by Peter A. Rona

Marine minerals for the 21st century

Institute of Marine and Coastal Sciences and Department of Geological Sciences, Rutgers University, 71 Dudley Road, New Brunswick, New Jersey 08901-8521, USA; E-mail: rona@imcs.rutgers.edu

Nonfuel marine minerals are briefly surveyed in context of advances in our understanding of Earth processes and the United Nations Convention on the Law of the Sea framework for their development. Prior to the theory of plate tectonics ocean basins were considered passive containers for materials eroded from land that produced placer deposits of heavy metals, gemstones, and certain chemical precipitates (phosphorite). Plate tectonics recognized boundaries in ocean basins which became active sources for massive sulfide deposits and, in concert with continental sources, for manganese nodules and cobalt-rich ferromanganese crusts and associated chemosynthetic ecosystems. Considering the full spectrum of marine minerals, freshwater that can be extracted from seawater by desalination processes, is the most important because it is vital for life and depletion exceeds replenishment on land.

Introduction

At the new millennium utilization of marine minerals is accelerating and knowledge of new types of marine mineral resources is expanding with significant present and potential scientific and economic benefits. The utilization of marine minerals is driven by growing societal and industrial needs, which may be met by turning to the sea for materials that are in short supply, strategically vulnerable, environmentally sensitive to recover on land, or can be recovered more economically from the seafloor. Recognizing the resource potential of marine minerals, the United Nations Convention on the Law of the Sea (UNCLOS), which entered into force in 1994, divides the ocean into an Exclusive Economic Zone (EEZ) 200 nautical miles wide with resources under the jurisdiction of the adjacent coastal state, and an international Area beyond the 200 mile zone with mineral resources regulated by the International Seabed Authority as the "common heritage of mankind" (United Nations, 1997). The scientific definition of a mineral is a naturally occurring substance with a definite chemical composition and crystal structure. Energy resources including oil, gas, and gas hydrates do not fit this definition, but are treated as minerals by general usage. This paper presents a brief survey of nonfuel marine minerals in context of advances in our understanding of Earth processes and the UNCLOS framework for their development.

Marine minerals and earth processes

Our vision of marine mineral resources is expanding rapidly as our understanding of the Earth advances. Ocean basins were regarded as passive containers of the ocean until the advent of the theory of plate tectonics in the 1960's. According to the view of the ocean basins as

passive containers, marine metal and non-metal non-fuel mineral deposits were considered to be primarily derived by erosion of continental rocks and transported to the ocean by rivers in solid (sediment) or dissolved phases. This view adequately explains the marine minerals known at that time. These comprise placer deposits of various relatively dense metallic minerals and gemstones of terrigenous origin, that is, derived from erosion of continental rocks and mechanically transported, sorted, and concentrated by flowing water in offshore sediments (Table 1; Figure 1). River input is considered to be an adequate source of the dissolved chemicals that form manganese nodules and crusts, phosphorite, and other types of authigenic deposits precipitated from seawater (Table 1; Edmond et al., 1979).

The theory of plate tectonics changed our view of the ocean basins from passive sinks for material eroded from land to active sources of mineralization in addition to the land sources. Focus switched from erosional processes on land to tectonic and magmatic processes at plate boundaries (divergent and convergent), largely submerged beneath the oceans, as the loci of a global system of exchange of heat and chemicals between the mantle, crust and the oceans (Figure 2). The ocean basins are leaky as containers of the oceans because volcanic rocks of ocean crust are penetrated by fractures. Cold, dense, heavy seawater flows kilometers downward through the fractures and a mass approaching that of the ocean is assimilated into the mantle beneath much of the ocean basin (Meade and Jeanloz, 1991). However, where the cold, heavy seawater flows in proximity to magma upwelling at plate boundaries, the seawater is heated, expands, and the lighter fluid buoyantly rises. As the heated seawater rises, it dissolves and transports as chloride complexes metals that are present in low concentrations in the rocks through which it flows with a component contributed by magmatic fluids (Yang and Scott, 2000). The metals concentrated in the upwelling solutions link with sulfur primarily from seawater sulfate to precipitate as metallic sulfide deposits beneath and on the seafloor. The remaining high-temperature (up to 400°C), metal-rich solutions discharge at the seafloor and almost instantaneously precipitate the remaining metals that form the cloud of black metallic mineral particles of "black smokers" that may buoyantly rise up to hundreds of meters into the overlying water column. Marine minerals are now viewed as the product of both continental sources of material external to the ocean and sources at submerged plate boundaries internal to the ocean.

