## Manganese Nodules (I): Mineral Resources on the Deep Seabed

Fishing and offshore oil drilling are still the most significant of man's efforts to tap the resources of the 70 percent of the earth covered by oceans, although minerals such as salt, tin, and limestone are extracted from the sea or dredged from the continental shelf in growing quantities. The most glamorous and perhaps the most mysterious marine resource, however, is the billions of tons of metals contained in manganese nodules that lie scattered over the seabed in the once inaccessible depths of the open ocean.

The nodules contain iron, nickel, copper, cobalt (and traces of two dozen other metals) in addition to manganese, often in concentrations comparable to those in land ores. This wealth of metals and the prospect of deep sea mining operations to recover them have stirred up interest among oceanographers and industrialists alike. Indeed, to judge from newspaper stories about the inexhaustible riches of the deep sea floor and from the intensity of the international debate over the ownership of these resources (Science, 25 May 1973, p. 849), a new gold rush might be beginning. But despite investments estimated at \$100 million in the development of mining and processing tech-

nology, the economic viability of exploiting the nodules is still uncertain. (Mining and processing will be the subject of a second article.) Nor is the resource unlimited. Although nodules occur on the seabed in many parts of the world, they are unevenly distributed. Only a few areas have nodules with a high metallic content in sufficient abundance to make mining feasible. Efforts to explain this distribution pattern and to account for the formation of the nodules are leading, however, to a better understanding of deep ocean geochemistry. Among the more intriguing results is recent evidence that manganese nodules, much like coral reefs, are habitats for a variety of life forms (protozoans and other microorganisms) and seem to grow in part through biological action.

Manganese deposits on the sea floor occur as thick slabs or crusts, as thin coatings on basalt rocks, and as nodules, some of which were recovered as early as the 1872 expedition of the *Challen*ger. Nodules, the commercially significant type of deposit, are black or brown agglomerations of manganese oxide and iron oxide minerals. The nodules range in size from about 1 to 15 cm across. They are extremely porous, and differ



Fig. 1. Map of part of the North Pacific seabed showing sedimentary provinces, major geologic features, and manganese deposits. [Source: D. R. and B. M. Horn, Lamont-Doherty Geological Observatory]

widely in shape, internal structure, and composition from one deposit to another—even within the space of a few hundred meters. Nodules are found predominantly in areas of oxygen-rich waters and low sedimentation.

The nodule beds most favorable for mining appear to lie in the Pacific Ocean, southwest of Hawaii and just north of the equatorial zone of high biological productivity, according to D. R. Horn and B. M. Horn of Lamont-Doherty Geological Observatory (Fig. 1). The richest deposits occur in a narrow band, perhaps 200 km across and 1500 km long, running roughly east-west around 9° latitude (1). Not only are the nodules in this band high in copper and nickel content, but they are also very abundant (cover photo). The seabed in this area is about 5000 m deep and the sediments include silicon-rich remains of plankton (Radiolaria). High concentrations of nodules are also found along the southern edge of the equatorial belt, but the deposits, like those of the Atlantic and Indian oceans, are relatively poor in copper and nickel. (Deposits high in cobalt, however, have been discovered in the South Pacific.) As a result, both scientific and commercial interest have been focused on the North Pacific beds.

The structure of nodules from different regions varies widely, but most appear to be layered, often in the form of concentric rings around a small nucleus (2). According to R. K. Sorem of Washington State University, the layers represent compositional and mineralogical boundaries and range in size from rings visible with the eye down to microscopic structures. The layers as they are originally laid down on the nodule surface are honeycombed, Sorem finds, but as the nodules age they become more compact, the pores fill in with clay, and the materials reorganize. He finds no clear age pattern in the layers, but in some samples the layers are thicker on the bottom of the nodule (the side in contact with the sediments).

On a finer scale the structure of many nodules is close to amorphous; they are composed of fine-grained but inhomogeneous materials that include some recognizable crystals of manganese and iron minerals, often segregated in discrete layers. Sorem finds that most nodule material gives no x-ray diffraction pattern at all, and the patterns that do appear are characteristic of crystal sizes less than a few micrometers.

Radiometric dating of nodules indicates that they grow very slowly. Growth rates between 1 and 100 mm per million years have been reported. By comparison, sediment accumulates on the ocean floor at a rate exceeding 1 m per million years even far from sources of continental debris and outside the equatorial zone of high biological productivity (where the rate of accumulation is much higher). Nodules are mostly found on the surface of the sediments or only partially submerged, however, and there is little agreement as to what keeps them from being buried. Some investigators believe that deep sea organisms that feed on protozoans nudge the nodules, while others believe that the protozoans themselves buoy up the nodules.

