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Ferromanganese micronodules from the surficial sediments of Georges Bank

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ABSTRACT

Ferromanganese micronodules have been found on Georges Bank, off the U.S. northeast coast, distributed throughout the surficial sediments within an area about 125 km long and at least 12 km wide. These coarse, sand-sized concretions have precipitated from metal-rich interstitial waters and contain many of the textural and structural features common to other neritic nodules. Most of the nodules have accreted around detrital grains, and X-ray powder diffraction analyses indicate the presence of goethite and vernadite (δ -MnO₂) in the ferromanganese layers. Chemical analyses of the micronodules, when compared with similar data on deep-sea manganese nodules, reveal lower Mn/Fe ratios, significantly higher concentrations of V and As, comparable values of Mo, and an order of magnitude less of Co, Ni, Ce and most other metals.

1. Introduction

In recent years, manganese concretions have attracted considerable interest as possible commercial sources of Mn, Co, Ni, Cu, Zn, and other minor elements. These nodules consist of hydrated ferromanganese oxide precipitates, which form under a variety of conditions in many parts of the world. Because of distinctive geochemical and morphological characteristics, marine ferromanganese concretions can be placed into two categories: deep-sea nodules and shallow-water (<200 m) nodules. The major differences between neritic and deep-sea nodules have been described in the literature by Manheim (1965), Price (1967), and Cronan (1972). Shallow-water marine nodules form at a faster rate and have a lower trace-element content than the abyssal types. Many of the shallow-water marine ferromanganese deposits are not in the form of large nodules but occur as sand-sized micronodules and thin crusts on individual detrital grains. Owing to their inconspicuous nature, many micronodule occurrences may have gone unnoticed and information on their composition is scarce.

Manheim (1965) reported manganese stains and thin crusts on coarse sediments in the Gulf of Maine in areas swept free of finer detritus, and tube-like oxide masses were found along the coast of Maine by Medcof (1963). Dredgings contained and

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photographs showed nodules and thick encrustations of ferromanganese oxides on the New England Seamount Chain (Pratt and Thompson, 1962) and in Lydonia Canyon (D. W. O'Leary, oral commun., 1983). During July 1981, we observed micronodules in van Veen grab samples collected as part of the Biological Task Force study monitoring the exploratory drilling on Georges Bank (Bothner *et al.*, 1982). The purpose of this paper is to report on the external and internal morphology, mineralogy, chemical composition, and origin of the ferromanganese micronodules found on Georges Bank.

2. Methods

Grab samples collected on Georges Bank by the U.S. Geological Survey and archived at the Woods Hole Oceanographic Institution were examined to delineate the areal distribution of the micronodules. As part of the present study, three short gravity cores (17 cm, 15.5 cm, and 20.5 cm in length) were collected at station 1 (Fig. 1) to determine the occurrence of micronodules with depth in the sediment. Some nodules were thin-sectioned and their internal and external morphologies were examined by both optical and scanning electron microscopy. X-ray powder diffraction analyses were performed on micronodule samples prepared as wet, air-dried, and heated-to-60°C randomly oriented aggregates. The micronodules and visible shell fragments were removed from two composite samples collected at station 1 and the remaining host sediments were leached using hot (100°C) 6 M HCl. Major- and trace-element analyses were performed on the micronodules and leachates. Cd and As contents were determined by graphite-furnace atomic-absorption spectroscopy; determinations of the other metals listed in Table 1 were made by inductively coupled plasma (ICP). An energy dispersive X-ray spectrometer attached to a scanning electron microscope was used to determine the elemental composition of microstructures within the nodules. Summation for the chemical composition of the micronodules utilized total MnO₂ values recalculated as Mn₃O₄ to compensate for oxygen loss at the 1000°C ignition temperature. Other sums were calculated from the values as shown.

