## **OCEAN RAW MATERIALS**

#### 1. Introduction

The ocean is host to a variety and quantity of inorganic raw materials equal to or surpassing the resources of these materials available on land. Inorganic raw materials are defined here as any mineral deposit found in the marine environment. The mineral resources are classified generally as industrial minerals, mineral sands, phosphorites, metalliferous oxides, metalliferous sulfides, and dissolved minerals and include geothermal resources, gas hydrates precious corals, and some algae. The resources are mostly unconsolidated, consolidated, or fluid materials that are chemically enriched in certain elements and are found in or upon the seabeds of the continental shelves and ocean basins. These may be classified according to the environment and form in which they occur (Table 1) and with few exceptions are similar to traditional mineral deposits on land.

1.1. Global Ocean Resources. The nature and distribution of the apparent global marine mineral resources are shown in Figure 1. Although quantitative determinations are for the most part speculative, several publications have addressed the issue in some detail (3–5). Moreover, geological research and exploration support many of the forecasts that the oceans may contain mineral deposits of even greater potential than those found onshore (6). Comparative values for apparent marine mineral resources for 86 mineral commodities (7) have been tracked by the U.S. Bureau of Mines. Alternative marine resources exceeding existing land resources exist for each mineral except platinum, asbestos, graphite, and quartz crystal (8).

The terms ore, mineral resources, and ore reserves appear commonly in the literature and are often misunderstood. As defined by the American Geological Institute (AGI) in 1980, ore is a natural aggregate of mineral materials which can be mined at a profit (9). Prices of metals and other mineral-derived commodities fluctuate owing to a variety of technical, economic, political, and social factors such as engineering capabilities, supply and demand, wars and embargoes, or needs and fashions. Elasticity of price can be seen for gold, cobalt, copper, silver, and other metals. Ore reserves are currently economic mineral resources that have been measured, indicated, or inferred from acquired geological data. Only those reserves that are measured or indicated are used in the evaluation of a mineral property. There are few ore reserves in the marine environment other than those of operating mines because by definition the deposit must be currently mineable. As of this writing (2005) most marine mining technology is in the development stage. Mineral resources include all potentially recoverable minerals in a specified area, including measured ore reserves and undiscovered speculative deposits. Most marine mineral deposits are speculative and are classed as mineral resources. A more definitive discussion of the principles of the resource/reserve classification for minerals and forecasting methods used in the United States is given in Ref. (10) (see also Minerals recovery and PROCESSING).

# 2. Unconsolidated Deposits

Deposits that can be recovered without having to use explosives or other primary energy sources to break up the material in place are called unconsolidated deposits. These may be found stratified or disseminated as surficial or subsurface deposits on the continental shelf or in deep ocean basins.

**2.1. Continental Shelf.** A variety of terms may be applied to deposits in the continental shelf (conshelf) including beach, bank, alluvial, strand-line, heavy mineral, or placer. These contain mostly industrial materials, mineral sands, or precious metals (Table 1).

Industrial Minerals. Industrial minerals are bulk materials recovered for use directly as an industrial commodity rather than for their metal content. These include sand and gravel derived from glacial and alluvial sources that are predominantly siliceous; biogenic carbonate materials such as shell, coral, and carbonate sands; aragonite [14791-73-2], a denser and harder form of calcium carbonate, commonly of marine origin; salt; sulfur; and precious corals. A key distinguishing feature of the industrial mineral class is that a large percentage (60–100%) of the deposits is composed of saleable material and only simple beneficiation may be required to prepare the commodity for market. Within the United States, the most important commodity appears to be unconsolidated deposits of sand and gravel for use in coastal protection, beach replenishment, and industrial construction. Phosphorites are treated as a special case because of the maturity and complexity of the U.S. phosphate industry.

Sand and Gravel. Sand and gravel are terms used for different size classifications of unconsolidated sedimentary material composed of numerous rock types. The principal constituent of sand is normally quartz, although other minerals such as rock fragments or carbonates may be present, and may even be dominant, as is the case in tropical reef-derived sands. Gravel, because of its larger size, usually consists of multigrained rock fragments. Sand is generally defined as material that passes through a No. 4 mesh (4.75-mm) U.S. Standard seive and is retained on a No. 200 mesh (74-µm) U.S. Standard seive. Gravel is sized in the range of 4.75-76.2 mm in diameter. Resources of sand and gravel in the U.S. Exclusive Economic Zone (EEZ) appear to be not only adequate, but almost ubiquitous. More than 2 trillion metric tons of resources may be available (11). However, in the outer continental shelf (OCS), ie, U.S. seabeds seaward of the territorial limits of the States, it is doubtful if there are many known deposits that could be classed as commercial reserves as of this writing (2005). To evaluate a deposit for commercial use, it is necessary to know the specifications of the material needed for sale in a particular market. Similarly, it is necessary to ascertain that sufficient tonnage of saleable material exists within the deposit to sustain a profitable operation, ie, not only the areal extent, but the volume of the deposit, the grain size, the nature and quality of the grains and the percentage and location of unsaleable material within the deposit must all be ascertained. Of the vast quantities that are indicated as resources, a considerably lesser amount is expected to be mineable. Nevertheless, substantial mineable resources of sand and gravel aggregates exist off the U.S. coasts (12). Deposits of pure silica [7631-86-9] (qv) sand, valuable for optical and other special

purposes, are found in certain environments. Methods for the exploration of sand and gravel deposits are both conventional and satisfactory. Many references to such exploration technology are available (13–15). Some 20% of total sand and gravel production in Japan (16) and 15% in the United Kingdom (5) was obtained from offshore as of the mid-1990s.

