Reports

Manganese and Biotic Debris Associations in Some Deep-Sea Sediments

Abstract. *Incipient manganese concretions occur in microcavities of planktonic skeletal debris (especially diatom frustules) in some Pacific Basin deep-sea sediments. These concretions contain over 50 percent manganese and very little iron (<1 percent). There is a continuum of growth stages in the concretions having a diameter between 0 and approximately 2 millimeters, and a genetic relationship is suggested between the very small and the centimeter sized concretions.*

My purpose here is to report some observations on the character of some Pacific Basin sedimentary particles within which manganese, nickel, and copper are concentrated (*1*). The rationale for examining the particles themselves rather than studying these metals by indirect techniques is as follows:

1) In addition to the basal formation and the surface deposits of large nodules or crusts, manganese and other associated elements occur in sediments as microscopic concretions of oxyhydrates. The small concretions may be structurally less complex than the large nodules, and their ratio of growth surface to volume is large. Therefore, they should provide a promising opportunity to study the depositional substructures by which the manganese is added, be the process organic or inorganic.

2) Incipient concretions within the sediments must nucleate within microcavities. Since microfossils provide many such cavities that are free of other solid sedimentary particles and since these cavities can be preserved intact during the sampling process, the concretions found within them can be assumed to have formed there. Such internal concretions, not only of oxyhydrates but also of other materials, would thus be truly authigenic and would have formed in an aqueous environment.

In applying this reasoning, I found that much of the manganese in the sediment I studied (*1*) is localized in ferromanganese micronodules (0.1 to 1 mm) typically like that shown in Fig. 1A. These particles are present in a broad range of sizes and shapes, nearly all of which display biotically derived structures on their surfaces (for example, see the inset of Fig. 1A). The structures are fragile and easily destroyed, particularly by sonic dispersion techniques (*2*). Concretions of this size hereafter will be called juveniles.

That portion of the manganese not localized in juvenile concretions was found in still smaller units. These embryonic concretions, most of which range from 1 to 30 μm in diameter, are those within plankton skeletal remains, particularly in the interior of diatom frustules. When concretion growth transgresses the valve faces of the frustules, other sedimentary debris such as small skeletal fragments and mineral grains outside the diatom is incorporated. Figure 1C pictures the embryonic concretions shown in Fig. 1B after the free parts of the diatom frustule had been broken away. Note the complete lack of included debris in that portion of the concretion that was within the frustule. Upon complete encapsulation of the skeleton within which embryonic nucleation took place, the concretions enter their juvenile stage. All the juveniles that I have examined (great care must be taken in the examination) have yielded a nucleus of an intact plankton skeleton.

Table 1. Manganese concentrations (in percentages by weight) and manganese/minor element ratios for this station (*1*). Sediment analysis and adult nodule analysis were done by x-ray energy spectrometry, embryo analysis by electron microprobe. No other elements were detected (< 0.1 percent) in the embryos; in particular, no sulfur was found. Data correction closure for the microprobe results was 82 percent under the assumption that MnO_2, Fe_2O_3, NiO, and CuO were present. The 18 percent remainder was assumed to be OH^- and water.

Component	Sediment	Nodule	
		Embryo	Adult
Mn	0.3	50.5	26.8
Mn/Fe	0.05	72	2.6
Mn/Ni	30	168	14
Mn/Cu	10	126	24

Electron microprobe analysis of the particles (Table 1) shows that their minor element composition is dissimilar to that of the large ferromanganese nodules occurring in the same region (*3*). The material found within the diatom frustules is composed entirely of oxyhydrates of manganese with a total of less than 2 percent iron, nickel, and copper incorporated in the structure. That the earliest stages of concretion take place within the diatom frustule, primarily within substructural voids in the skeletal wall, is inferred from examination of diatom sections in the transmission electron microscope (TEM) (Fig. 1D). Analysis of the sections based upon the use of x-ray energy spectrometry in conjunction with scanning electron microscopy confirms that the material marked Mn is composed primarily of manganese oxide. Electron diffraction data show the individual manganese oxyhydrate particles to be crystalline. The interpretation of the diffraction patterns is complicated by the dehydration of crystals while under the electron beam. Details of these electron diffraction investigations will be reported elsewhere (*4*).