3. Results

Ferromanganese micronodules occur in the surficial sediments of Georges Bank (Fig. 1) between the 60–100 m contours, over an area at least 125 km long and 12 km wide. These sediments are subarkosic quartz sands that are well sorted, medium to coarse grained, and iron oxide stained. Silts and clays typically constitute less than one percent of the samples, a reflection of the strong winnowing processes associated with the tidal and storm generated currents on Georges Bank (Butman *et al.*, 1982). Sediment is not accumulating in this area at the present time. The sources of these relict nodule-bearing sediments were the Mesozoic sedimentary and Paleozoic metamorphic rocks of New England, which were eroded and transported to the shelf during Pleistocene glaciation (Hathaway, 1972).

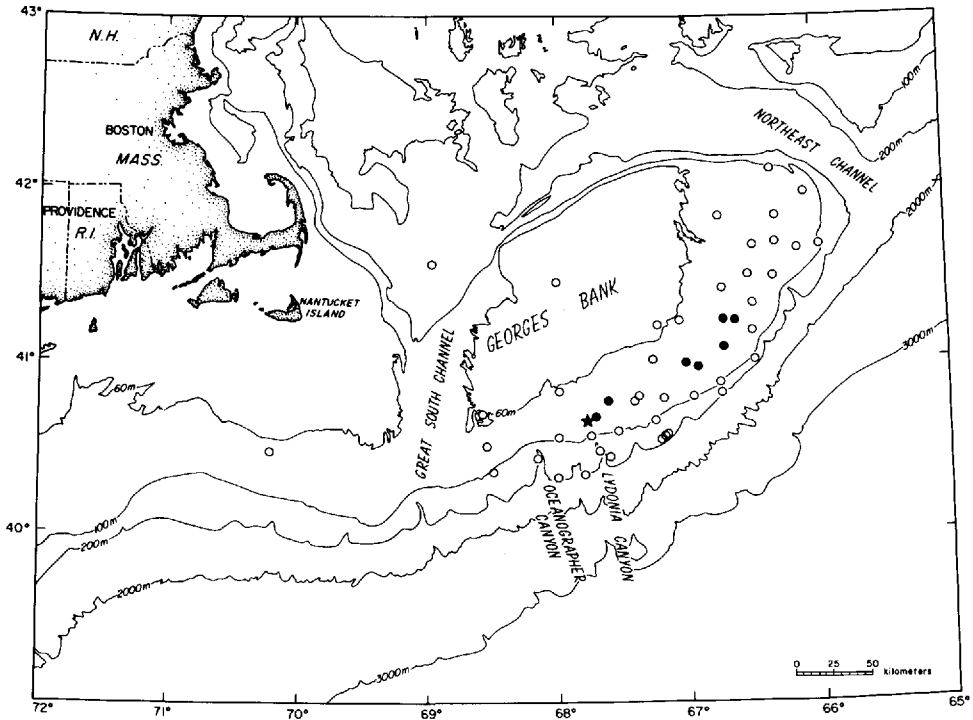


Figure 1. Sample locations. Solid symbols: Fe-Mn micronodules present; Open symbols: Fe-Mn micronodules not found. Gravity cores were collected at station no. 1 (solid star).

Unlike manganese stains and crusts in the Gulf of Maine (Manheim, 1965), which occur mostly on surfaces exposed to the bottom waters, the micronodules in the gravity cores were equally distributed vertically throughout the upper 20.5 cm of the surficial sediments. This distribution suggests that oxidizing conditions exist at least to 20 cm; the color of the sediments and absence of H_2S odors in freshly collected vibracores in the area indicate that they extend much deeper, perhaps 1–3 m (M. H. Bothner, oral comm., 1983). Although the sediments below the upper part of the oxidized layer were not sampled and no Eh profiles are available for the study area, we believe that sediments having a negative Eh probably underlie the study area and that the reducing conditions in these sediments caused the original mobilization of Mn and Fe. These reduced sediments would not be expected to contain micronodules because manganese is largely removed from the sediments after burial by reduction (Price, 1967). The rust-brown color of the sediments and the distribution of the nodules within this surficial oxidized layer suggest that the interstitial pore waters contain high concentrations of iron and manganese ions. Ferromanganese stained detrital grains (Table 1), partially encrusted grains, and fully encrusted micronodules were all observed in these surficial sediments.