*Biogenic Materials*. Living creatures form shells, reef corals, foraminiferal, and associated carbonate sands. Deposits of oyster, clam, and mollusc shells are commonly found in temperate waters in embayments or near the coast (17). Reef corals form coastal deposits in tropical or subtropical waters (18).

*Aragonite*. Calcium carbonate is a common deposit in shallow tropical waters as a constituent of muds, or in the upper part of coral reefs where it precipitates from carbon dioxide-rich waters supersaturated with carbonate from intense biological photosynthesis and solar heating. Deposits of oolitic aragonite, CaCO<sub>3</sub>, covering >250,000 km<sup>2</sup> in water <5-m deep are mined for industrial purposes in the Bahamas for export to the United States (19).

Precious Corals. One important deep seabed resource having worldwide distribution is precious coral. The industry extends worldwide, but the richest beds are found on seamounts in the western North Pacific Ocean and the western Mediterranean Sea. The U.S. Bureau of Mines listed corals in its mineral statistics reports although most countries, including the United States, regulate the industry as fisheries. Precious coral fisheries have existed in the Mediterranean Sea since ancient times. Beds of commercial density were not developed elsewhere until the early nineteenth century off Japan. In  $1966 \sim 95\%$  of the world's coral was dredged off Japan, Okinawa, and Taiwan. Overfishing led to stock depletion. Intensive exploration led to discoveries off Hawaii at the junction of the Emperor Seamounts and the Hawaii Ridge system,  $\sim 800$  km west of Midway. In 1980 these corals represented  $\sim$ 90% of the world's precious coral production. Throughout history, precious coral production has followed the pattern of exploration, discovery, exploitation, and depletion. Although the production of pink coral from Midway was  $\sim 140 \times 10^3$ kg in 1983, only  $\sim 10\%$  of the beds lie within the U.S. EEZ and the Pacific fishery is virtually unregulated. There has been no production of precious corals from within U.S. waters as of 1995.

Mineral Sands. Mineral sands is the generic industrial term for sands containing gold, precious gemstones, or minerals of tin, ie, cassiterite [1317-45-9], SnO<sub>2</sub>; titanium, ie, rutile [1317-80-2] TiO<sub>2</sub>; leucoxene [1358-95-8] (altered rutile); ilmenite [12168-52-4], FeTiO<sub>3</sub>; and other metals derived from the breakdown of rocks by weathering. Development activities for these minerals are well summarized (20). Other terms commonly used in the literature are placer, alluvial, and heavy mineral deposits. The principal distinction between industrial minerals and mineral sands is that the commercially valuable portion of the latter is rarely more than a few percent of the amount dredged. The waste product from these operations is therefore generally >95% of the total mined and processed. For the special cases of gold and platinum, the amount of saleable metal is measured in parts per million (ppm) and for diamonds in parts per billion (ppb). For all mineral sands or placers the beneficiation processes rarely employ chemical additives and are usually based on physical differences, such as specific gravity, grain size, color, and magnetic, radioactive or electrical properties, between the ore mineral and the waste materials. Mineral sands are widely distributed throughout the world generally in coastal areas, eg, tin has been mined offshore in southeast Asia since 1910 (1), but the occurrence of many mineral sands deposits also has been indicated in the U.S. OCS (21). In the early 1990s, significant discoveries were made of high quality diamonds in water depths >100 m off the coast of Namibia and South West Africa. This discovery sparked a minor diamond rush there and in Canada, where geologic conditions were similar. Namibia is now a major diamond produces. The occurrence of continentally derived gold placers in submarine sand channels at depths >2500 m has been postulated, based on new side scan imagery of the U.S. EEZ off southeastern Alaska (22). This offers an interesting potential for future deep-seabed activities.

Phosphorites and Glauconite. Phosphorites, or marine apatites,  $Ca_5(F,Cl,\ OH,1/2CO_3)(PO_4)_3$ , are commonly, though not predominantly, found as oolitic sands or as nodules in areas of upwelling of phosphorus-rich deep water (23). Glauconite [1317-57-3] is an authigenic form of mica (qv) having a high potassium content, ie, 2.5-8.5%  $K_2O$ , and some rubidium, lithium, and boron. It is widely distributed and commonly found as a beach sand. It is often associated with phosphorites in both ancient and recent marine sediments. Its occurrence as rounded dark-green grains <1 mm in diameter have earned it the sobriquet green sands.

**2.2. Ocean Basins.** Ocean basins are primarily formed from oceanic basalts and may be interspersed with continental remnants, ridges, seamounts, or volcanic islands rising from the depths. Average water depth is  $\sim\!4000$  m, but the most significant mineralization is generally found at 5000 m for manganese nodules, 4000 m for biogenic oozes, and 3000 m for hydrothermal metalliferous sulfides. The area is poorly explored, however.

Metalliferous Oxides. Marine oxide deposits occurring as unconsolidated nodules or consolidated crusts primarily of manganese and iron are termed metalliferous oxides. The ubiquitous unconsolidated deposits may contain potentially commercial quantities of manganese (20-30%), copper, nickel, and cobalt (<3% combined), and are found in all oceans primarily as discrete potato-sized nodules overlying soft sediments in water depths between 4000 and 6000 m. The nodules, commonly referred to as manganese nodules or polymetallic nodules, are primarily valued for the nickel content (Table 2). Nodules apparently form directly on the seabed through chemical precipitation from seawater and sediment pore-water fluids. Iron and manganese are the two most common transition metals in the earth's crust. The precipitation process, which seems to occur everywhere on the seabed, where the bottom water is oxygenated, represents the result of the transport of these metals from terrigenous rocks. Such deposits seem to form commonly where natural sedimentation rates are not high enough to overwhelm the chemical accretion processes. Extensive research has been conducted to elucidate and quantify the deposit formation processes because of the prevalence of these deposits in the oceans of the world and the apparent links to the global processes of weathering, primary production, and transport of metals through the world's marine ecosystems.

