

Reductive microbial dissolution of manganese nodules as a possible hazard of deep-sea mining

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ABSTRACT: The microbial lysis of deep-sea nodules as a possible result of large-scale, deep-sea mining is considered. It is assumed that the Mn (IV) and Fe (III) compounds of the manganese nodules are reduced by the numerous aerobic bacteria at the sediment/water interface as soon as the adjacent nodule area is buried by sedimentation of the disturbed deposits and the organic-rich debris from the blooming surface plankton. Intensive mineralization processes in the resettled sediments cause oxygen depletion. Subsequently, the aerobic (and anaerobic) microorganisms will switch to Mn (IV) and Fe (III) oxides as alternative electron acceptors in order to continue their energy-conserving (ATP synthesis) reactions (anaerobic respiration). The higher the amount of decomposable organic matter, the more intensive are these processes. Consequently, buried manganese nodules may be dissolved, thereby liberating mobile Mn (II), Fe (II) and several trace elements (Ni, Cu, Co and others). This possible hazard and its ecological consequences should be evaluated carefully before deep-sea mining is started on a large scale.

INTRODUCTION

Approximately 100 years ago, the first manganese nodules were discovered by the British research vessel "Challenger" on the bottom of the Atlantic Ocean at depths between 4000 and 5000 m. However, not until the mid-sixties was the economic importance of these – in fact polymetallic – concretions recognized (Mero, 1962). Because of the relatively high content of nickel, copper, cobalt and manganese (Table 1), these mineral accretions may become increasingly important, since the terrestrial sources of these essential elements may run short within a very limited period of time. At present, the reserves of Cu have been estimated 38 times, those of Ni even 200 times higher than the actual continental supplies (Schneider, 1977). Based on conservative calculations the resources recoverable from the Pacific nodule belt have been estimated to account for 170 million tons of nickel, 155 million tons of copper, 30 million tons of cobalt and even 3.7 billion tons of manganese (Fellerer, 1975). The economic significance of these potential sources of raw material has been recognized and international associations have been established (Hubred, 1975; Mero, 1977; Schneider, 1977). Such consortia are required to develop appropriate mining technologies as well as to share the considerable economical risks. Meanwhile, different pilot projects for testing the deep-sea mining systems with mining ships such as "Sedco 445" were undertaken successfully during 1978 (Summerer, 1978). There seems to be no doubt that we may expect deep-sea mining on a large scale within the next 10–30 years.

DISTRIBUTION AND COMPOSITION

Manganese nodules are widely distributed (25–80 % coverage) on the bottom of the deep sea, particularly in the Pacific Ocean. Generally speaking, they may occur at almost all depths and latitudes both in the oceans and in certain fresh-water lakes. However, the most abundant deposits are found on the surface of the pelagic sediments in the deep sea (Hubred, 1975; Cronan, 1978). These areas of genesis are characterized by (a) an extremely low sedimentation rate, (b) a relatively low biological productivity and (c) by a continuous supply of oxygen by (arctic) bottom waters. These features are usually restricted to the central regions of oceans far from terrigenous (organic) supply. It is only at a low mineralization rate, a restricted supply of Mn and Fe, and a permanent aerobic environment (reflected by the relatively high Eh of + 400 to + 565 mV) that nodules may develop at a slow, but steady accretion rate (a few mm/10⁶ years). These ecological prerequisites may explain why the most abundant (and economically interesting) deposits have been recorded north and south of the equator in the Pacific Ocean. So far, the minimum abundance of nodules required to start mining has been estimated as

Table 1. Survey of the average dry-weight percentages of 26 different elements* in 54 manganese nodules collected from the Pacific Ocean