Table 1. Chemical composition of micronodules and comparative materials. Data are referred to oven-dried material. (1) Average of composite samples of Georges Bank micronodules. (2) Average stain leached from host sediments on Georges Bank. (3) Average Georges Bank sediment (Bothner *et al.*, 1982; and Manheim, 1972). (4) Mean composition of 702 micronodules from world oceans (Addy and Lindsay, 1977). (5) Average deep-ocean nodules (McKelvey *et al.*, 1982; and Cronan, 1980). See text for discussion of calculation methods.

Major Elements (Weight percent)

	1	2	3	4	5
SiO ₂	21.4	—	92.6	—	16.44
TiO ₂	0.055	0.17	0.23	—	1.15
MnO ₂ (tot.)	10.5	1.7	.037	23.1	25.6
Fe ₂ O ₃ (tot.)	46.3	35.5	.72	19.0	18.05
Al ₂ O ₃	1.12	—	2.6	—	5.57
CaO	2.6	23.9	.18	—	3.12
MgO	2.0	4.1	.40	—	2.60
NiO	.043	.0073	.0007	0.52	0.62
CoO	.045	.0081	—	.27	.39
CuO	<.01	.0013	.0026	.36	.32
K ₂ O	.35	5.0	.63	—	.87
Na ₂ O	.48	—	.50	—	2.64
P ₂ O ₅	2.4	1.82	.03	—	.85
Ig. Loss	9.0	—	1.6	—	—
Sum	96.3	72.2	99.5	43.3	78.2

Minor and Trace Elements (PPM)

As	880	470	—	—	140
Ba	770	1065	105	—	2300
Cd	4.2	—	0.04	—	10
Ce	108	—	—	—	720
Co	350	63	—	2130	3000
Cr	55	—	18	—	70
Cu	4	10	21	3600	2600
Li	87	—	—	—	100
Mo	400	—	—	—	380
Ni	340	58	6	4060	4900
Pb	86	273	6	—	930
Pr	26	—	—	—	—
Sr	760	—	—	—	850
V	1320	960	18	0	520
Y	66	79	—	—	150
Yb	9.3	—	—	—	30
Zn	270	295	9	—	2200
Zr	111	—	—	—	160

The mean grain size of the sediment within which the nodules occur is 0.34 mm, and the mean diameter of the micronodules is 0.84 mm, a coarse sand. In addition to their larger size, the micronodules also have a higher mineral specific gravity ($2.98 \pm .08$) than the host sediments. However, they have a porosity of approximately 51% (corresponding to a water content of 25.8%), which yields a bulk density of 1.97 g/cc. Thus, because the density of the micronodules is well below that of quartz grains (2.62 g/cc), the micronodule grains may well be in hydraulic equilibrium with the remainder of the sand fraction. Because of this hydrodynamic relationship, the softness of the manganese crusts which would abrade during transport, and the brown stain on the host sediments, we believe that the micronodules formed *in situ*. Although the nodules represented slightly less than 1% of the sediment, they were the major authigenic component.

If the micronodules have formed since Georges Bank was submerged during the Holocene transgression, about 10,000 years ago, then the measured thickness of the ferromanganese crusts indicates that the minimum accretion rate for the micronodules is $0.3 \text{ mm}/10^4 \text{ years}$. This rate is rapid when compared with rates of accumulation for open-ocean nodules, but slow relative to the accumulation rates of shallow-water marine and freshwater-lake ferromanganese nodules (Manheim, 1965).

The concretions typically have smooth surface textures (Fig. 2). However, a few of the nodules show a granular botryoidal surface. Although the external shape of the micronodules generally ranges from rounded to well rounded and from elongate to equant, some of the nodules are saucer shaped, colloform, or joined by ferromanganese cement.