Large deposits of manganese nodules having relatively large concentrations of nickel, copper, and cobalt are found on the seabed surface in the principal oceanic basins. Deposits in several areas have been investigated for commercial

recovery potential, including the Clarion-Clipperton region of the Northeastern Tropical Pacific  $\sim 5-20^{\circ}$  North latitude,  $110-155^{\circ}$  West longitude (25,26); in the Central Indian Ocean south of India ~5-10° South latitude, 75-88° East longitude (27); in the EEZ of the Cook Islands in the South Pacific ~15-25° South latitude, 155–165° West longitude (28); and the Blake Plateau off the Atlantic coast of the United States  $\sim 30-35^{\circ}$  North latitude,  $65-80^{\circ}$  West longitude (29).

Other excellent summaries describing what is known of the formation processes and geological setting of these deposits have also been assembled (30-32). Listings of nodule compositions for these and other areas have been compiled (33,34). For many sites these data are available as computer databases (qv) maintained by the NOAA National Geophysical Data Center in Boulder, Colorado.

Biogenic Materials. Deep ocean calcareous or siliceous oozes are sediments containing 30% of biogenic material. Foraminifera, the skeletal remains of calcareous plankton, are found extensively in deep equatorial waters above the calcium carbonate compensation depth of 4000-5000 m. Similar deposits of radiolaria or diatoms composed of siliceous skeletal remains are widespread in more temperate areas in deep water below 5000 m. The deposits may be very pure. The diatoms recovered from deposits on land are used as fillers or filter materials or as a source of high quality carbonate or silica (see Diatomite).

Metalliferous Sulfides. Hydrothermal discharges are found extensively in the vicinity of active oceanic plate boundaries. Precipitates from these discharges may form sediments or muds highly enriched in sulfides of lead, zinc, copper, silver, and gold. A prime example of these metalliferous muds is a series of deposits in the Red Sea overlain by hot pools of metalliferous brines. The Atlantis Deep deposit was discovered in 1976 in water depth of  $\sim$ 2200 m. The sediments, overlying oceanic basalt, are 2–25 m thick and cover  $\sim$ 60 km<sup>2</sup>. They are estimated to contain  $30 \times 10^6$ t Fe,  $2.5 \times 10^6$ t Zn,  $50 \times 10^3$ t Cu, and  $9 \times 10^3$ t Ag. The sediment is compacted to the consistency of shoe polish at depth. On the surface it is quite soft and the water content can be as high as 200%. The wet density is  $\sim$ 1.25 g/ cm<sup>3</sup>, the shear strength from 60-250 N/m<sup>2</sup>. To mobilize the required daily metals throughput in a full-scale operation it would be necessary to extract  $10 \times 10^3$ t/d of in situ mud, creating  $100 \times 10^3$ t/d of slurry in the process. This slurry would then need to be diluted with an equal amount of seawater before it could be pumped to the ship. Recovered as a relatively dilute slurry containing not >100 g/L solids of fine particle size (80% at  $\leq 2\mu m$ ), the metalliferous muds are unlike any of the feeds usually supplied to mineral-processing facilities. The muds contain only 3-6% zinc, up to 1% copper, and about 50 g/t silver; thus concentration prior to extractive metallurgy is essential. Further diluting the slurry to limit the solids content to <30 g/L immediately prior to the slurry entering the flotation (qv) circuit poses no particular problems on the mining vessel. Direct leaching and thermal beneficiation are too costly.

Authigenic barium sulfate or barite [13462-86-7] is found in relatively high concentrations in sediments covering active diverging oceanic plate boundaries. It occurs as rounded masses containing up to 75% BaSO<sub>4</sub> or as a dispersed constituent of the sediment. Its origins are uncertain, but it is likely that it is associated with hydrothermal actions.

# 3. Consolidated Deposits

Consolidated deposits are those that occur as solid masses upon or within the structure of the seabeds. These may be removed only by fracturing, fluidizing, or dissolving the materials to be recovered.

**3.1. Continental Shelf.** Most consolidated mineral deposits found on the continental shelf are identical to those found on land and are only fortuitously submerged. Exceptions include those laid down in shallow marine seas or basins in earlier geochemical environments such as bedded ironstones, limestone, potash, coals, phosphorites, and, more recently recognized, gas hydrates.

Phosphorites. Phosphorites are of special significance. These constitute an already established and somewhat complex industry and a variety of technologies proposed for offshore mining. The deposits are most commonly bedded marine rocks of carbonate fluorapatite in the form of laminae, nodules, oolites, pellets, and skeletal or shell fragments. The commercial term phosphate rock includes phosphatized limestones, sandstones, shales, and igneous rocks containing apatite. Marine phosphorites, widely distributed in continental margins, vary in character depending on their genesis. They are found consolidated as crusts and indurated sands, sands in shallow basins, submerged plateaux, on the slopes of islands, and in tropical lagoons. Extensive bedded deposits are indicated offshore of the eastern United States. Marine phosphorites commonly contain minor quantities of uranium—thorium, platinum, cadmium, and rare earths (35,36).