I am not aware of any earlier report of an occurrence within diatom frustules of embryo manganese oxyhydrate concretions. The origin of the concretions is unclear; I have found no compelling evidence indicating whether they are produced organically or inorganically.

Living diatoms are not known to contain sufficient manganese to account for that found within the frustules in this sediment. The apparent extra-diatom source of the manganese necessitates the assumption of manganese transport into the frustule during deposition of the embryonic concretion. It is noteworthy that no spheroidal concretions seem to nucleate outside of skeletons, since manganese concretions of microscopic size (≲ 100 μm) not having a skeleton sur-

---

Scoreboard for Reports: In the past few weeks the editors have received an average of 63 Reports per week and have accepted 11 (17 percent). We plan to accept about 10 reports per week for the next several weeks. In the selection of papers to be published we must deal with several factors: the number of good papers submitted, the number of accepted papers that have not yet been published, the balance of subjects, and length of individual papers.

Authors of Reports published in *Science* find that their results receive good attention from an interdisciplinary audience. Most contributors send us excellent papers that meet high scientific standards. We seek to publish papers on a wide range of subjects, but financial limitations restrict the number of Reports published to about 12 per week. Certain fields are overrepresented. In order to achieve better balance of content, the acceptance rate of items dealing with physical science will be greater than average.

rounding their nuclei are rare in this sediment. Those uncontaminated embryos occasionally observed without a surrounding protective skeleton are thought to have been released from within skeletons during specimen preparation. The spherical embryos are similar to the birnessite spheres reported by Brown *et al.* (*5*), but they have a significantly different surface texture. The electron diffraction data do not suggest birnessite as being present within the embryonic concretions I have examined.