Energy-dispersive X-ray analyses and petrographic observation of thin sections reveal an internal structure composed of alternating concentric layers of iron- and manganese-rich compositions. These shell-like layers differ in both color and texture and commonly surround the entire micronodule. Abrasion within the shifting host sands often causes these soft ferromanganese layers to separate, resulting in the spherical weathering observed in many of the micronodules. Such abrasion apparently limits the size of the concretions and is probably responsible for the low minimum accretion rate. The concretions show no internal transverse or radial fractures filled with oxides, or other evidence suggesting diagenetic changes.

Most deep-sea ferromanganese nodules form about a nucleus of volcanic material, rock, or biologic debris. We crushed 50 micronodules from Georges Bank to determine the composition of their nuclei and found that 68% of them (34) had formed around detrital grains. Most of the seed grains were quartz or feldspar, but one nucleus was an opaque heavy mineral. No evidence of alteration was observed in any of the detrital core grains. The remainder of the micronodules had formed around fragments of ferromanganese crusts apparently broken off other nodules. Such micronodules tended to be less spherical than those accreting around detrital grains, probably because the ferromanganese fragments were not as well rounded. Therefore, the external size and

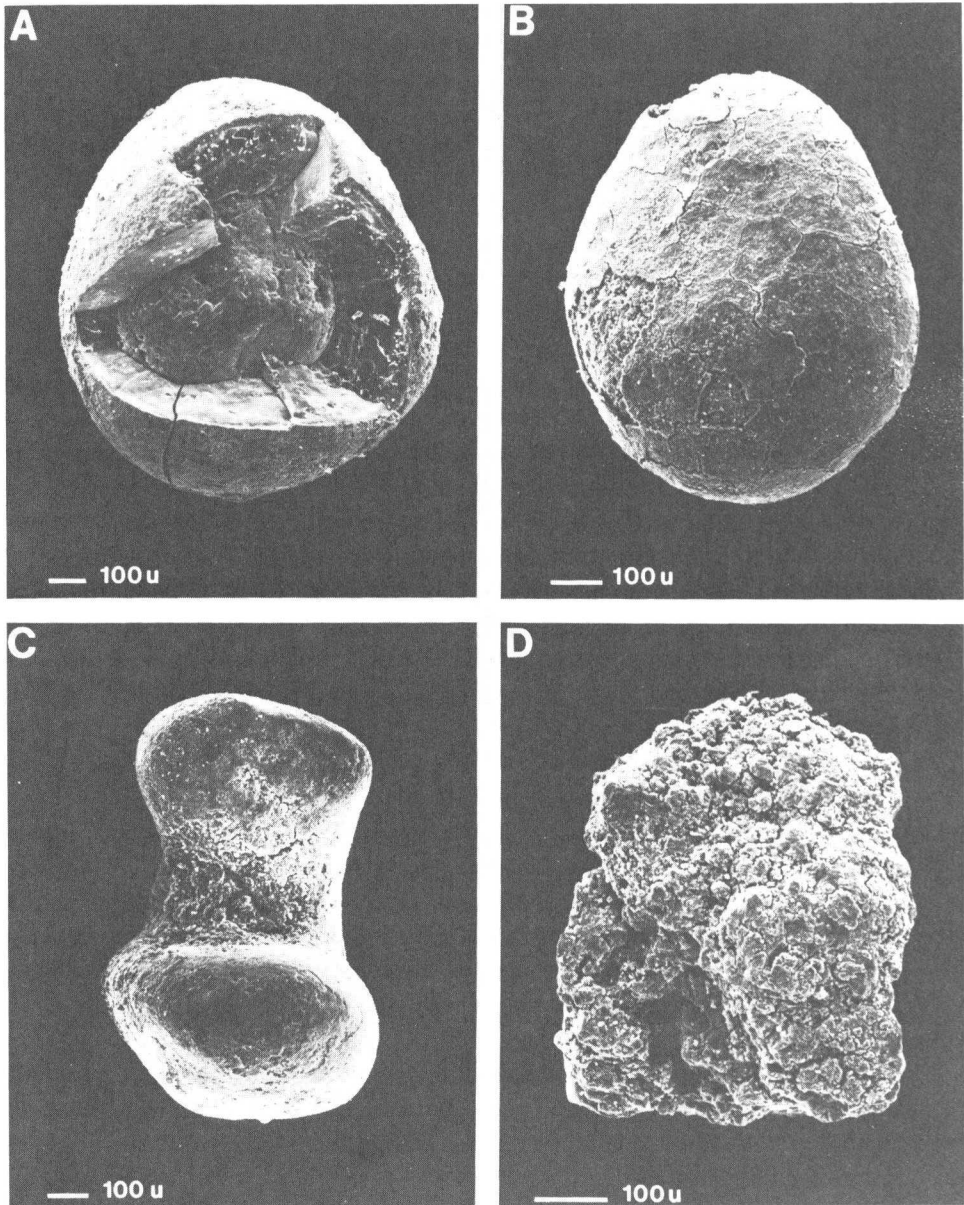


Figure 2. Scanning electron micrographs of ferromanganese micronodules found on Georges Bank. (A) Broken nodule showing detrital grain core. (B) Separation of alternating Mn and Fe rich layers caused by spheroidal weathering. (C) Ferromanganese cement connecting two micronodules. (D) Micronodule exhibiting botryoidal surface texture.

shape of a micronodule from Georges Bank are governed by the dimensions of its nucleus.