Gas Hydrates. Gas hydrates are solid, ice-like substances composed of water and natural gas, commonly methane. They occur naturally in areas of the world where methane and water can combine at appropriate conditions of temperature and pressure. The methane hydrates  $[CH_4*6.1(\pm 0.1\%) H_2O]$  are found in low temperature, low pressure regimes of permafrost regions, and high pressure, moderate temperature regimes in ocean sediments. Methane hydrate is stable in seabeds below ~450 m water depth in open ocean with an average temperate hydrothermal profile that gives hydrate a wide pressuretemperature field of stability. These conditions are found in deep water basins adjacent to continental shelves, and in deep ocean basins where the sediment thickness is at least one kilometer. Methane molecules are compressed closely together in the hydrate lattice. One cubic meter of hydrate yields  $\sim 160 \text{ m}^3$  of methane at STP, and ~0.87 m<sup>3</sup> of water. Their widespread occurrence in the world's oceans and seas, their ability to change phase from solid to gas when their natural state of equilibrium is disturbed, and other characteristics have resulted in the recognition of four distinct areas in which more information is sought. These are their potential as an energy resource, their influence on seabed stability when disturbed by activities such as drilling, their suspected influence on global climate when massively disturbed by natural causes such as earthquakes or slumps, and the implication of indicated unique acoustic properties (37).

The immense volumes of gas and the richness of selected deposits so far indicated have resulted in an important global increase in interest in the deposits as a potential clean energy source. Conservative estimates by the US Geological Survey and others have resulted in projections for the marine hydrates of from 100,000 trillion ft<sup>3</sup> (TCF) to 270,000,000 TCF. In terms of available energy reported, they would represent an undeveloped source of fuel more than twice that of all other known fossil fuels together. In U.S. areas alone the mean value of the projected quantities would supply, at the present rate of consumption, all U.S. energy need for 64,000 years.

Artificially induced methane hydrate has been known in the oil industry for decades as a formidable nuisance in the clogging of pipelines much like cholesterol in human arteries. It was only in the 1960s that natural hydrates were recognized in the Siberian permafrost and some years later serendipitously identified in seismic records in the seabeds. Now (2005) research and development activities directed to the development of hydrates as an alternative fuel source are being given priority funding in many countries including Canada, Chile, China, India, Korea, Norway, Russia, and the United Kingdom, In the United States, congress passed the Methane Hydrate Research and Development Act in 1999, to fund cooperative work among the Departments of Energy and Interior, and the National Science Foundation. Oil companies are now cooperating or funding there own research programs and other independent organizations are preparing to field test their own patented recovery systems. The developments that have taken place in Industry in the acquisition and processing of seismic data and the development of other techniques have prepared a broad technological base on which to build. Characterization of the deposits and determination of their economic value may now be very rapid.

Seafloor stability is an important aspect of large hydrate deposits whether disturbances are caused by natural events or by production operations. As with the energy issue, much is still to be learned about the stability of gas hydrates in the seabeds, especially in a period of apparently accelerating global climate change. Methane, as a greenhouse gas has ten times the impact of carbon dioxide when released to the atmosphere. Exact mechanisms for methane release are not yet fully established. Release from the seabeds as a result of sealevel fall, or from the permafrost as a result of sea level rise would warm the global climate. This might counteract cooling trends to stabilize the climate or it might exacerbate warming trends to create further destabilization. Either way there are significant questions to be addressed.

The velocity of sound in hydrate is very high and significantly alters the properties of surface layers of hydrate-cemented sediments. Changes in acoustic characteristics have important implications for the use of sonar devises for defense, seismic exploration, and research.

**3.2. Ocean Basins.** Known consolidated mineral deposits in the deep ocean basins are limited to high cobalt metalliferous oxide crusts precipitated from seawater and hydrothermal deposits of sulfide minerals which are being formed in the vicinity of ocean plate boundaries. Technology for drilling at depth in the seabeds is not yet adequately advanced, and most deposits identified have been sampled only within a few centimeters of the surface.

Metalliferous Oxides. Cobalt crusts, commonly referred to as ferromanganese crust, manganese crust, or high cobalt manganese crust, are relatively rich in cobalt, nickel, and platinum. These are found on hard-substrate seabed elevations, such as seamounts, and the submerged flanks of islands. They

occur as encrustations up to 40 cm, but are more commonly 3–5 cm thick, on the exposed rocks of island slopes, seamounts, or submerged plateaux in water depths between 800 and 2400 m. Research into the genesis, composition, and distribution of these deposits has been significant since the early 1980s (38). The crusts, primarily evaluated on the basis of cobalt content, are commonly associated with platinum and phosphorites. Two general sources for the metals seem to dominate: pore-water solutions and colloidal suspensions within the host sediments, and seawater itself. Manganese, nickel, and copper seem to be relatively more important components in the pore-water source; cobalt and iron are relatively more important in the seawater source. The crust deposits seem to be composed almost entirely of material derived directly from seawater. Growth rates vary between 1 and  $20 \times 10^6$  mm/year and are generally at the lower rate.

Because crust deposits are derived almost completely from direct precipitation from seawater, these offer a potentially important record of the ocean's chemical environment during the past 80 to 100 million years. Work on Pacific deposits (39–41) indicate that the layers of deep ocean seamount deposits show significant differences related to regional, and perhaps global, changes in the marine chemical environment. Future research on the crusts can be expected to produce at least a partial history of seabed chemistry. As the links between the deposit formation and seawater chemistry become more fully understood, it is quite possible that the stratigraphic record of crust deposition could permit a better understanding of the constraints on variability of oceanographic parameters. Of particular interest are the long-term oceanic rates of absorption of CO<sub>2</sub>, heavy metals, and other pollutants. The association of crusts with the rare-earth metals has been described (40).