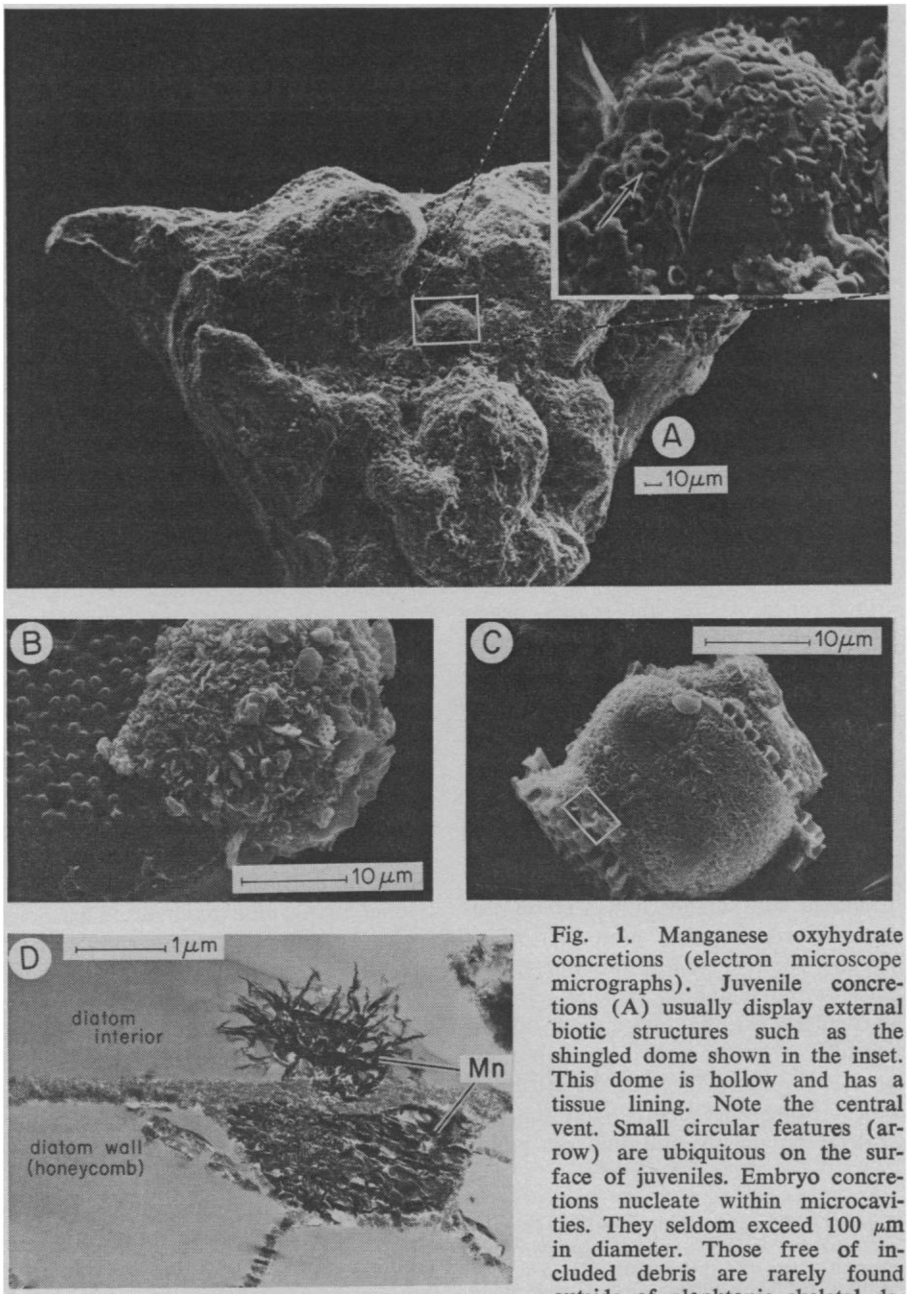

Fig. 1. Manganese oxyhydrate concretions (electron microscope micrographs). Juvenile concretions (A) usually display external biotic structures such as the shingled dome shown in the inset. This dome is hollow and has a tissue lining. Note the central vent. Small circular features (arrow) are ubiquitous on the surface of juveniles. Embryo concretions nucleate within microcavities. They seldom exceed 100 µm in diameter. Those free of included debris are rarely found outside of planktonic skeletal debris and are composed almost entirely of manganese oxyhydrates (see Table 1). Embryos in this sediment occur most frequently within centric diatoms appearing under the light microscope as brown to black opaque material. Once the concretion diameter equals the diatom dimension, the concretion transgresses the valve faces and assimilates the adjacent sedimentary debris (B). That portion of the concretion held within the frustule remains free of contaminants (C). The small rectangle in (C) represents a region like that in the TEM micrograph (D) showing a portion of the frustule wall honeycomb structure. Several microtome sections were examined in a scanning electron microscope equipped with an x-ray energy spectrometer; this examination confirmed manganese to be the only element present above system detection limits in the area marked Mn. The manganese deposit is inferred to have nucleated in the subcellular structural cavity and to have grown progressively into the diatom's interior. The manganese material is crystalline; that is, it yields distinctive electron diffraction patterns (*4*). The diagonal line in the upper right of the micrograph is due to a fold in the sectioned embedding plastic.

In light of Ehrlich's (*6*) studies of manganese-precipitating bacteria on concretions of larger size, the possibility exists that the spherical concretions found in diatom frustules are of a bacterial origin. Many living algae contain significant concentrations of bacteria (*7*). Perhaps, upon the diatom's demise, some of the bacteria first consume the immediately accessible organic compounds of the dead diatom and then metabolize and deposit manganese. This discussion is clearly speculative, but I believe not without sufficient merit to warrant investigation, especially since the shape and surface texture of the embryos are quite similar to the spherical manganese concretions resulting from bacterial activity in laboratory culture experiments (*8*).

