton of Ore ($)
Cobalt	39.60	6899	273.20
Titanium	7.70	12035	92.67
Cerium	28.00	1605	44.94
Zirconium	44.62	618	27.58
Nickel	6.60	4125	27.23
Platinum	13,024.00	0.489	6.37
Molybdenum	8.80	445	3.92
Tellurium	44.00	60	2.64
Copper	1.65	896	1.48
Total	--	--	480.03

**Mean of data in Table 6 for columns 2, 4, and 6; ppm is parts per million, which equals micrograms per gram and grams per ton*

However, it has recently been determined that Fe-Mn crusts contain metals other than manganese, cobalt, nickel, copper, and platinum that may offer additional incentive in recovery (*Table 8*). For example, titanium has the highest value after cobalt, the rare-earth elements (represented by cerium in *Table 8*) have a greater value than nickel, zirconium is equivalent to nickel, and tellurium has nearly twice the value of copper. Manganese is not shown in *Table 8* as it could be recovered in several different forms depending on demand. This analysis assumes that economic extractive metallurgy can be developed for each of those metals.

Outside of Japan, there has been limited research and development on mining technologies for Fe-Mn crusts and therefore current economic analyses are highly speculative. Despite these uncertainties, China has held discussions with the State of Hawaii about the possibility of placing a plant on the islands for the processing of iron-manganese oxide materials. Over the past decade, at least three companies have expressed interest in Fe-Mn crust mining, including the International Hard Minerals Company, Bluewater Marine, and Oceanx. In addition, the Republic of the Marshall Islands leased its EEZ for minerals exploration, primarily for cobalt-rich crusts. Several evolving circumstances may change the economic environment and promote mining in the oceans, for example land-use priorities, fresh-water issues, and environmental concerns in areas of mining on land.

Based on grade, tonnage, and oceanographic conditions, the central-equatorial Pacific region offers the best potential for Fe-Mn crust mining, particularly the EEZ of Johnston Island (USA), the Marshall Islands, and international waters in the Mid-Pacific Mountains, although the EEZs of French Polynesia, Kiribati, and the Federated States of Micronesia should also be considered. Adding political and international issues to that mix, the EEZ of the Marshall Islands likely offers the best potential for Fe-Mn crust mining in the future, and to date has been the region most extensively studied.

There is a growing recognition that cobalt-rich Fe-Mn crusts are an important potential resource. Accordingly, it is necessary to fill the information gap concerning various aspects of crust mining through research, exploration, and technology development.

6. RECOMMENDATIONS FOR RESEARCH

At the end of the 20th century, 20 years will have gone into studies of cobalt-rich Fe-Mn crusts. However, many questions remain to be answered and it is recommended that research in the 21st century should include:

- Detailed mapping of selected seamounts, including analysis of microtopography
- Development of better dating techniques for crusts
- Determining the oceanographic and geologic conditions that produce very thick crusts
- Determining what controls the concentration of PGEs and other rare elements in crusts
- Determining how much burial by sediment is required to inhibit crust growth; and to what extent crusts occur on seamounts under a thin blanket of sediment
- Determining the role of microbiota in the formation and growth of crusts
- Determining the extent and significance of organic complexing of metals that comprise crusts
- Studying currents, internal tides, and upwelling (physical oceanography) around seamounts
- Complete environmental and ecological studies of seamount communities
- Development of new mining technologies and processes of extractive metallurgy

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Appendix 1.: Key to symbols in Table 6

Element	Name	Element	Name
Fe	Iron	Se	Selenium
Mn	Manganese	Sn	Tin
Si	Silicon	Sr	Strontium
Na	Sodium	Te	Tellurium
Al	Aluminium	Tl	Thallium
K	Potassium	Th	Thorium
Mg	Magnesium	U	Uranium
Ca	Calcium	V	Vanadium
Ti	Titanium	W	Tungsten
P	Phosphorus	Y	Yttrium
S	Sulphur	Zn	Zinc
Cl	Chlorine	Zr	Zirconium
H_2O^+	Structural water	La	Lanthanum*
H_2O^-	Hygroscopic water	Ce	Cerium
CO_2	Carbon dioxide	Pr	Praseodymium
LOI	Loss On Ignition	Nd	Neodymium
Ag	Silver	Sm	Samarium
As	Arsenic	Eu	Europium
B	Boron	Gd	Gadolinium
Ba	Barium	Tb	Terbium
Be	Beryllium	Dy	Dysprosium
Bi	Bismuth	Ho	Holmium
Br	Bromine	Er	Erbium
Cd	Cadmium	Tm	Thulium
Co	Cobalt	Yb	Ytterbium
Cr	Chromium	Lu	Lutetium
Cu	Copper	Hg	Mercury
Ga	Gallium	Au	Gold
Hf	Hafnium	Ir	Iridium
Li	Lithium	Pd	Palladium
Mo	Molybdenum	Pt	Platinum
Nb	Niobium	Rh	Rhodium
Ni	Nickel	Ru	Ruthenium
Pb	Lead	Wt%	Weight percent
Rb	Rubidium	ppm	Parts per million
Sb	Antimony	ppb	Parts per billion
Sc	Scandium		

** La through Lu are rare-earth elements (REEs); Ir through Ru are platinum-group elements (PGEs); ppm = grams per ton*

Technical Requirements for the Exploration and Mining of Seafloor Massive Sulphide Deposits and Cobalt-Rich Ferromanganese Crusts

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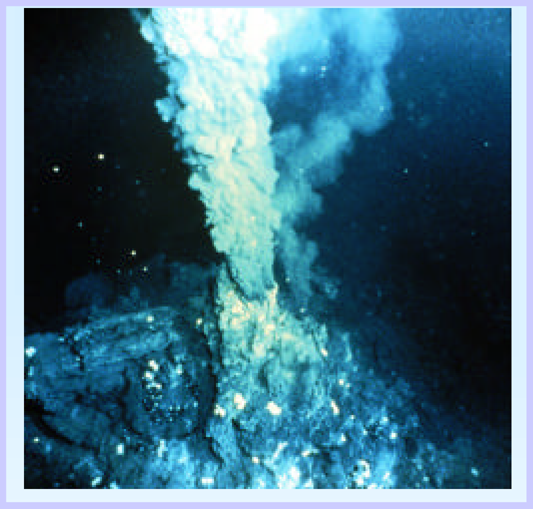

Technical Requirements for the Exploration and mining of Seafloor Massive Sulphide Deposits and Cobalt-rich Ferromanganese Crusts

During the past decade, marine mineral exploration programs have been significantly enhanced through the development and availability of state-of-the-art exploration tools and equipment. Today, multi-purpose research vessels with swath mapping capabilities, deep-towed camera and video systems, TV-guided grab samplers, as well as deep-diving submersibles and remotely operated vehicles (ROVs) are almost routinely used. A first order technical requirement for a new era of scientific research and resource assessment of polymetallic massive sulphide deposits is the availability of portable seafloor drilling and coring devices which can be deployed from a research vessel rather than a specifically designed drill ship. So far, most research results and resource assessments are based on surface samples only and thus are not sufficiently reliable. The development of mining systems for massive sulphide and precious metal deposits needs to focus on continuous recovery through rotating cutter heads and airlift of an ore slurry to the mining vessel. Recovery technologies for cobalt-rich ferromanganese including hydrojet and heavy-duty rollers need to be tested in order to demonstrate that the crusts can be efficiently separated from the substrate rock.