Metalliferous Sulfides. Hydrothermal mineral deposits are formed by the action of circulating waters in seabed rocks which dissolve, transport, and redeposit elements and compounds in the earth's crust. Most of the familiar hard rock mineral lodes of tin, copper, barite, lead, silver, and gold on land or in the submerged continental shelves are of this type. More recently discovered, and potentially a significant resource, are deep seabed hydrothermal sulfide deposits (42), commonly referred to as metalliferous or polymetallic sulfides (PMS). These deposits may carry sulfides of almost any of the metallic elements, including copper, lead, zinc, silver, and gold. They are formed in the vicinity of active diverging plate boundaries throughout the world's oceans. Figure 2 indicates their known distribution in the Pacific. Knowledge of the grades, sizes, occurrences, and settings of these marine deposits is rudimentary, but consistent with the notion that this type of deposit should ultimately be as important as, or more important than, any other type of marine deposit (44–46).

Deposits that are forming are frequently characterized by venting streams of hot  $(300^{\circ}\mathrm{C})$  mineralized fluid known as smokers. These result in the local formation of metalliferous mud, rock chimneys, or mounds rich in sulfides. In the upper fractured zone or deep in the rock mass beneath the vents, vein or massive sulfide deposits may be formed by the circulating fluids and preserved as the crustal plates move across the oceans. These off-axis deposits are potentially the most significant resources of hydrothermal deposits, even though none has yet been located.

# 4. Fluid Deposits

Fluid deposits are defined as those which can be recovered in fluid form by pumping, in solution, or as particles in a slurry. Petroleum products and Frasch process sulfur are special cases. At this time no valid distinction is made between resources on the continental shelf and in the deep oceans. However, deep seabed deposits of minerals which can be separated by differential solution are expected to be amenable to fluid mining methods in either environment.

**4.1. Dissolved Minerals.** The most significant source of minerals for sustainable recovery may be ocean waters which contain nearly all the known elements in some degree of solution. Production of dissolved minerals from seawater is limited to fresh water, magnesium, magnesium compounds (qv), salt, bromine, and heavy water, ie, deuterium oxide. Considerable development of techniques for recovery of copper, gold, and uranium by solution or bacterial methods has been carried out in several countries for application onshore. These methods are expected to be fully transferable to the marine environment (5). The potential for extraction of dissolved materials from naturally enriched sources, such as hydrothermal vents, may be high.

# 5. Minerals Recovery

- **5.1. Technology.** There are four basic methods of mining solid minerals: scraping the surface, excavating a pit or trench, removal through a borehole in the form of a slurry or fluid, and tunneling into the deposit (Fig. 3). All deposits on land are mined by one or more adaptations of these methods. Marine mining is amenable to the same basic approaches whether on the continental shelf or in the deep seabeds. Each mining method has variations that may be tailored to a specific situation. Most of the deposit types can be mined by more than one method. Similarly, any one method can be applied to more than one deposit type. These systems are described in a number of publications (1,5).
- **5.2. Environmental Considerations.** A significant advantage that appears to accrue from the recovery of mineral raw materials from the marine environment is the apparently benign effects of these activities when compared to the recovery of the same materials from land. Although a great deal of work remains to confirm this assumption (8), limited testing and monitoring on existing producing operations indicate an environmental advantage to ocean mining (48,49). Regulatory constraints in the U.S. regarding limits for potential toxic contaminants are given in Table 3.
- **5.3. Economic Aspects.** To be useful the raw materials must be recoverable at a cost not greater than the cost of similar terrestrial materials. These costs must include transportation to the point of sale. Comparative costs of recovery are strongly influenced by secondary environmental or imputed costs, such as legal costs or compensatory levies.

#### **BIBLIOGRAPHY**

"Ocean Raw Materials" in *ECT* 2nd ed., Vol. 14, pp. 150–170, by W. F. McIlhenny, The Dow Chemical Co.; in *ECT* 3rd ed., Vol. 16, pp. 277–296, by W. F. McIlhenny, Dow Chemical U.S.A., in ECT 4th ed., Vol. 17, pp. 580–593, by Michael J. Cruickshank, University of Hawaii at Manoa; "Ocean Raw Materials" in *ECT* (online), posting date: December 4, 2000, by Michael J. Cruickshank, University of Hawaii at Manoa.