Marine minerals from continental sources

Metals

Numerous sites are known on continental shelves around the world where heavy minerals containing metals and non-metals are concentrated (Figure 1; Table 1), but of these only a small number are or have been actually mined. As noted, these materials are eroded from rocks exposed on land and transported by rivers to the ocean where they are concentrated by waves, tides and currents as placer deposits. With reference to metals, the outstanding resource is tin, which is dredged from shallow water (water depth less than 30 meters) under

Figure 1 Global distribution of marine mineral resources (Cronan, 1980; Rona, 1981; Lenoble, 1995; Cruickshank, 1998; Ghosh and Mukhopadhyay, 2000).

Table 1 Marine mineral resources

REGION	ORIGIN	MODE OF OCCURRENCE			
		Unconsolidated (mineral)	Consolidated	Fluid	Heat
Continental Margin (shelf, slope and rise)	Terrigenous (derived by erosion and weathering of rocks on land)	Non-metals:			
		Beach deposit: siliceous sand and gravel (quartz)			
		Placer deposit: diamond			
		Metals			
		Placer deposit: heavy mineral and native metal concentrates			
		Barium (barite, witherite)			
		Chromium (chromite)			
		Gold			
		Iron (hematite, magnetite, siderite)			
		Rare Earth Elements (monazite, basanite)			
		Tin (cassiterite)			
		Titanium (ilmenite, rutile)			
		Thorium (monazite)			
		Tungsten (scheelite, wolframite)			
		Zirconium (zircon)			
				Seawater solutes:	
				Salt (halite; sodium chloride)	
				Magnesium	
				Magnesium compounds	
				Bromine	
				Others	
				Bicarbonate	
				Boric acid	
				Calcium	
				Fluorite	
				Potassium	
				Strontium	
				Sulfate	
				Thorium	
	Biogenic (derived from organisms)	Beach deposit: Lime (calcite, aragonite) mud, sand shells			
		Precious coral			
		Pearl (primarily cultured)			
			Coal		
			Limestone		
			Gas hydrates (methane)		
	Authigenic (precipitated from seawater)		Sulfur (pure and as sulfate)		
				Petroleum (oil & gas)	
		Lime (calcite, aragonite), mud, sand shells			
		Beach or placer deposit: Iron sands (glaucinite)			
		Particulate deposit: Phosphorite (apatite, fluorapatite, etc.)	Solid layered deposit: phosphorite (apatite, fluorapatite, etc.)		
			Cobalt-rich ferromanganese crusts		
			Phosphorite		
			Potash		
	Diagenetic (produced by alteration of existing material)		Salt (halite; sodium chloride)		
			Sulfur (pure and as sulfate)		
		Particulate deposit: Phosphorite (apatite, fluorapatite, etc.)			
			Solid layered deposit: Phosphorite		

(continued)

REGION	ORIGIN	MODE OF OCCURRENCE			
		Unconsolidated (mineral)	Consolidated	Fluid	Heat
Continental Margin (shelf, slope and rise)	Volcanogenic (derived from volcanoes)		Lode and vein deposits (all elements)		
			Massive sulfide deposits (copper, iron, zinc, silver, gold)		
					Geothermal energy
				Water	
Ocean Basin	Meteoric (derived from the atmosphere)			Fresh water (desalination of seawater)	
	Biogenic (derived from organisms)			Petroleum (oil & gas)	
	Authigenic (accumulated from seawater)	Manganese nodules (manganese, iron, nickel, cobalt, copper)			
			Cobalt-rich ferromanganese crusts		
	Volcanogenic (derived from volcanoes)	Metalliferous sediments (manganese, iron, copper, lead, zinc, gold, silver)			
			Manganese encrustations		
			Polymetallic massive sulfides (copper, iron, zinc, silver, gold)		
			Nickel-platinum sulfides		
			Nickel-platinum sulfides		
			Chromium (chromite)		
			Sulfur (pure and as sulfate and sulfide)		
				Hydrothermal fluids (heat and metals)	
					Geothermal energy
				Water

Figure 2 World map showing plate boundaries, the 200 nautical mile (370 km) offshore zone extending from coastal states zone (dashed line around land; Office of the Geographer, 1978; McBryde, 1982), and sites at plate boundaries where some of the larger massive sulfide deposits have been found (Rona and Scott, 1993). Only a small percentage of prospective areas of the deep seafloor has been explored in sufficient detail to find such deposits. Numbers indicate locations where the divergent plate boundaries (ocean ridges) lie within the 200 nautical mile zone of a coastal state, as listed in Table 4.

calm coastal conditions at several sites offshore Thailand, Indonesia, and Myanmar. The tin mineral (cassiterite) was derived by erosion and fluvial transportation from Mesozoic continental granites (Lenoble et al., 1995; Yim, 2000). Other tin deposits off northeastern Tasmania, Queensland, southern China, and eastern England (Cornwall) have yet to be exploited. Gold-bearing sands and gravels have been intermittently (depending on the market price) dredged from shallow water (water depth less than 15 meters) at several sites subject to rough sea conditions primarily from buried fluvial channels offshore Alaska, New Zealand and the Philippines (Garnett, 2000a). Titanium (minerals ilmenite and rutile), zirconium (zircon), Rare Earth Elements (monazite), and the radioactive element thorium (monazite) have been recovered at several shallow water sites (water depth less than 5 m) offshore South Africa, Madagascar, and India (Lenoble et al., 1995). Chromium (chromite) is recovered at a shallow water site offshore Central Sulawesi island, Indonesia, and barium (barite) at a site offshore Alaska (Lenoble et al., 1995).