1. INTRODUCTION

Since the first discovery of black smokers, massive sulphides and vent biota in 1979[1], exploration of seafloor massive sulphide deposits at oceanic spreading centres is carried out by numerous academic and government institutions worldwide. Leading countries in this field are the United States, France, Germany, the United Kingdom, Japan, Canada, Russia, and Australia (cf., *Table 1*). In some countries, such as Portugal and Italy, marine exploration programs for massive sulphides have newly been developed over the past few years. Cobalt-rich ferromanganese crusts in the Pacific Ocean have been the focus of exploration and evaluation in the mid 1980s led by the United States, Germany, and Japan[2]. Technical developments of marine research and exploration equipment that paralleled geological research programs were critical factors in advancing scientific and resource-oriented studies of hydrothermal systems and cobalt crusts. Today, a large number of different tools and systems are available for the efficient search and evaluation of marine mineral deposits as a whole. State-of-the-art equipment includes modern multi-purpose research vessels with multibeam swath mapping systems and DGPS-navigation, side-scan sonar devices, deep-towed camera and video systems with on-line capability, TV-guided grabs for controlled large-scale geological sampling, shallow and deep-diving research submersibles, and remotely operated vehicles (ROVs). In the future, autonomous underwater vehicles (AUVs) will become available on a routine basis. Recently, a first generation of portable drilling and coring devices for shallow drilling at the seafloor has been developed but needs significant improvement with respect to drilling depth and core recovery in order to reveal reliable information on the third dimension of polymetallic massive sulphide deposits. Mining tools for massive sulphides so far have not been specifically designed but may be adopted from the offshore diamond mining industry. For cobalt-rich ferromanganese crusts, two different mining systems (hydrojet and roller) have been designed but not yet fully tested.

Table 1. Selected Research Programs for Seafloor Massive Sulphide Deposits 1980-2000

Program	Countries	Ocean Area
FAMOUS	France/USA	Mid-Atlantic Ridge
TAG	USA/France	Mid-Atlantic Ridge, 26°N
FARA	France/USA	Mid-Atlantic Ridge, Azores
DIVA	France/USA	Mid-Atlantic Ridge, Azores
BRIDGE	United Kingdom	Mid-Atlantic Ridge
CYAMEX	France/USA	East Pacific Rise, 21°N
GEOMETEP	Germany	East Pacific Rise, South
GARIMAS	Germany	Galapagos Rift, 86°W
HYDROTRACE	Germany/Canada	Juan de Fuca Ridge, Axial Seamount
VENTS	USA/Canada	Juan de Fuca Ridge
GEMINO	Germany	Central Indian Ridge
HIFIFLUX	Germany	Southwest Pacific, North Fiji Basin
STARMER	France/Japan	Southwest Pacific, North Fiji Basin
PACMANUS	Australia/Canada	Southwest Pacific, Manus Basin
PACLARK	Australia/Canada	Southwest Pacific, Woodlark Basin
NAUTILAU	France/Germany	Southwest Pacific, Lau Basin
EDISON	Germany/Canada	Southwest Pacific, Tabar-Feni Arc

2. EXPLORATION TOOLS AND SYSTEMS

Marine mineral exploration programs for massive sulphides and cobalt-rich ferromanganese crusts require state-of-the-art multi-purpose research vessels that allow time and cost efficient exploration of large areas. A prerequisite are permanently installed multibeam swath mapping systems (up to 121 beams) which are capable of mapping the seafloor down to several thousand meters depth. Modern systems are able to map a swath width of more than 3 times the water depth along the ships track. On-board computer processing usually produces a coloured or even 3D bathymetric map with down to 5 m contour intervals. In addition, ship-mounted sediment echosounder are being routinely used to determine the thickness and nature of the upper part of the sedimentary column, whereas seismic reflection surveys reveal information about the deeper part of the sedimentary pile. Side-scan sonar systems, which are towed behind the ship, obtain information about tectonic features at the seafloor. Gravity, magnetic, and heat flow surveys are also routinely run.

On-line real-time observation of the seafloor in the search for hydrothermal sulphides at oceanic spreading ridges or for cobalt-rich ferromanganese crusts at seamount flanks is achieved by using deep-towed camera-systems (rated up to 5.000 m depth) which are equipped with lamps and flashes in combination with high-resolution colour video cameras and still cameras for up to 700 colour slides. The data transfer from the seafloor to the ship is achieved via a fibre optic cable while the energy for cameras, lamps and flashes is transmitted via a co-axial cable.

Basic sampling devices include various corers (spade, piston and gravity corer) and dredges (barrel, box and chain-bag dredge) as well as free-fall grabs known from manganese nodule exploration. An excellent development is TV-guided grab systems (rated up to 5.000 m depth) for precise large-scale (up to about 3 tonnes) sampling of rocks, massive sulphides or cobalt crusts. Due to a high-resolution video camera and several lights mounted in the centre of the grab, the system can be used for small scale mapping of the seafloor as well as for sample selection and finally sampling. If the sample is not sufficient, the grab can be reopened and closed several times before the batteries are exhausted and need to be recharged. TV-grabs are usually also operated on a fibre optic cable to enhance the camera signal and to trigger the closing and opening mechanism of the grab. The power necessary to close and open the claws, however, is provided by deep-sea batteries.

For water sampling in the search for geochemical signals (methane, manganese, helium isotopes) of active hydrothermal vents, several CTD (conductivity-temperature-depth) and rosette sampler systems with up to 24 bottles are in use. Each bottle can be closed remotely at a certain water depth. Chemical analyses of the water samples are usually performed on board ship with only limited time delays. In recent years, geochemical scanner (e.g., SUAVE: NOAA/USA; ZAPS: Oregon State University/USA; ALCHEMIST: IFREMER/France) became available which are used in a towed mode and provide continuous (on-line) registration of various pathfinder elements for active hydrothermal vents. The advantage over conventional hydrocast surveys is obvious as large areas can be covered in a reconnaissance mode in relatively short periods of time.