Element	Maximum	Minimum	Average (dry weight %)
B	0.06	0.007	0.029
Na	4.7	1.5	2.6
Mg	2.4	1.0	1.7
Al	6.9	0.8	2.9
Si	20.1	1.3	9.4
K	3.1	0.3	0.8
Ca	4.4	0.8	1.9
Sc	0.003	0.001	0.001
Ti	1.7	0.11	0.67
V	0.11	0.021	0.054
Cr	0.007	0.001	0.001
Mn	50.1	8.2	24.2
Fe	26.6	2.4	14.0
Co	2.3	0.014	0.35
Ni	2.0	0.16	0.99
Cu	1.6	0.028	0.53
Zn	0.08	0.04	0.047
Ga	0.003	0.0002	0.001
Sr	0.16	0.024	0.081
Y	0.045	0.0033	0.016
Zr	0.12	0.009	0.063
Mo	0.15	0.01	0.052
Ba	0.64	0.08	0.18
La	0.024	0.009	0.016
Yb	0.0066	0.0013	0.0031
Pb	0.36	0.02	0.09

* Data taken from Mero (1962); see also Hubred (1975) and Cronan (1977, 1978)

8000 tons/km² with metal contents (weight % of dry material) of 1.25–1.40 % Ni, 0.05–1.35 % Cu, 0.18–0.25 % Co and 25–28 % Mn (Fellerer, 1975; Cronan, 1978). These trace elements are intimately intermixed with the concentric layered amorphous and (crypto)-crystalline Mn (IV) and Fe (III) oxides as well as with other Mn and Fe phases (Crerar & Barnes, 1974; Hubred, 1975; Friedrich et al., 1977). The interior of the manganese nodules is characterized by high porosity (Halbach et al., 1975) and a great variety of small-scale columnar cups orientated with their long axes in the radial plane of the nodules (Hubred, 1975; Cronan, 1978). This high porosity and internal surface area makes post-depositional redissolution and migration of metals possible. Because of the lower activation energy required to reduce Mn (IV) compounds (mainly birnessite = δ -MnO₂ and todorokite) compared with the amorphous and crystalline Fe (III) oxides (McKenzie, 1972; Crerar & Barnes, 1974), we may expect the Mn (IV) components to be dissolved much more rapidly and earlier than the corresponding Fe (III) structures. Such a selective dissolution of different constituents would disintegrate the nodule considerably. Indeed, such internal "erosional features" have been observed repeatedly (Hubred, 1975; Cronan, 1978).

ROLE OF MICROORGANISMS IN GENESIS

In general, areas with high nodule densities have lower metal contents and vice versa. However, nodules of a single restricted region may also differ considerably in their chemical composition, although some remarkable relationships between certain elements have been observed (Friedrich et al., 1973; Marchig and Gundlach, 1976; Friedrich et al., 1977; Halbach et al., 1979). Thus, Fe, Mg (and Co) on the one hand, and Mn, Ni, Cu and Co on the other, are usually well correlated. The highly significant correlation between Mn and Ni (with a Mn/Ni ratio of 23) indirectly supports the view that positively charged ions (such as Ni⁺) are adsorbed physico-chemically onto the primarily negatively loaded Mn colloids by extracting these cations from the sea water. Although this scavenging theory of Goldberg (1954) has been generally accepted (Crerar & Barnes, 1974), the mechanism of Mn (IV) oxide formation has not yet been completely elucidated. This is caused by the fact that Mn (II) is both undersaturated (with an average concentration of 2 ppb) and chemically stable (at pH 7.7–8.1 and Eh values between +400 to 565 mV) (Crerar & Barnes, 1974; Hartmann et al., 1975; Müller, 1977) at the pelagic sediment/water interface. Even if Mn (II) is extracted from the undersaturated sea water by (weakly) positively charged Fe (III) colloids and mineral-sorbed particles, the oxidation and precipitation of Mn (II) may be explained only by assuming an autocatalytic surface effect (caused by an increased Eh) (Crerar & Barnes, 1974) and/or by the biocatalytic activity of certain bacteria (Ehrlich et al., 1972; Kuznetsov, 1975; Schütt & Ottow, 1977; Nealson, 1978). The possible role of microorganisms in the formation of iron-manganese concretions (nodules) has been a point of considerable discussion ever since the suggestions of Butkewitsch (1928). These arguments can be ascribed to the poor knowledge of the microflora in the sediment/water interface of the pelagic sediments. Differentiated quantitative and qualitative microbiological population studies with freshly taken, non-contaminated manganese nodules and sediment samples showed that this area is inhabited abundantly by a specific, mainly aerobic bacterial flora, lacking actinomycetes and fungi (Table 2) (Schütt & Ottow, 1977, 1978;