Non-metals

A viable industry with estimated annual production value of about US\$ 1 billion has developed exploring for and dredging diamond-bearing gravels on the continental shelf and upper slope offshore Namibia and South Africa in shallow water subject to rough sea states (exploration water depth to 400 meters; dredging water depth to 140 meters; Lenoble et al., 1995; Garnett, 2000b). The diamonds were eroded from kimberlites of Cretaceous age in southern Africa and transported hundreds of kilometers by river systems over the past 100 million years where they are concentrated in onshore paleobeaches and offshore drowned paleoriver channels and depressions in the bedrock/sediment interface (Garnett, 2000b). Diamond recovery has also been attempted at shallow water sites offshore northwestern Australia, Kalimantan, Indonesia, and Sierra Leone, West Africa.

The most widely recovered marine minerals are aggregates (sand and gravel) and water. Aggregates are dredged from beaches and shallow offshore bars at numerous sites worldwide for use in construction materials (concrete) and restoration of beaches for recreation and shore protection. Freshwater can be extracted from seawater by various desalination processes and exists in crystalline phase in the ice sheets of Antarctica and Greenland. Desalination is an energy intensive process, which is mainly being used in the oil-based economies of arid Middle Eastern maritime states. Desalination plants are spreading to other parts of the world. Another mineral with large potential is phosphorite for use in agricultural fertilizers. Phosphorite is precipitated from seawater primarily on present and past continental shelves where the easterly trade winds blow water offshore causing upwelling of deep water enriched in phosphorous (0 to 30 degrees North and South latitude). Present mining of phosphorite is from land deposits that were precipitated during past higher stands of sea level, but extensive untapped deposits exist on continental shelves of agriculture-intensive countries like India.

Marine minerals from ocean sources

Hydrothermal deposits: metalliferous sediments

The metalliferous sediments of the Atlantis II Deep in the northern Red Sea are not only the first hydrothermal deposit found at a divergent plate boundary in the ocean (Degens and Ross, 1969), but remain the most efficient ore-forming system and the largest such deposit found to date. The Atlantis II Deep is a trough roughly 10 km in diameter at a water depth of 2 km that lies on the divergent plate

Table 2 Resource potential of metalliferous sediments of the Atlantis II Deep of the Red Sea (Nawab, 2002; 1 metric ton = 1,000 kilograms)

Metal	Grade (weight percent; dry salt-free basis)	Weight (metric tons; dry salt-free basis)
Metalliferous sediments		89,500,000
Zn	2.06	1,838,000
Cu	0.45	402,000
Ag	38 grams/metric ton	3,432

boundary that rifted Africa from the Arabian peninsula about 10 x 10⁶ years ago and generated lithosphere at a slow full-spreading rate (2 cm/y) to account for the present width of the northern Red Sea (200 km). The ore-forming system entails downwelling of seawater through permeable ocean crust; an order of magnitude increase in salinity over normal seawater salinity (35 parts per thousand) by flow in proximity to marginal salt deposits up to kilometers in thickness that precipitated at an early stage in opening of the Red Sea when evaporation exceeded inflow through narrow shallow straits; heating by flow in proximity to axial magmatic intrusions; upwelling of the thermally expanded highly saline solutions; dissolution and transport of metals from the volcanic rocks and magmatic solutions as chloride complexes; ponding of the solutions by density stratification in the axial trough; and precipitation of metallic sulfides, oxides and hydroxides that settle to form layers of unconsolidated metalliferous sediments up to 30 m thick (Table 2). The Atlantis II Deep is the largest of a number of such troughs subsequently found along the axis of the northern Red Sea.

The Saudi-Sudanese Red Sea Commission oversees development of the Atlantis II Deep deposit located within the overlapping 200 nautical mile zones of these two coastal states (Mustafa, 1979). The Commission sponsored a pre-pilot mining test in 1979, which demonstrated the feasibility of using hydraulic dredging to recover the metalliferous sediments and shipboard flotation to separate out zinc, copper and silver. Estimated grades and tonnages based on statistical analysis of the composition of 605 cores are presented in Table 2 (Nawab, 2002). The fine size of the sediment will require modification of existing refining techniques. As seafloor spreading continues, the Red Sea may widen into an ocean like the Atlantic, and hydrothermal deposits may be aligned along flow lines of spreading depending on the persistence, periodicity, and position of axial hydrothermal activity (Rona, 1985). Deposits of metalliferous sediments like those forming in the Atlantis II Deep are expected to be present buried beneath sediments at sites along rifted continental margins of ocean basins that underwent a stage like the Red Sea early in their opening, like the Atlantic Ocean.