3. SUBMERSIBLES AND ROVs

For detailed mapping of particular seafloor sites ("round truthing"), for precise small-scale sampling, and in particular for direct sampling of hydrothermal fluids at active black smoker chimneys, manned research submersibles and/or remotely operated vehicles (ROVs) are required. There are currently several research submersibles available (*Table 2*) that have operation depths of 400-6,500 m, which equals a pressure of 40-650 bar or 4-65 MPa. The various submersibles commonly accommodate two pilots and one scientist and are being launched from a mother ship. Individual dives last about 8-10 hours in total, however, dives up to more than 16 hours have been reported. Most submersibles are equipped with two 5 to 7-function manipulators for sampling and measurements. Remotely operated vehicles (ROVs) have several advantages over manned submersibles including (i) longer bottom time (up to a week and more), (ii) reduced cost, (iii) no risk for pilots and scientists. ROVs are equipped with camera/video systems, which transfer video images via fibre-optic cable onto the ship. This enables a larger group of scientists to participate in a dive and to discuss the selection of sampling locations etc. Similar to submersibles, ROVs are also fitted with two robot arms for manipulations at the seafloor. Currently, the Canadian ROPOS (Remotely Operated Platform for Ocean Sciences) operated by the Canadian Scientific Submersible Facility, the American JASON operated by Woods Hole Oceanographic Institution, and the French VICTOR operated by IFREMER, are leading in this field together with the Japanese KAIKO which has a maximum depth range of 11,000 m (*Table 2*)

Table 2. Research Submersibles and Remotely Operated Vehicles

Name	Organisation	Country	Depth Capability
NAUTILE	IFREMER	France	6,000 m
CYANA	IFREMER	France	3,000 m
MIR 1 & 2	Shirshov Institute	Russia	6,000 m
SHINKAI 6500	JAMSTEC	Japan	6,500 m
SHINKAI 2000	JAMSTEC	Japan	2,000 m
ALVIN	WHOI	USA	4,500 m
PISCES IV & V	SOEST	USA	2,000 m
PISCES	-	Russia	2,000 m
JAGO	MPI Seewiesen	Germany	400 m

ROPOS (ROV)	CSSF	Canada	6,000 m
JASON (ROV)	WHOI	USA	6,000 m
VICTOR (ROV)	IFREMER	France	6,000 m
ROBIN (ROV)	IFREMER	France	3,000 m
DOLPHIN 3K (ROV)	JAMSTEC	Japan	3,300 m
KAIKO (ROV)	JAMSTEC	Japan	11,000 m

4 SEAFLOOR DRILLING AND CORING DEVICES

Drilling of seafloor polymetallic sulphide deposits is essential to obtain samples and information from the interior of hydrothermal mounds and chimney complexes. The drilling vessel JOIDES RESOLUTION which is operated by the Ocean Drilling Program at Texas A&M University, USA, has already carried out scientific drilling at the Middle Valley sulphide deposit on the Juan de Fuca Ridge off-shore Canada during Legs 139 and 169 and the active TAG hydrothermal mound at the Mid-Atlantic Ridge 26°N (Leg 158). A further drilling leg is planned for 2000/2001 (Leg 193) in the eastern Manus Basin offshore Papua New Guinea to explore the third dimension of the Pacmanus hydrothermal field.

In addition to drilling vessels such as the JOIDES RESOLUTION, the first generation of portable seafloor drilling and coring systems is available including the PROD (Portable Remotely Operated Drill), which was jointly developed and constructed by an US-Australian group consisting of Benthic GeoTech Pty. Ltd., Williamson and Ass. Inc., and the University of Sydney. Performance specifications for PROD include a maximum penetration of 100 m at an operating depth of up to 2,000 m, a rock core diameter of 40 mm with individual core lengths of 2.2 m. So far, however, the drill has not yet been fully tested and longer cores have not been retrieved. A second drill, the BMS (Benthic Multicoring System) was built by Williamson and Ass. Inc. for the Metal Mining Agency of Japan (MMAJ) in 1996 and is presently installed on the research vessel Hakurei Maru No. 2. The BMS uses conventional diamond rotary-rock and soil sampling tools and can be operated from ships-of-opportunity at water depths of up to 6,000 m. Individual cores have a diameter of 44 mm at a maximum coring depth of 20 m. The system has been successfully used by the MMAJ to drill in the submarine caldera of Suiyo Seamount at the Izu-Bonin Arc down to a maximum depth of 9.8 m achieving a core recovery of 26%[3].

5. TECHNICAL REQUIREMENTS

For research and resource assessment of polymetallic massive sulphide deposits, technological advances are a critical factor. In the present state of research and commercialisation, information on the depth extent and therefore the size of the deposit and the type of mineralisation and alteration are extremely important. Drilling by the Ocean Drilling Program Leg 158 at the active TAG hydrothermal mound at the Mid-Atlantic Ridge[4] has indicated a total tonnage of 2.7 million tonnes of sulphide above and 1.2 million tonnes below the seafloor[5]. It was also found that high concentrations of base and precious metals are confined to the upper few metres of the mound, which basically consists of breccias with varying proportions of pyrite, silica, and anhydrite that would not be economically recoverable. Initially it was though that the mound entirely consists of polymetallic massive sulphides.

Except for the TAG mound, the Middle Valley site at the Juan de Fuca Ridge, and the Atlantis II Deep in the Red Sea, depth information is not available for any of the known seafloor sulphide deposits. Research and resource assessment of these deposits rely on surface samples only. As drilling of hydrothermal systems by the Ocean Drilling Program will be the exception rather than the rule, reliable portable drilling and coring devices are required for research and industry. It has to be demonstrated that these systems are actually capable of drilling and coring several tens of meters of massive sulphide and rock at the seafloor. The presently available technology is an encouraging start but needs to be further developed in order to make drilling at the seafloor to depths of 50-100 m a routine operation by any research vessel and to reveal reliable information on the depth extent of mound and chimney complexes.

After the resource potential has been adequately established by grid drilling similar to land-based operations, exploitation and recovery will be the next challenges. Selective mining using large TV-controlled grabs similar to those used for exploration are an option, however, continuous mining appears to be the only economic alternative. Continuous mining systems used by De Beers Marine offshore Namibia for the recovery of diamonds from water depths of about 100-150 m appear to be convertible to massive sulphide mining. These systems consist of large (7 m diameter) rotating cutter heads that are attached to a flexible drill string through which the diamond-bearing sediment is airlifted onto the ship where further processing takes place. The redesign of such a system for massive sulphides and/or altered gold-bearing rocks seems possible. A weight on head of several tens of tonnes controlled by the ships drill rig in combination with a heave compensator would allow to crush sulphides and altered rock in situ and to convert them to a slurry which can than be airlifted to the mining vessel from which the ore slurry would be transferred to a cargo freighter for transport to a processing plant. There is no question that the design and construction of suitable seafloor mining systems for polymetallic massive sulphides and gold-rich rocks are major tasks for research institutions and the off-shore industry which need to be met within the next few years.