Schütt, 1979). These studies further clearly demonstrated the presence of a great number of bacteria, potentially capable of precipitating Mn (II) to Mn (IV), both in and on the nodules as well as in the surrounding water and sediments. However, none of the isolated organisms developed with Mn (II) only, but all precipitated Mn (IV) readily in the presence of a low amount of glycerol as the carbon source (Schütt, 1979). A portion of the manganese-precipitating bacteria (such as *Vibrio* spp.) even dissolved nodule material by using Mn (IV) as an alternative electron acceptor if the amount of organic carbon was increased significantly. Obviously, it is the amount of degradable organic matter rather than the actual presence of these bacteria that determine whether Mn (II) precipitation or Mn (IV) reduction will occur.

ROLE OF ORGANIC SUPPLY

In Figure 1 the conditions and processes in the neritic and pelagic sediments are summarized and compared. There is no doubt that the differences are caused primarily by the significant variation in the supply of degradable organic matter. In the neritic zone, a continuous supply of organic matter (due to continental erosion and high primary

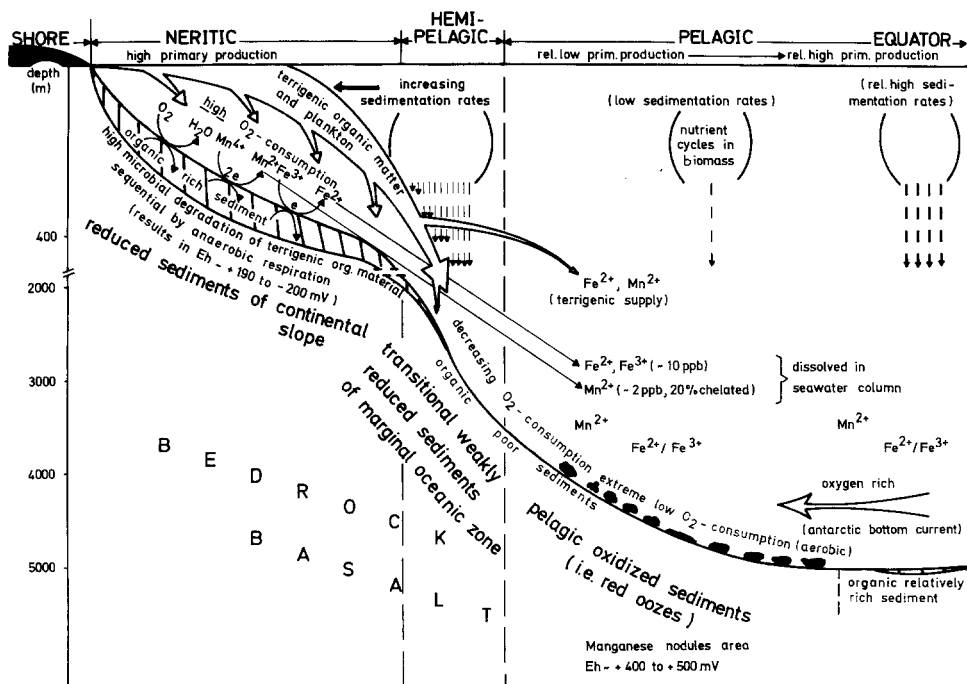


Fig. 1. Fate of the Mn and Fe compounds in the neritic zone compared with the pelagic sediments. In the neritic zone Mn (IV) and Fe (III) oxides (and hydroxides) are reduced microbiologically by acting as alternative electron acceptors. In the pelagic sediments far from the continental slope Mn (II) and Fe (II, III) compounds are immobilized (nodule genesis) by chemical and/or microbial activity. These opposite processes are essentially caused by the significant differences in organic supply (energy source for mineralization)

Table 2. Survey of various groups of bacteria determined on the top side (T), bottom (B) and in the center (C) of 6 ferromanganese nodules collected from the bottom of the Pacific Ocean