- M. J. Cruickshank, in *Mining Engineering Handbook*, Society of Mining Engineers, Littleton, Colo., 1992, Chapt. 28, pp. 1985–2028.
- P. Hoagland and J. M. Broadus, Seabed Commodity and Resource Summaries, Technical Report WHOI 87–43, Woods Hole Oceanographic Institute, Woods Hole, Mass., 1987.
- 3. M. J. Cruickshank, in *Proceedings of the International Symposium on Minerals and the Environment*, Vol. 18, paper No. 20, Institution of Mining and Metallurgy, London. 1974.
- V. E. McKelvey and co-workers, Subsea Mineral Resources, Bulletin 1689-A, U.S. Geological Survey, Woods Hole, Mass., 1986.
- 5. F. C. F. Earney, Marine Mineral Resources, Routledge, London, 1990.
- 6. M. J. Cruickshank and R. Kincaid, in *Minerals, Materials and Industry: Proceedings* of the Fourteenth Congress of the Council of Mining and Metallurgical Institutions, Edinburgh, Scotland, July 2–6, 1990, Institution of Mining and Metallurgy, London, 1990, pp. 197–206.
- 7. M. J. Cruickshank, *Technological and Environmental Considerations in the Exploration and Exploitation of Marine Minerals*, Ph.D. dissertation, University of Wisconsin, Madison, 1978.
- 8. M. J. Cruickshank and C. L. Morgan, *Synthesis and Analysis of Existing Information Regarding Environmental Effects of Marine Mining*, consulting report to Continental Shelf Associates for U.S. MMS Contract No. 14-35-0001-30588, U.S. Dept. of the Interior, Washington, D.C., 1992.
- Dictionary of Geological Terms, American Geological Institute (AGI), Washington, D.C., 1980.
- Principals of a Resource/Reserve Classification for Minerals, Circular 831, U.S. Department of the Interior, Washington, D.C., 1980.
- 11. Ref. (4), p. 106.
- 12. M. J. Cruickshank, Mar. Mining 7, 149 (1988).
- 13. L. E. Parkinson, Underwater Sci. Technol. J., 63 (June 1970).
- 14. M. J. Cruickshank and R. W. Marsden, eds., *SME Engineering Handbook*, Society of Mining Engineers, New York, 1973, pp. 1–200.
- 15. E. H. Macdonald, Alluvial Mining: The Geology, Technology and Economics of Placers, Chapman and Hall, New York, 1983.
- H. Okamura, J. Mining Min. Inst. Jpn. (1992); Engl. summary in unpub. proceedings of 14th Joint Meeting of the U.S.—Japan Cooperative Program in Natural Resources, Marine Mining Panel, Honolulu, Hawaii, June 6, 1992.
- 17. A. H. Bouma, Shell Dredging and Its Influence on Gulf Coast Environments, Gulf Publishing Co., Houston, Tex., 1976.
- S. J. Dollar, Sand Mining in Hawaii: Research, Restrictions, and Choices for the Future, UNIHI-SEAGRANT-79-01, Sea Grant Program, University of Hawaii, Honolulu, 1979.
- 19. Carib 1:np (1978).
- 20. Ref. 5, 387 pp.

- 21. A. E. Grosz and E. C. Escowitz, in W. F. Tanner, ed., *Proceedings of the 6th Symposium on Coastal Sedimentology*, Florida State University, Tallahassee, Fla., 1983, pp. 231–242.
- 22. M. R. Dobson, Mar. Mining 9, 495 (1990).
- M. J. Cruickshank and T. J. Rowland, Mineral Deposits at the Shelf Break, Publication No. 33, Society of Economic Paleontologists and Mineralogists, 1983, pp. 429

  436.
- P. G. Telecki, M. R. Dobson, J. R. Moore, and U. von Stackelberg, eds., Marine Minerals, Vol. 194, C. D. Reidel, Dordrecht, The Netherlands, 1987.
- J. L. Bischoff and D. Z. Piper, eds., Marine Geology and Oceanography of the Pacific Manganese Nodule Province, Plenum Press, New York, 1979.
- P. Halbach, G. Friedrich, and U. von Stackelberg, eds., The Manganese Nodule Belt of the Pacific Ocean, Stuttgart, Ferdinand Enke Verlag, 1988.
- A. B. Valansangkar and N. V. Ambre, Ocean Technology Perspectives, Publications and Information Directorate, New Delhi, India, pp. 827–841.
- A. L. Clark and co-workers, Cook Islands Manganese Nodule Resource Assessment, Pacific Islands Development Program, Honolulu, Hawaii, Feb. 28, 1993.
- 29. F. T. Manheim, Science 232, 601 (1986).
- N. A. Wogman, K. Chave, R. K. Sarem, eds., Inter-University Program of Research on Ferromanganese Deposits of the Ocean Floor, Seabed Assessment Program, Washington, D.C., 1973.
- 31. D. S. Cronan, Underwater Minerals, Academic Press, London, 1980.
- P. G. Teleki, M. R. Dobson, J. R. Moore, and U. von Stackelberg, eds., *Marine Minerals*, NATO ASI Series, Vol. 194, C. D. Reidel Publishing Co., the Netherlands, 1987, p. 588.
- 33. J. M. Botbol and G. I. Evenden, U.S. Geolog. Surv. Bull., 1863 (1989).
- 34. Japan International Cooperation Agency, in *Metal Mining Agency of Japan*, South Pacific Applied Geoscience Commission (SOPAC), Suva, Fiji, 1991.
- 35. F. T. Manheim, R. M. Prat, and P. V. McFarlin, Soc. Econ. Paleontol. Mineralog. SP 29, 117 (1980).
- 36. S. Riggs and co-workers, in Ref. 32, pp. 9–27.
- 37. M. J. Cruickshank, and S. M. Masutani, Methane hydrate research and development: Sea Technology, Aug. 1999, pp. 69-74.
- F. T. Manheim and D. M. Lane-Bostwick, eds., in U.S. Geological Survey, Open File Report 89-020, 1989; Final Environmental Impact Statement, EIS/EA MMS 90-0029, 2 vols., U.S. Dept. of the Interior, Washington, D.C., Aug. 1990.
- 39. P. Halbach and D. Puteanus, Earth Planet. Sci. Lett. 68, 73 (1984).
- 40. E. H. DeCarlo, Marine Geol. 98, 449 (1991).
- 41. J. R. Hein and co-workers, Paleoceanography 7(1), 63 (1992).
- G. R. McMurray, Proceedings of the Gorda Ridge Symposium, May 1987, Springer-Verlag, New York, 1990.
- 43. S. D. Scott, in Ref. 32, pp. 189-204.
- 44. R. A. Koski, W. R. Normark, and J. L. Morton, Mar. Mining 4(2), 147 (1985).
- 45. A. Malahoff, *Marine Mining: A New Beginning*, State of Hawaii, Honolulu, 1985, pp. 31–61.
- 46. P. A. Rona, Marine Mining 5(2), 117 (1985).
- 47. M. J. Cruickshank and co-workers, *Marine Mining on the Outer Continental Shelf*, Report 87–0035, U.S. Dept. of the Interior, Washington, D.C., 1987.
- 48. P. C. Rusanowski, *Alluvial Mining*, Institution of Mining and Metallurgy, London, 1991, pp. 586–601.