6. PROCESSING TECHNOLOGIES

The physical properties of seafloor sulphide deposits are an important consideration for future evaluation of their mineability and the recoverability of their contained metals. The bulk dry density of sulphide chimneys, hydrothermal crusts, and sediments from the outer surface of the deposits are very low. Sulphide chimneys from East Pacific Rise 21°N have a dry density of only 1-2 gm/cm^3 and an in situ water content of 25-50%[6]. Higher densities due to compaction, open-space filling, and hydrothermal re-crystallisation of the sulphides can be expected in the interiors of the mounds. Most recovered samples are fine-grained, complex intergrowths of sulphide minerals and gangue (silica, barite, anhydrite). Their fine-grained nature is partly a consequence of the manner in which the sulphides are precipitated from the hydrothermal fluids. Rapid quenching of the solutions as they mix with seawater results in poor nucleation of minerals and limited growth of large crystals. Particle size analysis of sulphide chimneys from East Pacific Rise 21°N, crushed to their individual grains, shows that 93% of the material is in the 10 micron-to-1 millimetre range (silt-to-sand sized particles[7]). Analyses of samples from East Pacific Rise 11°N and Southern Explorer Ridge also indicate a range of grain sizes for pyrite, sphalerite and chalcopyrite from 1-600 microns with averages of 22-37 microns; 90-95% of the particles in the -400 mesh range (smaller than 37 microns) are free of interlocking[7]. Some degree of natural coarsening of the sulphides may occur in large deposits, where early-formed minerals are continuously re-crystallised by hydrothermal reworking.

The technology for treating fine-grained ores is poorly developed, and fine grinding of the kind required to liberate individual grains of pyrite, sphalerite, and chalcopyrite is energy intensive. Significant losses of the ultra-fine fraction (particles <10 microns in size) are commonly encountered in processing of fine-grained ores from land-based deposits. Some deposits are economic only because re-concentration of metals during structural deformation and thermal metamorphism has upgraded the ore and increased the grain size of the minerals of interest to a range amenable to processing. Flotation is the most important method in current use for the production of sulphide concentrates at base metal mines on land, but there are also serious limitations to the effectiveness of this technique in separating fine-grained particles (<10 microns). Ultra-fine particle flotation with seawater has been tested to produce a bulk sulphide concentrate from the Red Sea muds[8,9], but other novel methods of mineral processing may be warranted. Fine grinding and high inductance magnetic separation of seafloor massive sulphides has proved to yield a suitable copper and zinc concentrate with a recovery rate of 81%[7]. This technique could be used at sea to produce a pre-concentration that could be easily shipped to shore at reduced costs[10]. The complex polymetallic nature of the sulphides may require developments in extractive metallurgy before they could be adequately treated (e.g., hydrometallurgical processes such as oxidative pressure leaching).

Gold and silver are recovered as a casual by-product of base metal mining on land, most commonly during the smelting of copper, zinc, and lead concentrates. The recovery of silver depends largely on its mineralogical siting in the ore, usually as a trace constituent in galena, chalcopyrite, or sulphosalts such as tetrahedrite. Gold is recovered as free grains of native metal or electrum and usually reports to the copper concentrate during flotation. Current milling practices, however, recover only a fraction of the total contained gold in most massive sulphide ores (as little as 60% in some cases). This poor recovery is a consequence of the uniformly small grain size of gold particles (typically <10 microns) which are not adequately liberated by conventional methods of mineral processing. In primary (i.e., not oxidized, not re-crystallized) sulphides from the seafloor, coarse-grained gold has been documented in only a few deposits. The recovery of fine-grained gold from massive sulphides without compromising the recovery of copper and zinc and at a reasonable cost (determined by energy requirements for fine-grinding) represents a major challenge to mineral processors and metallurgists and will be an important consideration in the possible development of seafloor polymetallic sulphides as a precious metal resource

7. COBALT-BEARING FERROMANGANESE CRUSTS

In contrast to polymetallic massive sulphides, which mainly occur at or within volcanic rocks or sediments at oceanic rifts such as mid-ocean ridges and back-arc spreading centres, cobalt-bearing ferromanganese crusts form on the flanks of seamounts at water depths of 800-2,500 m and are growing on a substrate rock as a result of metal precipitation from cold ambient seawater close to the oxygen minimum zone[2]. Relative to ferromanganese nodules, the crusts contain elevated concentrations of Co (up to more than 2.0 wt.%) and Pt (up to 3 ppm). Research on cobalt-bearing ferromanganese crusts has largely been carried out in the 1980s by the United States, Germany and Japan[2]. It was found that economic grade crusts should be at least 4 cm thick and contain >1 wt.% Co on average[11]. The majority of the crust fields are found in the Exclusive Economic Zones of Micronesia, Marshall Islands, Kiribati, and the USA, as well as in international waters of the Central Pacific Mountains.

Mining of crust fields involves the efficient fragmentation and in situ separation of the crust from the substrate rock to avoid dilution of the crust metal grade, a problem which has still not been sufficiently resolved. However, hydrojet systems and heavy-duty roller combined with suction and hydraulic pipe lift or airlift devices have been designed but not yet fully tested. Any mining system to be developed needs to be capable of mining at least 1 million tonnes per year. This scenario allows for 80% separation efficiency and 25% dilution by substrate rock fragments[2]. As the interest in ferromanganese crust mining is currently relatively low, new technical developments of mining equipment such as advanced trench cutters have not taken place. This is also true for metallurgical processing which needs to focus on the efficient recovery not only of the cobalt but also of the platinum, which has been a major problem in the past.

8. CONCLUSIONS

First order technical requirements for polymetallic massive sulphide exploration include portable drilling and coring devices to be operated from ships-of-opportunity. These systems need to be capable of drilling several tens of meters into the seafloor with more than 50% core recovery. For mining of massive sulphides at and just below the seafloor, continuously operating devices with large-scale cutter heads in combination with airlift or hydraulic pumps need to be developed. Exploration tools for cobalt-bearing ferromanganese crusts such as deep-towed cameras, side-scan sonar, and TV-guided grabs are available. The problem of the efficient separation of the crusts from the substrate rock by suitable mining tools (hydrojet, rollers) has not been resolved and needs further consideration.