That living organisms do play a role in the development of the nodules seems to be clear. Work at Scripps Institution of Oceanography by J. Greenslate recently revealed small tubular structures on the surface of carefully collected nodules, some of which had been built by a genus of deep ocean Foraminifera (Saccorhiza) (3). The tubular structures, many of which were made of ferromanganese material (Fig. 2), were easily destroyed (even by washing the nodule). Greenslate thinks this fragility explains why they had not been found on nodules brought to the surface by normal dredging procedures. The tubules and other smaller structures found on nodules from all parts of the Pacific show, Greenslate believes, that the surface of the nodule is home to many different protozoan organisms, making it perhaps the most densely populated site on the deep sea floor. Moreover, he finds remnants of similar structures within the interior of the nodules. On the basis of these observations, Greenslate suggests that nodules are formed around a skeleton of biotically derived tubules and chambers. Originally built on the nodule surface, these structures are later buried by other tubules and filled in with manganese precipitated by inorganic or bacterial processes and with clay and other debris.

Bacteria that oxidize and precipitate manganese and others that can reduce manganese oxides do exist, according to H. L. Ehrlich of Rensselaer Polytechnic Institute. The bacteria produce an en-



Fig. 2. Micrograph of nodule surface (enlarged 155 times) showing small tube and dome structures of biological origin. [Source: J. Greenslate, Scripps Institution of Oceanography]

zyme system that catalyzes the reactions, he finds, and the reactions occur at the temperature and pressure of the deep ocean. Ehrlich believes that manganese oxides can precipitate and adsorb onto a growing nodule without bacteria but that the organisms accelerate the process through their catalytic role. The other constituents of the nodule, iron oxides and smaller amounts of copper, nickel, and other metals, probably precipitate inorganically, since they are known to adsorb strongly on manganese oxide. The bacterial reducing agents, he speculates, may be involved in the release of manganese and other elements adsorbed onto it from the sediments.

If biological structures built by communities of microorganisms are the basis around which nodules are formed, as Greenslate proposes, it may explain the occurrence of nodules in distinct patches and the relative similarity of nodules within a given patch. The variations in shape and composition from one patch of nodules to another may also be attributable to variations in the communities of microorganisms.

Where the metals found in the nodules come from and how they are concentrated are subjects of some debate. It is known that iron and manganese, along with other metals, are introduced into the oceans by submarine volcanic eruptions and as runoff from the continents. In oxygen-rich waters (away from continental margins), deposition of ferromanganese minerals is widespread on the ocean floor.

The immediate source of copper and nickel in the North Pacific band of nodules is less certain, but, according to G. Arrhenius of Scripps, these metals are concentrated from seawater by plankton and deposited in the sediments. There the decay of organic materials eventually releases the metallic ions, and they are transported to the surface of the sediments to be incorporated in the nodules. (Arrhenius and his colleagues point out that sediments in areas of nickel-rich nodules are depleted in the metal.) Others have proposed that metals in the nodules are concentrated directly from seawater.

If the underlying sediments are indeed the immediate source of metals for the nodules-and the preponderance of evidence seems to favor this hypothesis-then the high rate of accumulation of biologically derived sediments may well explain the high concentrations of copper and nickel in nodules near the equator. Relatively few nodules are found directly within the highproductivity belt (most are presumably buried because of the very high sedimentation rate), but those which are found, according to Arrhenius, do have high metal values. North of the belt, sediment accumulates much more slowly and the density of nodules is corresopndingly higher.

The occurrence of a belt of metalrich nodules also seems to be attributable to the geology of the region. Northward of the Clipperton Fracture Zone the water becomes much deeper, deep enough that calcium carbonate sediments-which make up much of the deposits farther south-dissolve, leaving primarily siliceous sediments. The removal of carbonate has the effect, Arrhenius believes, of increasing the concentrations of manganese, iron, copper, and other nodule metals in the sediments while keeping the net accumulation of sediment low enough to permit nodules to form in large numbers. It is on the siliceous clay that the best deposits appear to be found.

Study of the North Pacific nodule beds and their geochemistry has only begun. But enough is known to show that they are a unique phenomenon and, quite possibly, a mineral resource of considerable value.

-Allen L. Hammond

## **References and Additional Reading**

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