- 49. H. E. Thiel, E. J. Foell, and G. Schriever, *Berichte aus dem Zentrum für Meeres- und Klimaforshung der Universität Hamburg*, No. 26, Institut für Hydrobiologie und Fisserelwiessenschaft Hamburg, Hamburg, Germany, 1991.
- J. Clark, Coastal Ecosystems, The Conservation Foundation, Washington, D.C., 1974.

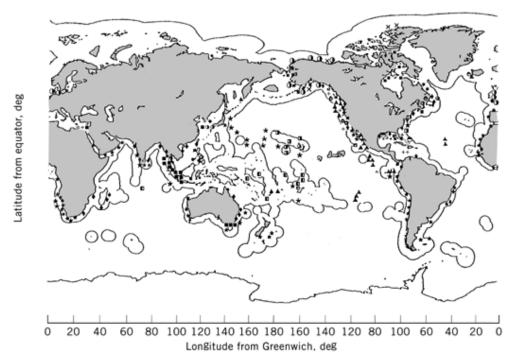
#### **GENERAL REFERENCES**

International Seabed Authority, 1999, Proceedings of the workshop on deep seabed polymetallic nodule exploration; development of environmental guidelines: Sanya, Hainan Island, PRC, 1–5 June, 1998, ISA, Kingston Jamaica, WI, January 1999, 289 pp.

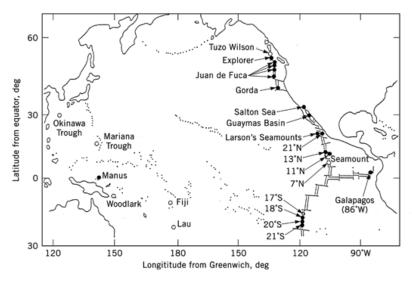
International Seabed Authority, 2000, Proceedings of the workshop on technology for deep seabed mining: ISA, Kingston, Jamaica, WI, July 1999 (www.isa.org.jm).

International Seabed Authority, 2004, Proceedings of a workshop on minerals other than polymetallic nodules of the international seabed area, in Kingston, Jamaica, June 26–30, 2000: ISA, Kingston, Jamaica, WI. Vol. 2., Parts 2, 3, and 4, pp. 466–918.

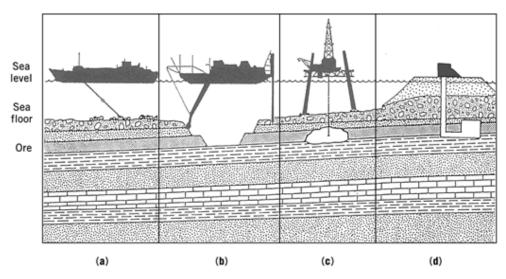
MICHAEL J. CRUICKSHANK MMTC Associates



**Fig. 1.** Global distribution of seabed mineral deposits, where  $\times$  represents chromite; + barite; v; titanium, zirconium, hafnium, and thorium;  $\bullet$  tin;  $\phi$  gold, platinum, and silver; sand and gravel; shell, calcium carbonate; \* gems;  $\rho$  marine polymetallic sulfides; H phosphorites; cobalt crusts; S sulfur; and ferromanganese nodules. Adapted from Ref. 2.



**Fig. 2.** Distribution of (•) known and (○) suspected metalliferous sulfide deposits and active hydrothermal vents in the Pacific Ocean (43).



 $\textbf{Fig. 3.} \quad \text{The four basic methods of mining: (a) scraping, (b) excavating, (c) fluidizing, and (d) tunneling (47).}$ 

Table 1. Classification of Global Marine Mineral Resources

	Resource classification					
Location	Unconsolidated	Consolidated	Fluid			
seabed	industrial materials sand and gravel shell sands aragonite coral sands mineral sands magnetite ilmenite rutile chromite monazite	Conshelf outcrops exposures of veins, etc	seawater magnesium sodium uranium bromide and salts of 26 other elements			
subseabed	mineral sands gold platinum cassiterite gem stones bedded deposits phosphorites	vein, stratified, disseminated or mas-sive deposits, coal phosphates carbonates potash ironstone limestone metal sulfides metal salts, gas hydrates Ocean basins	freshwater springs			
seabed	muds or oozes metalliferous carbonaceous siliceous calcareous baritic nodules manganese cobalt nickel copper	crusts phosphorite cobalt manganese mounds and stacks metal sulfides	seawater magnesium sodium uranium bromine and salts of 26 other elements			
subseabed		vein, stockwork, stratbound or massive deposits metal sulfides	hydrothermal fluids			

aRef. 1.