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Impact of the Development of Polymetallic Massive Sulphides on Deep-Sea Hydrothermal Vent Ecosystems

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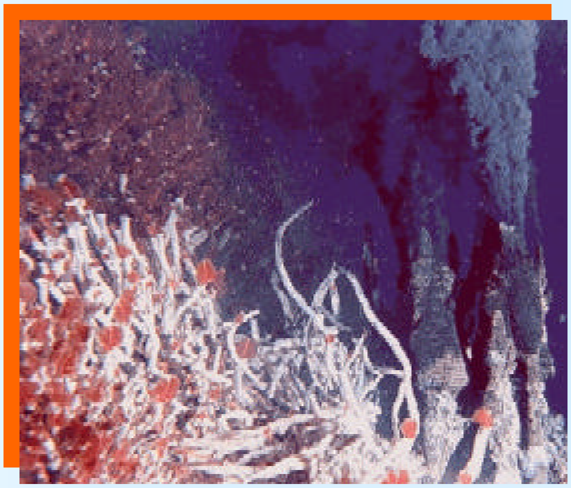

Impact of the Development of Seafloor Massive Sulphides on the Vent Ecosystem

The discovery of chemosynthetic-based ecosystems at hydrothermal vents in the deep ocean was arguably one of the most important biological findings of the 20th century. Nearly 500 new animal species have been described from this environment, most of which are endemic. Unusual, highly-evolved symbioses between invertebrates and chemolithoautotrophic bacteria are common at vents, and can produce concentrations of biomass that rival the most productive ecosystems on Earth. The abundance of ancient, extremophilic microbes in hydrothermal vent waters has stimulated new theories of the origin of life on Earth. It has also prompted astrobiologists to seriously consider underwater volcanoes as an likely source of energy for biosynthesis and maintenance of carbon-based life forms on other worlds. Hydrothermal vent science is now in its third decade of discovery. More than 100 vent fields have been documented along the 60,000km global mid-ocean ridge system. Species conservation and environmental stewardship are becoming issues of particular concern to vent scientists. Hydrothermal faunal communities occupy very small areas of the seafloor and many sites contain animal species found nowhere else. As vent sites become the focus of mineral exploration and deep-sea mining, oversight organisations will need to develop mitigative measures to avoid significant loss of habitat or extinction of populations. This paper will provide a brief overview of vent biology and ecology, and attempt to identify issues critical to the evaluation of the potential impact of mining operations on the productivity and biodiversity of vent communities.

1. INTRODUCTION

Plant life is impossible in the total darkness of the deep sea and food resources are consequently rare. Most deep-sea food chains are nourished by organic debris that sediments down from surface waters where phytoplankton carry out photosynthesis. Only a very small fraction (1% or less) of this surface productivity reaches the deep ocean floor. As a result, animal life is very scarce. The discovery of luxuriant oases of giant worms, clams and mussels clustering around hydrothermal vents >2000m deep came as a complete surprise to biologists who scrambled to identify the food source for this unusual ecosystem. Vent faunal biomass, measured as kg tissue/m^2, can be 500 to 1000 times that of the surrounding deep sea, and rivals values in the most productive marine ecosystems such as shellfish cultures[1]. Another surprise to biologists was the novel nature of the vent organisms, most previously unknown to science and many exhibiting unusual adaptations to the severe, potentially toxic nature of hydrothermal fluids. High animal density and the presence of unusual species are now known to be common characteristics of deep-sea hydrothermal vents all over the globe, with the composition of the fauna varying between sites and regions.

The presence of hydrogen sulphide in hydrothermal fluids and an abundance of sulphide-oxidizing bacteria were the first clues that led to the development of the hypothesis whereby biological productivity at hydrothermal vents is sustained not by photosynthetic products arriving from the sunlit surface ocean, but rather by the chemosynthesis of organic matter by vent microorganisms[2], using energy from chemical oxidations to produce organic matter from CO_2 and mineral nutrients. Hydrogen sulphide and other reducing substances present in hydrothermal fluids provide the 'fuel' for organic matter synthesis (*Fig.* 1). Since hydrothermal fluids are formed by reaction of seawater with hot rock, researchers quickly realized that vent ecosystems were ultimately powered by heat from the earth's mantle. This was a startling conceptual challenge to the long held view that all of our planet's ecosystems require sunlight and photosynthesis to create new biomass and nourish animal food chains.

Vent ecosystems are not completely independent of sunlight. All animals and many microorganisms at vents require dissolved oxygen for their metabolism (*Fig. 1*). Since dissolved oxygen in the world's oceans is a by-product of photosynthesis, there is a critical biogeochemical link between the vent ecosystems and the photosynthetic ecosystems in the upper layers of the sea and on land. Had photosynthesis not evolved on earth, hydrothermal vents would only be populated by micro-organisms that do not require dissolved oxygen - such as methanogens that derive energy for growth by converting hydrogen into methane using CO_2 as an oxidant.

2. VENT PRODUCTIVITY

At vent openings, local ecosystems are nourished by microbial growth that is coupled to the oxidation of H_2S, CH_4, H_2, Fe, Mn and other reducing substances. A recent thermodynamic modelling study[3] identifies hydrogen sulphide (H_2S) as the most important potential energy source for microbial growth in seafloor hydrothermal systems. Since both H_2S and dissolved oxygen are usually available in the mixing zone around vent openings, it is not surprising that the most visibly dominant forms of microbial growth around vent openings are dependent on hydrogen sulphide oxidation. What is unusual is the diversity of sources and locations of chemosynthetic activity within the hydrothermal system.

2.1 Symbiotic and free-living chemosynthesis

Seafloor vents

At vent openings, some chemosynthetic microorganisms live in symbiotic associations within the tissues of giant worms and bivalves[4], converting CO_2 into organic matter to nourish themselves and their hosts. Others grow freely as biofilms and filamentous mats on mineral and animal surfaces, providing food for grazing and deposit feeding animals. Predators and scavengers - some vent specialists, others attracted from the surrounding deep sea - complete the food web (*Fig. 2*). It is likely that at least some biological productivity from seafloor vents is exported to the surrounding deep sea through predation and advection of organic detritus but this food pathway remains unquantified (*Fig. 2*).

Other hydrothermal habitats

Microbial chemosynthesis also occurs in subsurface hydrothermal conduits[5], and in the plumes[6] that overlie vent fields, but faunal exploitation of microbial biomass produced in these two environments has not been extensively examined. Interaction between biological and geochemical processes has been most clearly documented in hydrothermal plumes. For example, recent studies show that oxidation of dissolved manganese in hydrothermal plumes is mostly microbially mediated[6,7]. High concentrations of zooplankton at the upper boundary of hydrothermal plumes in the northeast Pacific indicate that plume productivity may feed plankton food chains in the water column[8]; this remains to be quantified.

3. VENT ECOSYSTEMS

Mid-ocean ridges reveal an astonishing diversity of styles of seafloor spreading and associated geology and biology. One of the key variables that affect spreading style is the plate divergence rate: slow spreading ridges have very different characteristics from fast spreading ridges. Readers are referred to a theoretical paper[9] for detailed consideration of the relation between seafloor spreading rate, vent habitat frequency and vent faunal diversity. This section will briefly compare vent ecosystems on two parts of the ridge system that have formed the basis of much of our understanding: the East Pacific Rise (EPR), between 8° 30’ N and 13° 30’ N, which is spreading at approximately 100 mm/yr; and the Mid-Atlantic Ridge (MAR) between 33° N and 38° N, which is spreading at about a quarter of that rate.

