Manganese Nodules Grow by Rain from Above

The rain of plant and animal remains falling into the deep sea not only provides metals to nodules but also determines nodule growth rates and composition

Manganese nodules had always seemed unlikely geologic denizens of the deep. Solid tennis-ball-sized hunks of manganese and iron oxides and enticing traces of other metals, they lie on the sea floor thousands of meters below the surface where, except for the occasional fish or mud worm, nothing larger than a mote of clay or a speck of now-dead plant is ever likely to pass. And whatever part of this finely divided jetsam escapes dissolution into the sea is destined to be buried by the next millennium's load of detritus—except the metals that form the nodules. Somehow, the nodules must feed geochemically on the metals in their surroundings while avoiding drowning in the accumulating mud of the sea floor.

Although they have had some general ideas about how manganese nodules grow and survive, marine geochemists are only now reaching some consensus on the details. A consortium of American researchers that conducted the Manganese Nodule Project (MANOP)* made a major contribution to that consensus by confirming the central role of the debris raining from the surface. This debris carries metals to the sea floor and controls the geochemical conditions in the bottom sediment, which in turn determine the composition and rate of growth of the nodule. Ironically, the same debris that feeds nodule growth, if too abundant, will dilute economically attractive elements such as cobalt with less rewarding manganese. A further increase in the rain of debris will forever bury nodules beyond the reach of deep-sea miners.

As a part of MANOP, Jack Dymond and his colleagues at Oregon State University (OSU) have used a mathematical model to sort out the nodule accretion processes that combine to produce the distinctive variations in nodule chemical and mineralogical composition seen around the Pacific. Drawing on previous studies, the Oregon group inferred that only three processes add iron and manganese to nodules. The first of these has nothing to do with the sediment on which nodules are couched. Termed hydrogenous precipitation, this process deposits metals present in seawater at concentrations of parts per billion onto nodules, which consist of roughly 15 percent iron and manganese. As the best example of such deposits, the group chose manganese crusts formed on sea-floor rocks that stand high above the sediment.

According to the model, two different processes operate within sediments, depending on whether any oxygen remains below the sediment surface. Whether there is oxygen depends on how biologically productive the overlying surface waters are. If winds and currents mix the sea in the required manner, microscopic plants and animals will thrive and a portion of their inorganic skeletons and about 1 percent of their organic tissues will sink to the bottom along with the clay washed from the land. No matter how deep the sea floor, bacteria and animals dwelling on and in the sediment will oxidize all but a few percent of the organic matter that reaches the bottom.

> "Slowly" in nodule accretion is about one atomic layer of the manganese-oxygen structure per year.

When the rain of organic matter is light enough, it does not consume all of the sediment oxygen. Oxic chemical alteration, called oxic diagenesis, of the sediment can then supply metals to nodules. Oxic sediments presumably must be chemically altered to produce nodules because under such oxidizing conditions manganese and iron are usually tied up as insoluble oxides that cannot move to and be incorporated in nodules. A number of possible specific diagenetic reactions—including those involving volcanic ash and skeletal opal—have been suggested that could free metals and allow them to diffuse through sediment pore water to the nodules; different combinations of some or all of these reactions might occur on different parts of the sea floor, depending on prevailing conditions. The OSU group concluded that the nodule composition most typical of growth under oxic diagenesis is that of the nodule bottom most rich in trace metals from a siliceous sediment in the tropical North Pacific.

Mitchell Lyle, Ross Heath, and James Robbins of OSU now suggest that diagenetic reactions may not always be necessary to release enough of some metals for nodule growth. Rather than postulating that a nodule takes up dissolved metals that have diffused great distances from their point of release, a process that would be frustrated in the case of manganese by its oxidation, the OSU group suggests that sediment particles carry adsorbed metals to the nodules as feeding and burrowing animals stir the sediment. Once stirred close to the nodule, the metals need only desorb from a particle, adsorb to the nodule, and be incorporated into it. To judge by the rate of biological stirring and the amount of metals released from sediment by gentle leaching in the laboratory, the group says, nodule growth could be sustained by only 1 percent of the adsorbed manganese, nickel, and copper within about 5 centimeters of a nodule.

When so much organic matter falls to the sea floor that its decomposition consumes all the sediment oxygen, the burden of oxidizing it falls to other compounds, including manganese dioxide. The consequent reduction and dissolution of manganese creates a bountiful reservoir of mobile, reactive metal for nodule growth. For the composition of a nodule growing under these suboxic conditions, the OSU group chose that of the most manganese-rich nodule bottom from MANOP's most biologically productive site near the Galápagos Islands.

Given the assumed compositions produced by each of the three accretion processes, the OSU group then determined the proportion of each process that best accounted for the concentrations of 14 elements in nodules recovered from different varieties of Pacific sediments. Optimum apportioning of the three processes accounted for 90 percent of the variance of aluminum, silicon, calcium, titanium, the major element iron, and the potentially mineable elements cobalt and copper. The model accounted for 75 percent of the variance of manganese, magnesium, barium, and the potentially mineable element nickel. Zinc, an ill-behaved element in the mod-

*A group of major MANOP papers that includes the work reported here is in press in *Geochimica et Cosmochimica Acta*.

el, requires a fourth accretion process, probably release from decomposing organic matter under conditions intermediate between oxic and suboxic.