Hydrothermal deposits: massive sulfides and manganese deposits

Hydrothermal mineral deposits are a byproduct of the exchange of heat and chemicals between the lithosphere (upper mantle and crust) and ocean at divergent and convergent plate boundaries (Figure 2). However, seafloor hot springs and associated hydrothermal mineral deposits are highly localized at specific sites along plate boundaries where the right conditions exist. These conditions comprise magmatic intrusions connected to intersecting faults and fractures that drive the circulation of heated seawater through permeable pathways for the circulation of seawater to produce hot springs. Exothermic reactions produced by hydration of ultramafic rocks of the upper mantle (serpentinization reaction in peridotites) also can generate heat to drive seafloor hydrothermal systems (Fyfe and Lonsdale, 1981; Lowell and Rona, 2002). At divergent plate boundaries like the ocean ridge system of the slow-spreading Atlantic, Indian and Arctic oceans (full-rate 4 cm/y) and the intermediate- to fast-spreading ridges of the Pacific (> 4 to 18 cm/y) active sites generally occur at or within kilometers of the spreading axis and at spacings of tens of kilometers along axis, but most of the deposits are small (Rona and Scott, 1993).

Figure 3 A diagrammatic east-west cross-section of the Pacific Ocean between South America and eastern Asia shows the relation of potential mineral and energy resources to submerged divergent (East Pacific Rise) and convergent (Pacific margins) plate boundaries (Rona, 1983). Metal deposits concentrated by hydrothermal processes metal may occur at sites in ocean crust (black layer) and by magmatic processes in the upper mantle underlying the crust.

At convergent plate boundaries with volcanic island arcs, as in the western Pacific, the settings most favorable for the formation of massive sulfide deposits and associated manganese deposits are calderas of seafloor volcanoes in the fore-arc region and spreading axes in the back-arc basins (Figure 3). At convergent plate boundaries without volcanic island arcs, the deposits are concentrated in volcanic mountain ranges on land, like the Andes in western South America (Figure 3). Regardless of setting, seafloor hydrothermal fields are generally small, with diameters up to several hundred meters. Massive sulfides containing iron, copper, zinc, silver and gold in variable concentrations (also known as polymetallic massive sulfides; since all massive sulfides contain multiple metals, it is redundant to use the term "polymetallic") are precipitated beneath and on the seafloor where high-temperature hot springs discharge through mineralized chimneys. The term "massive sulfide" refers to metallic sulfide content (> 60 percent; Sangster and Scott, 1976) independent of texture, size and shape of the deposit. Deposits of relatively pure manganese oxide (c. 50 percent manganese by weight) may accumulate at warm springs (tens of degrees Celsius) peripheral to the hot springs. Once formed at a spreading axis, massive sulfide and manganese deposits may be destroyed by faulting and mass wasting or, may be carried away from the axis on diverging conveyor belts of spreading lithosphere and buried beneath lava flows and sediment.

The black smoker chimneys discharging high-temperature solutions are the surface expression of subseafloor hydrothermal systems. The TAG hydrothermal field, located at water depths up to 3,700 m in the rift valley of the Mid-Atlantic Ridge near 26°N (latitude of Miami, Florida), 45°W, is a good example to illustrate such a system, because it is the best studied and largest seafloor ore-forming hydrothermal system known (Figure 4; Rona et al., 1986; 1993). A cluster of black smokers discharges from the top of one of several mounds each the size and shape of the athletic stadium, the Houston Astrodome (200 meters diameter; 40 meters high), and composed primarily of massive sulfides (Figure 4). The subseafloor dimension was revealed by a suite of holes drilled into this active mound in 1994 by the drillship JOIDES RESOLUTION of the Ocean Drilling Program (ODP), a government-sponsored consortium of 20 nations. Partial cores (overall recovery 12 percent) recovered from 17 drill-holes up to 125 m below the seafloor revealed that the three-dimensional shape of the mound is that of a lens composed primarily of massive sulfides underlain by a stem-shaped feeder or stockwork zone where the hot solutions are welling up and replacing the volcanic rocks of the ocean crust (Figure 4; Humphris et al., 1995).