3.1 EPR Vent Ecosystems

A schematic representation of the general appearance of vent ecosystems on the northern EPR is shown in Figure 3. More vent species are known from sites on the northern EPR than from any other spreading ridge on the planet. This may in part be due to the longer history of research in the area, but there are legitimate theoretical arguments that relate this greater biodiversity to the history of seafloor spreading and the abundance of vent habitat along the northern EPR[9,10]. Chemosynthetic microbial growth provides the primary production of biomass, and occurs in three distinctly different habitats: endosymbioses, ectosymbioses, and free-living on animal and mineral surfaces.

Endosymbioses

There are three general models for the functioning of the most common forms of host-symbiont associations at EPR vents: vestimentiferan worms, clams and mussels. Microbial symbionts directly nourish their hosts through lysis (digestion of symbionts within host cells) or through secretion of organic matter that is subsequently absorbed by host tissues[4].

Type 1 - The most evolved symbiosis occurs in the vestimentiferan tube worms - which have no mouth or digestive system, and are entirely reliant on their symbiotic bacteria for nutrition. In the tubeworms the symbiotic bacteria are housed in a specialized organ known as the trophosome. Substrates for microbial metabolism (HS^-, CO_2, O_2, etc) are taken up at the gills and transported to the trophosome by the worm's blood[4]. Physiological and biochemical aspects of this symbiosis have been extensively studied in the vestimentiferan *Riftia pachytila*[4].

Type 2 - Vesicomyid clams found at vent sites are filter-feeding animals, but their digestive tract is highly reduced and experiments have shown that they are unable to survive without a supply of hydrogen sulphide for their symbionts. They host their symbionts in the tissue of their large modified gills. CO_2 and O_2 diffuse directly into the gills from the external environment, while the clams take up H_2S into their blood through their foot, which they extend into fractures, or sediments where there is diffuse hydrothermal flow[4]. The large size attained by the giant vent clam *Calyptogena magnifica* attests to the productive nature of this symbiosis.

Type 3 - Like the clams, the EPR vent mussel *Bathymodiolus thermophylus* also houses its symbionts in gill tissue, is a filter feeder and has a functional digestive system. Unlike the clams, filtration of particles of organic matter from the surrounding water appears to provide a significant supplement to the mussel's nutrition. When experimentally moved away from active venting these mussels do survive, although considerable weight loss occurs. The mussel blood lacks specific proteins for the binding and transport of sulphide and oxygen that are found in the vestimentifera and clams[4].

Ectosymbioses

The EPR Pompeii worm *Alvinella pompejana* represented in *Figure* 3, has specialized structures on its dorsal surface that are colonised by a diverse community of bacteria, including large filamentous forms visible to the naked eye. While described as the most highly evolved epibiotic association among all marine invertebrates, the functional role of the Pompeii worm's bacteria remains uncertain. They may serve as a source of nutrition for the worm or in detoxifying the microenvironment within the worm's tube[11]. The worm does have a functional digestive system and exhibits deposit-feeding behaviour. Since at least some of the epibiotic bacteria are know to be chemosynthetic, and are probably sulphide oxidizers, they could both provide a supplementary food source for *A. pompejana* and act as a barrier against the diffusion of hydrogen sulphide into the worm's tissues.

Free-living microbial growth

Microorganisms can also grow abundantly on animal and mineral surfaces that are exposed to hydrothermal fluids[12,13]. Filamentous bacteria often produce dense aggregations that are visible to the naked eye as fluffy tufts and mats. These surface-growing bacteria are a potential food source for grazing and deposit-feeding animals such as snails, limpets and worms. These same microbial films can be detached from surfaces by turbulence, and either consumed by filter or suspension feeding animals around the vent or exported to the surrounding deep sea.

3.2 MAR vent ecosystems

The visually spectacular vestimentiferan tubeworms, the archetypal organisms of vents in the eastern Pacific, are conspicuously absent from known vent sites on the Mid-Atlantic Ridge. Reasons for this do not appear to be strictly related to the geographic separation of the Atlantic and Pacific oceans, since tubeworms are abundant at cold seeps in the Gulf of Mexico.

Endosymbioses

Only mussel endosymbioses are known from vents on the Mid-Atlantic Ridge. The mussels are similar to the EPR species although some have been found to harbour methane-oxidizing bacteria in their gills[14]. Other vent mussels from the MAR host a dual symbiosis, containing both sulphide oxidising and methane oxidising bacteria in their gills[15]. This is a highly unusual condition in multicellular animals.

Ectosymbioses

Swarms of shrimp bearing ectosymbiotic bacteria on their legs and in specialised branchial (gill) cavities occur on hydrothermally active sulphide deposits on the MAR.

Different shrimp species occupy different habitats and there are at least two distinctive forms of ectosymbionts. The ectosymbiosis is most prominent in *Rimicaris exoculata*, which has an enlarged gill chamber housing a dense flora of bacterial filaments[16]. Two other common MAR shrimp species, *Alvinocaris markensis* and *Chorocaris chacei*, also carry some bacterial filaments on their carapace and appendages but these associations are much less developed compared to *Rimicaris exoculata*[16]. As in the case of the EPR alvinellid worms, the nutritional or detoxifying roles of these ectosymbioses remain uncertain. All shrimp can be observed to actively feed on chimney surfaces, and guts of collected specimens usually contain abundant mineral particles[16]. In addition, the two larger shrimp species (*Alvinocaris markensis* and *Chorocaris chacei)* are listed among the predators of the smaller *Rimicaris exoculata*[17].

Free-Living Microbial Growth

As on the EPR, microorganisms grow abundantly on mineral surfaces that are exposed to hydrothermal fluids[18]. Filamentous bacteria often produce dense aggregations that are visible to the naked eye as fluffy tufts and mats. These bacteria are a potential food source for grazing and deposit-feeding animals.

4. GENE FLOW ALONG THE GLOBAL RIDGE SYSTEM

From the time of the first discovery of hydrothermal vent communities, biologists have been asking how vent animals manage to persist in this ephemeral and spatially discontinuous habitat. How are new vents colonized? Why do we find the same species at vents hundreds and thousands of km apart? Why do other species have very restricted distributions? These questions lead to a fundamental point about how genetic information is transmitted along the global ridge system. Most hydrothermal vent species colonize new sites by producing larvae that have some swimming ability but, as for most marine larvae, are primarily transported by ocean currents. If there are barriers to the movement of larvae between different areas of the ridge crest, their species compositions will eventually begin to differentiate as a result of natural mutations or local extinctions. If gene flow is maintained through the exchange of larvae, then the populations and assemblages of species will continue to resemble each other.