Marine manganese oxides are commonly characterized by numerous structural defects, vacancies in the crystal structure which may or may not be ordered, domain overgrowths, extensive solid solution, cation exchange properties, and/or small sizes of the crystallites (Burns and Burns, 1979). The ferromanganese micronodules found on Georges Bank, like many marine manganese oxides, were also poorly crystallized or amorphous, which complicated the attempt to determine their mineralogy by X-ray powder diffraction. Diffraction patterns of the nodules indicated the presence of quartz, feldspar, goethite, and vernadite (δ -MnO₂). The quartz and feldspar can be attributed to the seed grains around which the nodules accreted. The goethite forms thin layers within and covering many of the nodules.

The identification of vernadite was based on diffraction maxima at 2.45 and 1.42 Å. According to Burns and Burns (1979), these peaks represent the diffraction of X-rays from the (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) planes of hexagonally packed oxygens that contain Mn ions in octahedral coordination. The vernadite was observed in the analyses of wet, air-dried, and heated (60°C) samples. In addition, an unexplained 10 Å peak appeared on the X-ray pattern of the heated samples. The abundance of iron in the micronodules has probably inhibited the formation of more ordered Mn structures (Calvert, 1978).

The results of trace- and major-element analyses performed on the ferromanganese micronodules and the leachates of the stained host sediments were compared with results averaged from analyses of Georges Bank sediments and earlier studies of deep-sea nodules from around the world (Table 1). Like most neritic nodules (Price, 1967), the concretions from Georges Bank had lower Mn/Fe ratios than pelagic nodules and micronodules. The average Mn/Fe ratio (Table 2) from three samples of the Georges Bank micronodules is only 0.23, whereas this ratio averages 1.1 in deep-ocean micronodules.

At least part, and perhaps most, of the Si, Al, Na, Ca, Mg, and K concentrations may be attributed to detrital silicate nuclei or detrital and possibly authigenic silicates incorporated into the ferromanganese layers of the micronodules. Energy-dispersive X-ray spectroscopy of the manganese crusts also indicated elevated concentrations of these elements which suggests that the Fe/Mn layers of the micronodules do contain trace amounts of silicate minerals.