The size of the mound-stockwork complex is about 4 million metric tonnes composed primarily of iron sulfide (pyrite). A long history of reworking by circulation of hydrothermal solutions through the mound has dissolved certain metals (Cu, Zn, Ag, Au, Sb and other trace elements) from the interior and concentrated them in the

upper 5 m of the deposit by the process of zone refining (Hannington et al., 1998). Radiometric dating of mound material reveals that it takes tens of thousands of years to form a sizable massive sulfide deposit, although the actual process is episodic with multiple relatively short intervals of deposition and sustained circulation that cumulatively build a large massive sulfide body and concentrate the economically interesting metals over the total age of the deposit (Lalou et al., 1995; You and Bickle, 1998; Hannington et al., 1998). Patchy, layered deposits of exceptionally pure manganese oxide (c. 52 weight percent manganese) as old as the massive sulfides are continuing to accumulate from warm springs along normal faults in the wall of the rift valley between 2 and 4 km upslope from the active high-temperature sulfide mound (Rona et al., 1993).

As noted, hydrothermal processes of concentration of massive sulfide and manganese deposits are similar at both divergent and

Figure 4 A schematic section through the TAG active massive sulfide mound based on drilling by the Ocean Drilling Program to show characteristic surface and subsurface features of a seafloor massive sulfide deposit based on drilling of the mound by the Ocean Drilling Program (Rona, 1992; Humphris et al., 1995). A massive sulfide mound the size and shape of the sports stadium, the Houston Astrodome, is underlain by a feeder/stockwork zone produced by the upflow of hot, buoyant, metal-rich solutions which discharge into the ocean as black smokers near the center of the mound. Radiometrically measured ages on massive sulfide samples recovered in cores from the drill holes range up to 37,000 years old (Lalou et al., 1998; You and Bickle, 1998).

Table 3 Composition of seafloor polymetallic massive sulfide deposits (Herzig and Hannington,

Microbes and hydrothermal mineral deposits

Chemosynthetic microbes use chemical energy derived primarily by oxidation of hydrogen sulfide dissolved in high-temperature hydrothermal solutions to combine carbon, hydrogen and oxygen from seawater into carbohydrates (sugars and starches) as their nutrients. The microbes, in turn, lie at the base of

Element	Mid-Ocean Ridges at Divergent Plate Boundaries	Volcanic Island Chains at Convergent Plate Boundaries (range of composition)
Lead (weight percent)	0.1	0.4 - 11.8
Iron	26.4	6.2 - 13
Zinc	8.5	16.5 - 20.2
Copper	4.8	3.3 - 4.0
Barium	1.8	7.2 - 12.6
Arsenic (parts per million)	235	845 - 17,500
Antimony	46	106 - 6,710
Silver	113	217 - 2,304
Gold	1.2	4.5 - 3.1
Number of samples analyzed	1,259	613

convergent plate boundaries. Massive sulfide deposits associated with settings at convergent boundary settings are enriched in metals relative to sites at mid-ocean ridges (Table 3; Herzig and Hannington, 1995). Examples of massive sulfide deposits in these settings at the front and back sides of volcanic island chains are, respectively: 1) the Sunrise deposit in the caldera of an active seafloor volcano in the forearc side of the Izu-Ogasawara Arc south of Japan (Iizasa et al., 1999); also, the crater of a volcanic seamount (Conical Seamount; water depth 1050 m) in the fore-arc region on the northeast side of New Ireland (Figure 5) is considered prospective because it contains hydrothermal minerals with gold content (43 ppm) comparable to commercial gold deposits on a neighboring island (Lihir island; Herzig and Hannington, 2000) and is relatively accessible and; 2) the PACMANUS hydrothermal field in the Manus back arc basin on the north side of Papua New Guinea (Binns and Scott, 1993). An Australian mining company (Nautilus Minerals Corporation) has leased two sites in this field (water depth c. 1700 m) within territorial waters of Papua New Guinea from that government to evaluate for mining (Figure 5; Broad, 1997). Convergent plate boundaries in the western Pacific generally lie within the 200 mile zones of adjacent coastal states and, in certain cases, the 200 mile zones overlap between adjacent coastal states. In contrast, over 80 percent of the length of divergent plate boundaries with the potential for the occurrence of massive sulfide and associated manganese deposits lies in the international seabed area with exceptions shown in Figure 2 and listed in Table 4 (Rona et al., 1983).

Figure 5 Map showing the location of two areas (water depth 1500 to 2500 m) covered by an exploration license for seafloor massive sulfide deposits from the Papua New Guinea government to an Australian mining company in the Manus back-arc basin southwest of New Ireland. The crater of a volcanic seamount (Conical Seamount; water depth 1050 m) in the fore-arc region on the northeast side of New Ireland contains hydrothermal minerals with gold content (43 ppm) comparable to commercial gold deposits on a neighboring island (Lihir; Herzig and Hannington, 2000).

the food chain in vent ecosystems (Jannasch, 1995). These microbes are hosted in the massive sulfide and basaltic rocks of seafloor hydrothermal systems (Deming and Baross, 1993). The microbes are of value to science and to industry. Analysis of their genome indicates that certain of the heat-loving microbes (thermophiles; Archaea and Bacteria) are at the base of the tree of life and their study may elucidate the origin of life. Enzymes found in certain of these microbes are already employed to replicate DNA for forensic and other genetic "fingerprinting" purposes (polymerase chain reaction); for high-temperature -pressure industrial processes such as enhancing flow in deep oil wells; and for bioactive compounds with potential for pharmaceuticals applicable to cancer and other diseases.