Part of the answer to questions about gene flow along ridges has come from sampling of vents around the world and comparing species inventories between geographic locations[19]. New techniques in molecular biology are also being applied to this problem, both to confirm differences between morphological species and to compare populations of the same species in order to quantify the rate of genetic exchange along the ridge axis. While published data are few and sampling of the global ridge system is still very incomplete, several interesting observations and hypotheses have emerged regarding the relationship between ridge crest processes and gene flow within the global vent fauna. First is a finding that species distribution along present day ridges is related to tectonic plate history. One model suggests that the global distribution of vent species and groups of species can be explained on the basis of a radiation away from an ancestral source on the mid-Tertiary ridges in the eastern Pacific. The entire global ridge fauna has ancestral ties to the eastern Pacific vent fauna, through shared species, genera and families, and can be seen as a subset of it since the greatest number of vent species is found on the northern EPR. When comparing the vent faunas of different regions, one study pointed out that taxonomic similarities reflect distance along the ridge system rather than shortest oceanic distance, implying a primarily along-ridge flow of genetic information[10]. These authors also showed that some present day relationships between vent faunas separated by major discontinuities in the global ridge system can be explained on the basis of past connections between ridges such as the northern EPR and the northeast Pacific ridges, and between the northeast Pacific ridges and the back-arc basins of the western Pacific[10].

At the scale of individual ridge systems, studies of the influence of distance and discontinuities on gene flow are indicating that high levels of long distance gene flow may be a pre-requisite for success of vent species. However, molecular work is also showing that the ability of species to move along and between segments can vary considerably. Eastern Pacific tube worms are very good at dispersing their genes along ridge axes although neighbouring populations are more similar than more distant ones, producing a quantifiable effect of along-axis geographic distance on gene flow[20,21]. Discontinuities between ridge axes can also have a measurable effect on gene flow, as has been shown by comparison of populations of the same species on either side of transform faults of different length. For the northeast Pacific tube worm, *Ridgeia piscesae*, no detectable genetic differentiation was found across the 160km offset between the Juan de Fuca and Explorer Ridges, while populations on either side of the 360km offset between the Juan de Fuca and Gorda Ridges had significant genetic differences[21]. Depth discontinuities may also act as a barrier to gene dispersal and confound interpretation of genetic differences between sites. Vertical mixing is limited in the deep sea so that water mass and larval transport tend to be horizontal. Mussel populations at the Snake Pit and Lucky Strike sites on the MAR show distinct genetic differences that may reflect their separation by transform faults but may also be influenced by depth differences between the two sites (3489m vs. 1650m)[22]. A clearer example of a likely depth effect is that of the amphipod crustacean *Ventiella sulfuris* in the eastern Pacific. The species shows low divergence along the EPR, even across the 240km Rivera Fracture Zone, while the 5000m deep, 50km wide Hess Deep between the Galapagos spreading centre and the EPR separates populations with major genetic differences[23].

5. RESPONSE TO PERTURBATIONS

Recent observations of the biological consequences of seafloor volcanic eruptions and the growth of hydrothermal sulphide chimneys and larger multi-chimney edifices provide new insight into the ability of vent communities to colonise newly-created habitat, to recover from major perturbations and to adapt to local-scale changes in habitat conditions.

5.1 Seafloor eruptions

Information on the effects of eruptions on vent fauna comes from time series observations at 9° 45' – 9° 52' N on the East Pacific Rise that followed the serendipitous discovery of a very new lava flow, and from similar studies on the Juan de Fuca and Gorda Ridges in the northeast Pacific. While the characteristics of the eruptions and the suites of observations made vary between sites, the post-eruptive periods have a number of consistent features that reveal the interconnection of magmatic, hydrothermal and biological processes.

Seafloor eruptions provoke rapid and significant changes in the location and style of venting. Widespread diffuse venting is usually observed soon after the event, with new vents being created in areas where there was no previous venting[24]. The biological consequences of this perturbation of the hydrothermal system are considerable. Existing vent communities can be destroyed by lava flows or as a result of the re-organization of hydrothermal venting. Both the 9° N and Coaxial eruptions initiated intense bursts of biological activity as organisms colonized new vents. Most immediate were blooms of free-living microorganisms. The ubiquity of microorganisms of most metabolic types in seawater and their ability to grow rapidly under favourable conditions result in their being the first life forms to exploit the new energy source. In the first few weeks after the eruptions, observers[24,25] reported the outpouring of particulate microbial material from the subsurface through "snowblower" vents and the massive accumulation of filamentous bacterial mats and flocculent microbial waste on the seafloor in areas of diffuse flow. The discharge of biogenic particulates from snowblower vents can be sustained for several months[24,25], suggesting continuous microbial production in the subsurface. Post-eruptive diffuse venting can initially be very widespread, supporting microbial growth over large areas of the seafloor. For example, following the 1993 Coaxial eruption there was a 21 ha. Zone of microbial growth on new lava flows[26].

Post-eruptive colonization or recolonisation by the vent fauna proceeds more slowly than the microbial response because most recruits must arrive as larvae that settle and grow into adult organisms. Some mobile predators and scavengers may recruit as adults from nearby hydrothermal sites if they survive the eruption[25]. Nevertheless, the rapidity with which faunal communities develop around new vents is astonishing. Within one year of the 9°N and Coaxial eruptions tube worm communities had appeared, requiring growth at several 10's of centimetres per year[24,27], the highest growth rates ever reported for multicellular animals. These observations bespeak the extent to which vent communities have adapted to exploit this ephemeral but energy-rich habitat through their capacities for reproduction, dispersal, colonization and growth. At Coaxial, one third of the regional pool of vent species had become established at the new vents within 2 years of the eruption[24].

5.2 Local habitat evolution

Active hydrothermal vents are extremely dynamic environments and studies of how vent communities respond to local environmental change provide an appreciation of their capacity to recover from human perturbation. Studies at 13°N on the East Pacific Rise and on the Juan de Fuca Ridge[28,29] found that alvinellid worms adapted quickly to sulphide chimney growth and were able to colonise new areas of chimney as they were formed. A more extensive, 4-year study of habitat and faunal community dynamics on a hydrothermal sulphide edifice on the Juan de Fuca Ridge showed that the composition of entire communities can be very plastic, shifting with fluid flow regimes at time scales of weeks to months[30]. These adaptations involve both recolonisation by more tolerant organisms where hydrothermal conditions become too severe for the previous community, as well as the progress colonisation of cooling surfaces by species less tolerant of severe conditions. All such observations contribute to an emerging picture of a fauna that is well adapted to the ever-changing habitat of active sulphide edifices. This capacity to keep up with environmental change is dependent on a ready supply of adults and larvae to recolonise disturbed or gradually changing surfaces.