The micronodules contain about 2.4% phosphate, which is typical of shallow-water marine concretions but is about twice as much as is found in deep-sea nodules (Manheim, 1965). The micronodules contain lower concentrations of Co, Cu, Ni, Pb, Ce, and most other minor elements in comparison with pelagic ferromanganese concretions. Notable exceptions include As and V, which occur in concentrations greater than are present in most open-ocean nodules, and Mo, which was found in amounts roughly equal to amounts typical of open-ocean nodules. The brown stain that coated the host sediments revealed considerably lower Mn/Fe ratios, but otherwise

Table 2. Selected metals and ratios for micronodules and others phases. Data refer to oven-dried material. World micronodule average from Addy and Lindsay (1977).

Component	Georges Bank micronodules	Georges Bank stains	World average micronodules
Fe (%)	32.0	24.5	13.1
Mn (%)	7.6	1.24	14.6
Ni (ppm)	340	58	4060
Co (ppm)	350	63	2130
Mn/Fe	.23	.050	1.1
Ni/Mn	.0044	.0046	.028
Co/Mn	.0046	.0051	.014

elemental compositions are in fair agreement with those of the micronodules. The high calcium content is attributed to carbonate shell fragments.

4. Discussion

The origin of the Georges Bank micronodules and the stain on the host sediments is consistent with a model (Price, 1967) in which reduced Mn and Fe ions migrate up through the sediment column in interstitial waters and are preferentially oxidized and subsequently precipitated on the nuclei as more stable, higher-valence oxides and hydroxides. Oxygen is provided by the overlying bottom waters; a dissolved oxygen analysis on water collected near the bottom in the middle of the nodule-bearing sand patch contained 243 $\mu\text{Mol/kg O}_2$.

Because iron is more readily precipitated than Mn in marine sediments, it is the first to form coatings on the sand grains. This Fe-rich coating forms a favorable catalytic substrate for nucleation and precipitation of MnO_2 (Burns and Burns, 1975). Similar Ni/Mn and Co/Mn ratios for both stain and micronodules (Table 2) support the supposition that the Ni and Co present are principally associated with the manganese precipitation. The high concentrations of V, As, and Pb in the Fe-rich stains are consistent with previously observed correlations among these elements (Cronan, 1972). In particular, the positive charge of Fe oxide colloidal surfaces may facilitate formation of initial ferric vanadates, arsenates, and plumbates, as well as phosphates (Murray and Brewer, 1977). Molybdenum content in the micronodules, on the same level as that in deep ocean nodules, is consistent with the virtually constant Mo/Cl ratio in sea water (Manheim and Landergren, 1978), and hence its availability for precipitation with MnO_2 in the interstitial sites. The concentrations of Co, Ni, Ce, Zn and other constituents in the Georges Bank micronodules are an order of magnitude lower than their average concentrations in deep ocean nodules and micronodules. This relationship probably results from the rapid accretion rates and the relatively greater supply of Mn and Fe from pore waters in the Georges Bank substrates.

Higher titanium concentrations in the stain than in the micronodules are not

explainable by the relatively constant Fe-Ti relationship in nodules (Calvert, 1978); the Ti concentration may be affected by Ti-rich particulate matter in the leachates, as the leachates were aspirated into the ICP without filtration. The high Ba concentrations (1065 ppm) in the host sediment leachates may reflect the presence of drilling mud used during the exploratory drilling for hydrocarbons on Georges Bank. The very low copper values remain unexplained.

The Georges Bank micronodules form between water depths of 60 to 100 m and in areas where the sands are periodically, but not constantly, agitated. Finite amounts of degradable organic matter are better preserved here than in the generally coarser sediments of shallower, higher energy environments and may create reducing microenvironments that further enhance interstitial metal content. Abrasion within the shifting host sands causes spheroidal weathering and separation of the poorly adhered, soft, Fe- and Mn-rich oxide layers. This abrasion apparently limits the size of the concretions.

Most of the Si, Al, Na, Ca, Mg, and K concentrations are attributable to detrital silicates in seed grains and were leached with the hot-concentrated HCl treatment. However, energy-dispersive X-ray spectroscopy shows locally elevated concentrations of these elements within the Fe-Mn layers of the micronodules. These concentrations suggest that the oxide phases may contain finely divided detrital and possibly authigenic admixtures of the above elements.

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