At MANOP's site in the central North Pacific, where there is little biological production to deliver metals to the bottom or to drive diagenesis, hydrogenous accretion slowly adds metals to nodule tops in the form of sheets of manganese dioxide accompanied by enough seawater ions to balance atomic charges in the crystal. Nickel, copper, and zinc seem to have a particular affinity for this accreting nodule surface, allowing them to compete with more abundant seawater ions. "Slowly" in nodule accretion is about 1 millimeter per million years, according to radiometric dating by Chi An Huh of Woods Hole Oceanographic Institution; that is, one atomic layer of the manganese-oxygen structure per year.

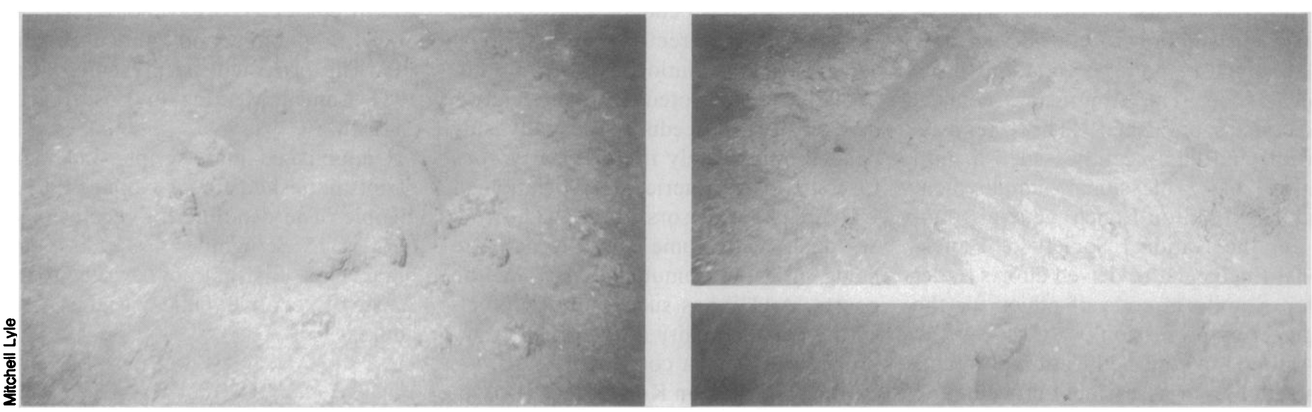
When the rain of biological debris is faster, oxic diagenesis can provide enough manganese to permit nodules to grow at least ten times faster than when only seawater manganese is available, according to the OSU group. Oxic diagenesis also releases copper and nickel fast enough to allow the production of the form of manganese oxide called todorokite, whose tunnel structure prefers to incorporate copper and nickel.

Suboxic diagenesis, as might be expected from its ability to dissolve sediment manganese oxides, drives the fastest nodule growth, on the order of 200 millimeters per million years. That should allow suboxic accretion to dominate nodule growth at MANOP's most productive site, but it does not. Hydrogenous accretion does produce less than 2 percent of nodule growth, but oxic accretion supplies 60 percent compared to suboxic's 40 percent. In fact, nodules at this site are at least 5 centimeters above the sediment zone where manganese is dissolved, a gap presenting a nearly impenetrable barrier to the diffusion of manganese.

The OSU group suggests that, although suboxic accretion may be fastest, it is intermittent, occurring only when a surge of biological production at the surface creates temporary suboxic conditions around the nodules, which seems to be only about 7 percent of the time at the MANOP site. The duration of these episodes could be as short as one season, Dymond says, to judge from the observed variations in the flux of debris from the surface and evidence in the sediment of free manganese lingering from the last episode. In the longer term, Bruce Finney of OSU, Heath, and Lyle found a jump in the growth rate of one nodule (from 50 to 200 millimeters per million years) that occurred about 40,000 years ago when the amount of organic matter in the sediment increased sharply.

Although biological debris greatly increases nodule growth, there can be too much of a good thing. At the most productive MANOP site, manganese markedly dilutes the economically desirable elements such as cobalt, and the rain of debris keeps most nodules slightly buried most of the time. A slightly heavier rain of debris (see box) would quickly bury manganese-plated shark's teeth and other nuclei that form the cores of infant nodules.—RICHARD A. KERR

Why Are There Any Nodules at All?



Mitchell Lyle

They shouldn't be there but they are. A typical manganese nodule can grow for millions of years at the glacial pace of 10 millimeters per million years or less, while the rain of clay and biological debris from the surface can pile up a thousand times faster. Why doesn't this avalanche of sediment, which actually nurtures the growth of nodules, totally bury all nodules? Proposed explanations have included shaking by earthquakes, rolling by deep-sea currents, and nudging by overly frisky bottom animals. The present favorite is the digging, tunneling, and churning of bottom sediment caused by animals as they create their shelters and search for food. Exactly what aspect of this bioturbation actually moves sediment underneath nodules and lifts them remains a mystery. Perhaps it is animals wedging beneath a nodule and backfilling, as suggested by David Piper and Bradford Fowler of the U.S. Geological Survey in Menlo Park, or merely a greater commotion in the sediment between nodules than beneath them that shuffles sediment under them, as recently suggested by Brian Sanderson of the University of British Columbia. The process remains a mystery because the net effect of thousands of years of bioturbation is difficult to record. Bottom photographs taken during MANOP at an eastern North Pacific site underlying high biological production hint at the kind of activity that might be responsible. In the upper right, the fanned pattern of feeding tracks made by a worm suggests why such populous sediments have been likened to a well-plowed Iowa cornfield. In the lower right, some sediment dweller has built its mound hard against a nodule. And on the left is a "fairy ring" of unknown origin that seems to be slipping and perhaps rolling nodules into its moat.—R.A.K.