The presence of spheroidal manganese oxyhydrate concretions in deep-sea sediments is also interesting in the context of recent reports on iron sulfide framboids from the California Borderland and the Red Sea (*9*). Here again, there are similarities between the gross external features of the embryonic manganese concretions and the sulfide-bearing framboids. However, the manganese concretions contain very little sulfur (< 0.2 percent). Sulfide framboids and manganese spheroids occur in vastly different sedimentary environments, but it is conceivable that one could be mistaken for the other, especially in older sediments.

Lougheed and Mancuso (*10*) have reported hematite framboids in Precambrian iron deposits and conclude that they are pseudomorphs of pyrite framboids. Many of the younger framboid structures they discussed were in the interior of biotic remains, especially within diatom frustules. The concretions reported here are, by contrast, most certainly not pseudomorphic structures. I have never observed and know of no other reports of the occurrence of any opaque material within diatom frustules of pelagic environments prior to their deposition on the sea floor and must conclude that nucleation of the internal concretions is entirely postdepositional. Lougheed and Mancuso's suggestion of pyrite formation during sedimentation followed by oxidation and pseudomorphic replacement after deposition (*10*, pp. 202 and 208) is not applicable here.

It appears that any assumed sequence involving the initial precipitation of colloidal iron oxyhydrates followed by an adsorption of aqueous manganese and other aqueous elements to account for the presence of ferromanganese deposits in the sediments is not necessary, although in some cases in the deep sea it may be sufficient. The low iron content (< 1 percent) and the fact that the iron is dispersed throughout the diatom-held spheres clearly indicates that manganese can be deposited in the deep ocean independently of iron. This observation differs considerably from the reported precursor iron layer found in some other samples (*11*). If the sediment interstitial fluids are near thermodynamic equilibrium, the small percentage of iron in the embryo concretions suggests either that the iron concentration in the solution is extremely low compared to that of manganese or that there is some catalytic process that is precipitating manganese preferentially. The relative enrichment of manganese versus iron in surface sediment fluids seems tenable, but then so does the probability of bacterial agents being involved in the manganese deposition. Further, it seems reasonable that the process responsible for manganese infilling of diatom frustules may well be the process responsible for manganese infilling of biotic structures recently reported to exist on the surface layer of large manganese nodules (*12*). The microenvironment within the voids of diatom frustules and other planktonic skeletal debris certainly have characteristics that are very similar to those of a vacant structure built on a large nodule's surface, that is, the presence of decaying organic materials, the exclusion of sedimentary particles, and permeability by ambient solutions.

I have stated the genetic relationship between the concretions I term embryos and those I call juveniles. It might be contested whether there exists any such relationship between these two types of smaller concretions and those larger ones that I would like to refer to as adults. Adult nodules are those of a size such that they may exhibit evidence of numerous benthic organisms having resided on their surfaces ($\gtrsim 1$ cm). The small and large concretions are at least related in that some benthic organisms actively add juvenile concretions to the surface of adult concretions (*12*). In addition, all three sizes of concretions are related if by nothing other than the fact that all have manganese as their principal component.