Magmatic deposits

The massive sulfide and manganese deposits precipitated from relatively high-and low-temperature hot springs, respectively, occur primarily in the volcanic rocks of the ocean crust. The metallic mineral potential of the upper mantle underlying the ocean crust are poorly known because of limited exposures of these deeper rocks in the ocean (Figure 6). However, the types of deposits that occur in the oceanic upper mantle are known from outcrops exposed in slices of ocean lithosphere that have been thrust and uplifted onto land (Nicolas, 1995). These types of deposits include podiform chromite and nickel- and platinum- group element-rich sulfide mineral phases of magmatic origin (Naldrett, 1989). The discovery of magmatic mineral deposits in mantle rocks exposed on the seafloor is anticipated.

Figure 6 Schematic block diagram showing potential occurrence of metal deposits in ocean crust (shaded) and the underlying upper mantle formed at a divergent plate boundary (modified from Bonatti, 1981 and Rona, 1983).

Table 4 Submerged divergent plate boundaries (ocean ridges) within 200 nautical miles (370 km) of land (location identified by number in Figure 2; Rona, 1983)

Location	Ocean	Oceanic Ridge	Land	Country
1	Greenland Sea-Norwegian Sea	Mohns Ridge	Svalbard Islands Jan Mayan Island	Norway Norway
2	Greenland Sea-Norwegian Sea	Iceland-Jan Mayan Ridge	Jan Mayan Island Greenland Iceland	Norway Denmark Iceland
3	Greenland Sea-Norwegian Sea	Kolbeinsey Ridge	Iceland	Iceland
4	North Atlantic	Reykjanes Ridge	Iceland	Iceland
5	North Atlantic	Mid-Atlantic Ridge	Azores Islands	Portugal
6	Caribbean Sea	Cayman Spreading Center	Cayman Islands Swan Island	Jamaica Honduras
7	Equatorial Atlantic	Mid-Atlantic Ridge	St. Peter and St. Paul Rocks	Brazil
8	South Atlantic	Mid-Atlantic Ridge	Ascension Island	United Kingdom
9	South Atlantic	Mid-Atlantic Ridge	Tristan de Cunha Gough Island	United Kingdom United Kingdom
10	South Atlantic	Mid-Atlantic Ridge	Bouvet Island	Norway
11	South Atlantic-Scotia Sea	Scotia Spreading Center	South Sandwich Islands	United Kingdom
12	Indian Ocean	South-West Indian Ridge	Prince Edward Islands; Marion Island	Republic of South Africa
13	Indian Ocean	Carlsberg Ridge	Chagos Archipelago	United Kingdom
14	Indian Ocean	Gulf of Aden Spreading Center	Democratic Republic of Yemen	Democratic Republic of Yemen
15	Red Sea	Red Sea Spreading Center	Yemen Saudi Arabia Ethiopia Sudan Egypt	Yemen Saudi Arabia Ethiopia Sudan Egypt
16	Indian Ocean	South-East Indian Ridge	Amsterdam Island St. Paul Island	France France
17	Antarctic Ocean	Pacific-Antarctic Rise	Antarctica Antarctica	Australian Claim New Zealand Claim
18	Pacific Ocean	Chile rise	Chile	Chile
19	Pacific Ocean	East Pacific Rise	Easter Island	Chile
20	Pacific Ocean	Galapagos Spreading Center	Galapagos Islands	Ecuador
21	Pacific Ocean	East Pacific Rise	Mexico	Mexico
22	Pacific Ocean	Gulf of California Spreading Center	Baja California	Mexico
23	Pacific Ocean	Gorda Ridge	Oregon, California	USA
24	Pacific Ocean	Juan de Fuca Ridge	British Columbia	Canada
25	Pacific Ocean	Endeavour Segment	British Columbia	Canada
26	Pacific Ocean	Explorer Ridge	British Columbia	Canada