6. POTENTIAL MINING IMPACTS

6.1 Nature of mining-related perturbations

Mining activities in the coming decades are likely to be concentrated in very limited areas where polymetallic sulphide deposits of commercial size are known to occur. At these locations, extracting ore will result in removal of the substratum and production of a particulate plume. Some organisms will be directly killed by mining machinery, while others nearby risk smothering by material settling from the particulate plume. Individuals surviving these perturbations would be subject to a radical change in habitat conditions with hard substrata being replaced by soft particulates settling from the mining plume. These particulates could also clog hydrothermal conduits, depriving established vent communities of their vital fluid supply. At sedimented hydrothermal sites, where much of the ore body lies within a sediment overburden, digging out the deposit would produce a much more extensive plume that could completely eradicate the local vent fauna.

6.2 Important biological considerations

The global hydrothermal vent fauna is one of the most unusually adapted assemblages of organisms found in the oceans, in terms of tolerance of extreme physico-chemical conditions and exploitation of chemosynthetic food sources. This high degree of uniqueness, together with the facts that most vent species do not occur outside of the hydrothermal environment and that many have restricted distributions along the global ridge system are important issues to be considered in developing strategies and regulations for the mining of seafloor polymetallic sulphide deposits. In contrast, microorganisms colonising hydrothermal sites are generally assumed to be drawn from a globally distributed gene pool and therefore little threatened by localised mining activities. The biogeography of marine microbes has been little studied and the present view of their global distribution may eventually change.

Studies of the rapid colonisation of new vents following seafloor eruptions demonstrate the ability of the vent communities to re-establish at a severely disturbed site, as long there are hydrothermal emissions to support microbial chemosynthesis. While time scales for the establishment of mature, multi-species communities remain uncertain, high biomass and faunal density levels are attained within a few years after eruptions. Observations of local shifting of vent species to adapt to changes in fluid flow reinforce this notion of resilience. While it may be tempting to apply the resilience argument to considerations of mining impact, it is important to point out that the mother populations that permit repopulation after perturbation are themselves particularly vulnerable to mining. There is some evidence that biodiversity within a given region is greatest at larger, longer-lived hydrothermal sites[9,31]. This is in keeping with what has been observed in other ecosystems on Earth. Long-lived 'mother populations' may be critical to the maintenance of vent species biodiversity within a region. These same long-lived hydrothermal sites are also the most likely locations for accumulation of large sulphide deposits and therefore will be prime targets for mining (see papers by P. Rona and P. Herzig, this volume). As well, many localised species many not have a nearby mother population or they may be unable to recolonise the altered substratum after mining. In the latter case, only the establishment of protected areas would prevent eradication of species.

Some large, seafloor polymetallic sulphide deposits are hydrothermally inactive and provide no habitat for a specialised vent fauna. There are some observations of the colonisation of inactive deposits by 'normal' deep-sea organisms. This would suggest that mining would pose little threat to the survival of individual species since its fauna is drawn from the surrounding deep sea. However, inactive sites have received little attention from biologists and more extensive sampling is required to establish that the nature of their fauna. Mining will effectively eliminate the habitat formed by extinct deposits, so it is important to confirm that they host only background deep-sea species.

Arguments for the conservation of vent species can be developed from the same sources that have led to the present global interest in the preservation of biodiversity. In addition, cutting edge biological science has become an important stakeholder in this resource and millions of research dollars are annually directed to laboratory and field studies of vent organisms. Vent biology, in its brief history, has made major contributions to the development of basic models of life processes. Most recent editions of university textbooks in biology and ecology now use examples from hydrothermal vents to illustrate points on symbiosis, detoxification, adaptation to extreme conditions and ecosystem function. The visually spectacular and extreme nature of vent communities also makes them popular subjects for the science media and science education sectors. Several of the world's leading natural history museums feature new exhibits on hydrothermal vents. While few of the novel species discovered at vents may be edible or of any immediate material value, any one may hold a priceless message of fundamental importance to basic science.

6.3 Development of guidelines and regulations

Any guidelines aimed at protection of vent species will require provision for site-specific issues such as whether mining will occur on active or inactive hydrothermal sites and the geographic range of the affected vent species. Standard criteria used in environmental assessment in other marine habitats will also have to be taken into account. These include:

i) *Characterisation of the type of disturbance* – in particular the destruction of the substratum and associated organisms, and the creation of particulate plumes that could bury or stress organisms in areas directly adjacent to mining activities.

ii) *Estimation of the percent loss of seafloor vent habitats* – most vent fields include several types of habitat that host different assemblages of organisms. Managing the impact of mining on individual species will thus require specific information on the fraction of individual types of habitat that remain undisturbed, as well as an estimation of the total disturbance

iii) *Identification of affected seafloor organisms* – this information is critical to evaluating the impact of mining activities on the survival of species. Species with a broad geographic range are less likely to be endangered by mining, which is expected to be very localised. On the other hand, sites containing species with restricted distribution will require more careful management to assure maintenance of biodiversity.

iv) *Dose-response characteristics of plume fallout* – many vent species are sessile or capable of little locomotion. Some feed by filtering particles from surrounding seawater. In both cases, the presence of particulate plumes or sediment fallout from adjacent mining could have adverse affects on their survival even if they are not directly disturbed by mineral extraction machinery. There is no published information on dose-response characteristics of vent organisms in relation to particulate plumes. Test or pilot mining operations would provide opportunities to conduct this type of study prior to full-scale mining operations. Such studies need not be site specific since much useful general information can be derived from monitoring burial of vent organisms or their food supply and particulate fouling of suspension feeders.

Development of management plans for individual mining sites will require baseline information on their biological characteristics. These include:

i) *Distribution of habitat within the affected area* – Hydrothermal emissions are often correlated with seafloor relief features. Sidescan or pencil-beam sonars provide detailed topographic information that can be used to develop a basemap. Submersible video surveys or digital photography can then be used for “ground truthing” sonar maps to relate relief and textural information to hydrothermal activity, occurrence of mineral deposits and presence/absence of visually distinct faunal assemblages.

ii) *Species composition and community structure* – complete information on species composition can only come from sampling. This information is vital to questions regarding the geographic range of the affected species. Since extensive sampling is costly and time-consuming, an approach that combines synoptic habitat mapping (see above) with targeted sampling will likely be the best strategy.

iii) *Basic biology of species* – key here is information concerning the feeding mode of individual species (i.e. how they will be affected by particulate plumes) and an understanding of their ability to recolonise a disturbed site (reproductive cycles, recolonisation potential).

There is no imminent threat to the entire global vent fauna from mining or any other human activity. Concentration of mining activities in areas such as the southwest Pacific back arc spreading centres will, however, produce local and even regional effects on vent organism abundance, to the point where the survival of some species could become an issue. The challenge to regulators, vent biologists and miners will be to use existing knowledge to develop strategies for managing these effects. A realistic overall goal for management could be the maintenance of biodiversity throughout the period of mineral extraction so that exploited sites could be repopulated. This may require managed protection of breeding populations within colonisable range of the affected site. Identification of a potential source of colonists for all affected species in nearby areas unaffected by mining operations would obviate the need for formal protection.

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