J. GREENSLATE
Geological Research Division,
Scripps Institution of Oceanography,
La Jolla, California 92037

References and Notes

1. This sediment was collected with a box corer during the Scripps Institution of Oceanography Benthiface Expedition in June 1973, at 14°35.2′N and 117°20.2′W and a water depth of 3980 m. The sediment is a radiolarian clay with a substantial diatomaceous component. The surface sediment is of Recent age. Ferromanganese nodules of centimeter size and larger are abundant in this region, and many were recovered. Many of these nodules were among those I examined for biotic structures and are discussed in (*12*).
2. Sample preparation techniques were designed to be as simple and gentle as possible so as to avoid alteration or elimination of interesting particles, particularly the ferromanganese phases. The generalized procedure involves dispersing the sediment in filtered (pore size, $0.2\ \mu$m) seawater, freeze-drying it, and then directly examining the individual particles. Some crushing or embedding and sectioning of larger particles was necessary for the TEM and microprobe studies.
3. J. Z. Frazer and G. Arrhenius, Technical Report 2 of the Interuniversity Program of Research on Ferromanganese Deposits on the Ocean Floor (International Decade of Oceanographic Exploration, National Science Foundation, Washington, D.C., 1972).
4. S. Asunmaa, G. Arrhenius, J. Greenslate, in preparation.
5. F. Brown, A. Pabst, D. Sawyer, *Am. Mineral.* **56**, 1057 (1971).
6. H. Ehrlich, in *Ferromanganese Deposits on the Ocean Floor*, D. R. Horn, Ed. (International Decade of Oceanographic Exploration, National Science Foundation, Washington, D.C., 1972), p. 63; see also references therein.
7. B. Berland, M. Bianchi, S. Maestrini, *Mar. Biol.* **2**, 350 (1969).
8. G. Zavarin, *Microbiology (USSR)* **30**, 343 (1961).
9. R. E. Sweeney and I. R. Kaplan, *Econ. Geol.* **68**, 618 (1973).
10. M. S. Longheed and J. J. Mancuso, *ibid.*, p. 202.
11. R. Burns and B. Brown, in *Ferromanganese Deposits on the Ocean Floor*, D. R. Horn, Ed. (International Decade of Oceanographic Exploration, National Science Foundation, Washington, D.C., 1972).
12. J. Greenslate, *Nature (Lond.)* **249**, 181 (1974).
13. I thank Dr. G. Arrhenius for stimulating discussion and constant encouragement; Drs. K. Towe and K. Nealson for constructive criticisms that improved the manuscript; and Dr. S. Asunmaa, H. Fujita, and M. Chiappino for assistance. Research was supported by the University Research Foundation.

19 March 1974; revised 22 July 1974

■

Baring High-Albedo Soils by Overgrazing: A Hypothesized Desertification Mechanism

Abstract. *Observations are reported of high-albedo soils denuded by overgrazing which appear bright, in high contrast to regions covered by natural vegetation. Measurements and modeling show that the denuded surfaces are cooler, when compared under sunlit conditions. This observed "thermal depression" effect should, on theoretical grounds, result in a decreased lifting of air necessary for cloud formation and precipitation, and thus lead to regional climatic desertification.*

Trewartha (*1*) has raised the question of why there can be sharp contrasts in the amounts of rainfall in regions with similar climatic controls, both dominated by the surface flow of maritime air. The possibility of regional aridity alongside regions of higher rainfall is ascribed here to a desertification mechanism in which overgrazing, which bares inherently high-albedo soils and lowers surface temperatures, is the underlying cause.

Aridity can arise from three general causes: (i) the separation of the region from oceanic moisture sources by distance or topography; (ii) the existence of dry stable air masses that resist convective currents; or (iii) the absence of influences that cause convergence, create unstable environments, and provide the lifting of air necessary for precipitation (*2*). A decrease in lifting is invoked in the mechanism discussed here.

A striking case of baring high-albedo soils can be observed in the Sinai-Negev region. In images of southwestern Israel and northern Sinai from the Earth Resources Technology Satellite (ERTS-1) (Fig. 1), one can discern a sharp demarcation line, with pronounced contrast, between the relatively dark Negev and the very bright Sinai and Gaza Strip. The line coincides with the 1948–1949 armistice line between Israel and Egypt, along which a fence was erected some 5 years ago.

Ground truth observations show that the effect stems from the denuding of the bright sandy soil, predominantly as a result of overgrazing by goats, camels, and sheep, on the formerly Egyptian-held side. Additional contributing causes include picking by the Bedouin of the prevalent inedible shrub *Artemisia* for the construction of their habitats and shallow ploughing by the Bedouin of some small isolated areas (*3*). On the protected dark side of northwestern Negev, only a few herds graze and the natural vegetation grows in relative abundance. The natural vegetation is definitely rain-limited, and the weakening of the contrast between Sinai and Negev in the inland direction can be attributed to the weakening of the natural vegetation cover in the Negev as a result of decreasing rainfall.

The contrast between the denuded bright side and the protected dark side has been measured with a Joyce-Loebel microdensitometer. The space contrast,