Marine minerals from combined continental and deep ocean sources

Manganese nodules

Manganese nodules have been the signature mineral of the deep ocean ever since John Mero published his book, "The Mineral Resources of the Sea", (Mero, 1965). Mero's high estimates of the in situ value of the suite of metals contained in manganese nodules without accounting for the substantial costs of recovery and refining created a "gold rush" mentality at that time, which contributed to drive the development of the UN Convention on the Law of the Sea (UNCLOS). The golf- to tennis ball-sized nodules lie on and in sediment on vast expanses of the abyssal plains that cover some 80 percent of the ocean basin at typical water depths of about 5 km (Figure 1). The portion of the nodules that protrudes above the surface of the seafloor sediment is precipitated from metals dissolved in seawater (authigenic or hydrogenous origin; Table 1), while the underside of the nodules accumulates from metals dissolved in the pore water of the sediment (diagenetic process) over millions of years (Cronan,

1980). The metals come from two sources. As noted, manganese and other metals are dissolved by weathering of rocks on continents and transported into the ocean by rivers. At the same time hot springs at sites along submerged plate boundaries discharge an equivalent amount of manganese and variable amounts of other dissolved metals into the ocean (Edmond et al. 1979). The result is a mixture of copper, nickel, manganese, cobalt and iron in the nodules that varies in different regions of the ocean related to proximity to sources and to concentration processes (Table 5).

The most prospective regions for the future recovery of manganese nodules based on metal content (combined Ni, Cu, and Co content >2.5 percent and an abundance on the seafloor >10 kg/m²) are the international Area between the Clarion and Clipperton fracture zones in the eastern equatorial Pacific between the Hawaiian islands and Central America and the Central Indian Ocean (Glasby, 2000). The International Seabed Authority (ISA) has licensed tracts within the Pacific Area to national government organizations (Russia, Japan, France, P.R. China, South Korea) and several industrial consortia designated pioneer investors and exploration contract holders for future nodule mining (International Seabed Authority, 1999).

Table 5 Average concentration of metals in manganese nodules from different oceans (Ghosh and Mukhopadhyay, 2000)

Element	Atlantic	Pacific	Indian	World Oceans
Manganese (weight percent)	13.25	20.10	15.25	18.60
Iron	16.97	11.40	14.23	12.40
Nickel	0.32	0.76	0.43	0.66
Copper	0.13	0.54	0.25	0.45
Cobalt	0.27	0.27	0.21	0.27
Zinc	0.12	0.16	0.15	0.12
Lead	0.14	0.08	0.10	0.09
Iridium	9.32	6.64	3.48	-
Uranium	7.4	7.68	6.20	-
Palladium (parts per million)	5.11	72	8.76	-
Thorium	55.00	32.06	40.75	-
Gold (parts per billion)	14.82	3.27	3.59	-

Cobalt-rich ferromanganese crusts

Cobalt-rich ferromanganese crusts of the deep ocean precipitate slowly over millions of years from metals dissolved in seawater derived from both chemical erosion of continents and discharge of seafloor hot springs (Hein, 1999) like manganese nodules. The metals comprise cobalt, nickel, platinum, and titanium in addition to iron and manganese depending on proximity to different sources (Table 6). These metals accumulate in crusts up to about 25 cm thick on volcanic substrates of seamounts and ocean ridges between ocean depths of 400 and 4000 meters. The most favorable setting for the occurrence of these crusts lies within and beyond the 200 nautical mile zones of the island nations of the western Pacific where extensive volcanic substrates exist. It is estimated that a single mine site on a seamount could complement land production to provide up to 25 percent of the annual global need for cobalt (Mangini, 1987; Hein, 2000). Recovery of these crusts is more challenging than manganese nodules, that lie loose on sediment, or massive sulfides, that form compact mounds, because the thin crusts are difficult to remove from the large areas of hard rock substrate to which they adhere.

Environmental considerations

Environmental regulations for marine exploration and mining are at an early stage of formulation and require understanding of ecosystems in different seafloor settings (Thiel et al., 1997). Observations of the nature of marine organisms to be considered in these settings include the following:

Ocean exclusive of hot springs:

Marine species diversity in the ocean is comparable to that in tropical rainforests (May, 1994).

The species diversity of marine life is so high that an investigation found new species in every square meter of seafloor sediment sampled (Grassle and Maciolek, 1992).

Deep ocean hot springs at massive sulfide deposits:

Table 6 Range of mean concentration of metals in cobalt-rich ferromanganese crusts from the Pacific, Atlantic and the Indian oceans (Hein, 2000).

Iron (weight percent)	15.1 - 22.9
Manganese	13.5 - 26.3
Nickel (parts per million)	3,255 - 5,716
Copper	713 - 1,075
Cobalt	3,006 - 7,888
Zinc	512 - 864
Barium	1,494 - 4,085
Molybdenum	334 - 569
Strontium	1,066 - 1,848
Cerium	696 - 1,684

Large biodiversity on the highest taxonomic level (phylum); smaller but significant biodiversity on lower taxonomic levels (Tunnicliffe et al., 1998).

Every seafloor hydrothermal field examined to date has some species that are not found in any other field (Tunnicliffe et al., 1998).