Table 2. Examples of Metal Grades and Values for Crusts and Nodules  $\!\!\!^a$ 

	$\mathrm{MPM}^b$ crusts				Line Island Ridge crusts				
Component	Price, \$/kg	% Dry	% Wet	\$/t Wet	$m^2$	% Dry	% Wet	\$/t Wet	\$/m <sup>2</sup>
Co	27.56	0.83	0.54	148.82	2.98	1.00	0.65	179.14	3.58
Ni	4.98	0.49	0.32	15.94	0.32	0.55	0.36	17.93	0.36
Cu	1.77	0.07	0.05	0.89	0.02	0.07	0.05	0.89	0.02
Mo	10.58	0.06	0.04	4.23	0.08	0.06	0.04	4.23	0.08
$\mathrm{Mn}^c$	1.52	25.0	16.25	247.00	4.94	25.0	16.25	247.00	4.94
d	0.58	25.0	16.25	94.25	1.89	25.0	16.25	94.25	1.89
Total									
c				416.88	8.34			449.19	8.98
d				264.13	5.29			296.44	5.93
_	$\mathrm{MIDPAC}^e$				$\operatorname{Nodule}^f$				
	% Dry	% Wet	\$/t Wet	$\frac{m^2}{m^2}$	% Dry	% Wet	\$/t Wet	$\frac{\text{\$/m}^2}{}$	
Co	0.79	0.51	140.56	2.81	0.24	0.16	44.10	0.44	
Ni	0.49	0.32	15.94	0.32	1.21	0.79	39.34	0.39	
Cu	0.07	0.04	0.71	0.01	1.00	0.65	11.51	0.12	
Mo	0.06	0.04	4.23	0.08	0.04	0.03	3.17	0.03	
$\mathrm{Mn}^c$	24.6	15.99	243.05	4.86	25.2	16.38	248.98	2.49	
d	24.6	15.99	92.74	1.85	25.2	16.38	95.00	0.95	
	Total		404.49	8.08			347.10	3.47	
			254.18	5.07			193.12	1.93	

<sup>&</sup>lt;sup>a</sup>Ref. 24.

 $<sup>{}^{</sup>b}MPM = mid - Pacific mountains.$ 

<sup>&</sup>lt;sup>c</sup>99.95% Mn.

 $<sup>^</sup>d\mathrm{Ferromanganese}$  (78% Mn) recalculated to 100% Mn basis.

<sup>&</sup>lt;sup>e</sup>MIDPAC 81 cruise.

fAbyssal manganese nodules from the nodule belt area in the northeast Pacific.

Table 3. Coastal Water Quality Criteria for Toxic Substances Other Than Biocides<sup>a</sup>

	Maximum acceptabl	3.6		
Substance	96 h LC <sub>50</sub> <sup>b,c</sup>	$\mu \mathrm{g/L}^c$	Minimum risk threshold, $\mu$ g/ $\mathrm{L}^d$	
aluminum	1/100	1500	200	
antimony	1/50	200		
arsenic	1/100	50	10	
barium	1/20	1000	500	
beryllium	1/100	1500	100	
boron	1/10		5000	
bromine <sup>e</sup>				
cadmium <sup>f</sup>	1/100	10	0.2	
${ m chromium}^g$	1/100	100	50	
copper	1/100	50	10	
fluorides	1/10	1500	500	
iron		300	50	
$\operatorname{lead}^g$	1/50	50	10	
manganęse	1/50	100	20	
$\operatorname{mercury}^h$	1/100	1.0		
molybdenum	1/20			
nickel	1/50	100	2	
phosphorus	1/100	0.1		
selenium	1/100	10	5	
silver	1/20	0.5		
thallium <sup>i</sup>		100	50	
uranium	1/100	500	100	
vanadium	1/20			
zinc	1/100	100	20	
cyanides <sup>/</sup>	1/10	10	5	
detergents	1/20	200		
phenolics	1/20	100		
phthalate		0.3		
esters				
$PCB^{k,l}$		0.002	_	
$ ext{sulfides}^{l,m}$	1/10	10	5	

<sup>&</sup>lt;sup>a</sup>Ref. 50.

 $<sup>^</sup>b$ Maximum acceptable concentration figures expressed as fractions of 96 h LC<sub>50</sub> for most sensitive species in given area. The 96 h LC<sub>50</sub> is that concentration of a substance that kills 50% of the test species within 96 h under standard bioassay conditions.

<sup>&</sup>lt;sup>c</sup>Data are U.S. EPA official criteria where available; National Academy of Sciences (NAS) data used where EPA data not available.

<sup>&</sup>lt;sup>d</sup>NAS data, for concentrations "below which there is a minimal risk of deleterious effects."

 $<sup>^{</sup>e}$ The maximum acceptable concentration for free (molecular) bromine is 0.1 mg/L; for ionic bromate, 100 mg/L.

fin the presence of copper or zinc in concentrations of 1 mg/L or more, the minimum risk threshold should be lower by a factor of 10.

gIn oyster growing areas, the minimum risk threshold should be lower.

<sup>&</sup>lt;sup>h</sup>According to NAS, "Fish-eating birds should be protected if mercury levels in fish do not exceed 0.5 mg/g."

 $<sup>^{</sup>i}1/20$  of the 20-day LC<sub>50</sub>.

<sup>&</sup>lt;sup>j</sup>Marine and estuarine aquatic and wildlife criteria not available; freshwater criteria are used (by EPA).

<sup>&</sup>lt;sup>k</sup>According to EPA, "The maximum acceptable concentrations of PCB in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, within the size range consumed is 0.5 mg/kg on a net weight basis."

<sup>&</sup>lt;sup>l</sup>Data supplied by NAS.

<sup>&</sup>lt;sup>m</sup>These concentrations are valid only if salt water pH is between 6.5 and 8.5.