Microbes that are hosted in massive sulfides and associated hot springs have great scientific, medical, and industrial value.

Conclusions: perspective on marine minerals

Our brief survey of marine minerals may be placed in perspective, as follows:

Placer deposits: The profitable mining of tin off southeast Asia and of diamonds off southwest Africa is literally only scratching the surface in terms of the potential that exists for heavy metals and gemstones in sediments of continental margins.

Phosphorites: Extensive deposits on continental shelves in past and present areas of oceanic upwelling in low latitudes constitute an untapped resource most accessible to developing countries that can fertilize agricultural crops as land deposits dwindle.

Aggregates: Sand and gravel are the most widely utilized and accessible of marine mineral resources with growing needs for construction materials, shore protection, and beach replenishment.

Water: The need for a reliable and adequate source of fresh water for consumption and agriculture in light of depletion by population growth, industrialization and climate change is considered to be the most pressing environmental problem for humankind (Revenga et al., 2000). The ocean is by far the largest reservoir on Earth contingent on development of cost-effective desalination processes.

Metalliferous sediments: The Atlantis II zinc-silver-copper metalliferous sediment deposit of the Red Sea is the only seafloor hydrothermal deposit in which grade and tonnage are known anywhere near to mining standards on land. Legally its recovery rests with the bordering coastal states that share the intervening 200 mile zone; a pilot mining test has been proposed that should address the issue of refining the fine-grained material. Initiation of commercial mining is subject to market forces. The metalliferous sediments of the Atlantis II Deep represent a type of deposit that should be present at sites buried under sediments of Atlantic and other rifted passive continental margins.

Massive sulfides: The immediate significance of massive sulfides concentrated by high-temperature hydrothermal systems at plate boundaries is as analogs to guide economic geologists in the search for and mining of ancient VMS (Volcanogenic Massive Sulfide) deposits that formed at similar seafloor settings in the geologic past and have subsequently been uplifted onto land. A surge of discovery of these VMS deposits on land in P.R. China (Rona and Hou,

1999) and other places is attributable to insights gained from the actual submarine ore-forming systems. The mining of seafloor massive sulfide deposits is likely to start at fore- and back-arc settings of volcanic island arcs within the 200 mile zone of coastal states of the western Pacific before those deposits on ocean ridges in the international Area. Present technical limitations on drilling to adequately determine grade and tonnage will have to be overcome and favorable market conditions relative to land sources must evolve. While individual min-

eralized chimneys have been observed to grow quickly (days to years), seafloor massive sulfide deposits as a whole are not renewable resources because they require thousands of years to accumulate prospective grade and tonnage. Furthermore, directly tapping the discharging metal-rich solutions would result in accumulating iron and little else.

Manganese nodules: The players are positioned with the International Seabed Authority in the richest international zone (nickel and copper content >2.5 weight percent) in the eastern equatorial Pacific. A strategic need and/or favorable market conditions relative to presently adequate land sources of these metals are conditions necessary to drive the considerable investment required to support production.

Cobalt-rich ferromanganese crusts: Cobalt is considered to be the potential driver, but the prospect of recovery and refining from a hard-rock substrate adds an extra challenge.

Economics: A lesson learned from manganese nodules that applies to all mineral deposits is that in-situ mineral resources are useless economically; the mineral deposits must be found, assessed, recovered, refined, and competitively marketed before they are economic assets.

Microbes: The present harvesting and utilization of this unanticipated living resource, which is hosted in the massive sulfide deposits and substrate of subseafloor hydrothermal systems, is presently outside the legal framework of UNCLOS. This situation is described as "the deepest of ironies" (Glowka, 1996). It raises pressing issues for development and implementation of codes for marine exploration and mining that will conserve the integrated living and non-living resource systems.

Placing these diverse mineral and microbial resources in perspective, the marine mineral that is most universally needed for survival of life and is most threatened on Earth is the fresh water that can be extracted from our oceans. This reinforces the importance to maintain clean oceans and to develop reasonable energy sources for desalination.

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Dr. Peter Rona served as senior research geophysicist with the U.S. National Oceanic and Atmospheric Administration (NOAA) before joining Rutgers University in 1994 as Professor of Marine Geology and Geophysics. He is a pioneer in investigation of seafloor hydrothermal systems and led the discovery of the first hot springs, mineral deposits, and vent animals in the deep Atlantic Ocean, as well as discoveries in the Pacific. He has organized and directed numerous multi-institutional, international, interdisciplinary projects investigating continental margins and ocean ridges in all the major ocean basins. He serves as a consultant to the United Nations on marine mineral resources and is actively involved in developing science centers for public education.

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Dipartimento di Scienze della Terra
Via La Pira, 4
50121 FIRENZE - ITALY
Tel/Fax +39 055 2382146
E-mail: cmanetti@geo.unifi.it