Bacterial groups tested* **	Top side (T)		Bottom (B)		Central core (C)	
	E/S-type (5)***	Kg-type (1)***	E/S-type	Kg-type	E/S-type	Kg-type
(A) Dilution tube method (MPN/g)						
Total number of aerobic bacteria (30 °C)	5.4×10^5 – 3.1×10^7	3.1×10^6	9.5×10^5 – 5.4×10^6	NT	1.2×10^5 – 5.4×10^6	1.2×10^6
Psychrophilic bacteria (5–6 °C)	3.1×10^4 – 3.1×10^5	1.2×10^6	1.2×10^5 – 5.4×10^5	NT	1.2×10^5 – 5.4×10^5	5.4×10^4
Halophilic bacteria (+ 20 % NaCl)	1.2×10^3 – 3.1×10^5	5.4×10^5	1.2×10^3 – 5.4×10^5	NT	5.4×10^3 – 5.4×10^4	3.1×10^5
Denitrifying bacteria (37 °C)	1.2×10^2 – 5.4×10^3	1.2×10^3	2.0×10^2 – 3.1×10^3	NT	1.2×10^2 – 5.4×10^3	1.2×10^2
Fe (III)–NH ₄ –citrate ⁺ precipitating bacteria (synthetic medium; 30 °C) ⁺	0 – 1.2×10^2	0	0 – 3.1×10	NT	0 – 1.2×10^2	0
Total number of anaerobic bacteria	1.2×10^3 – 5.4×10^4	1.2×10^3	1.2×10^2 – 1.2×10^4	NT	5.4×10^2 – 3.1×10^4	3.1×10^3
(B) Semiquantitative method = highest dilution with positive test on Mn (IV) when streaked on MnCO₃-yeast extract-citrate agar (Mulder & Van Veen, 1963)⁺⁺						
Mn (II)-precipitating ⁺⁺ mesophilic (30 °C) bacteria	ca. 10^4 – 10^5	$\sim 10^5$	$\sim 10^4$ – 10^6	NT	$\sim 10^3$ – 10^6	NT

* Population densities (highest and lowest values recorded) are expressed in Most Probable Number per g oven-dry material (MPN/g); for details see Schütt & Ottow (1977) and Schütt (1979)

** Neither fungi and actinomycetes, nor sulfate-reducing bacteria could be detected; nitrifying bacteria were irregularly distributed

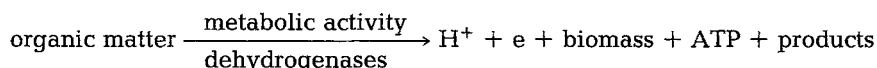
*** E/S-Type = ellipsoidal to spheroidal mono-nodule; Kg-Type = ellipsoidal to spheroidal poly-nodule; for classification consult Meyer (1973)

⁺ Fe(III)-NH₄-citrate was selected as a model compound for the capacity to mineralize Fe-organic chelates (= Fe-precipitating bacteria)

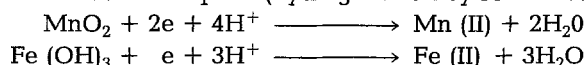
⁺⁺ Bacteria, potentially capable of precipitating Mn (II) (estimated semi-quantitatively); most abundant representatives were identified as members of *Pseudomonas* spp., *Alcaligenes* spp. and *Vibrio* spp. (see Schütt & Ottow, 1978; Schütt, 1979)

production) will lead to intensive mineralization processes. As soon as oxygen has been respired, aerobic and anaerobic bacteria switch to nitrate, Mn (IV) and Fe (III) as alternative electron acceptors in order to continue their energy conserving reactions (ATP synthesis) (Trimble & Ehrlich, 1968; Ottow & Glathe, 1973; Munch & Ottow, 1977; Munch et al., 1978). These processes may be summarized as follows.

Biological oxidation (= dehydrogenation):



Mn (IV) or Fe (III) oxides as H-acceptors (hydrogenation by reductases):



Oxygen depletion and the accumulation of reduced products are responsible for the rapid drop in Eh (in the range of +190 to 220 mV). It is important to realize that Mn (IV) and Fe (III) are reduced directly by metabolic activity rather than indirectly by a lowered redox potential. A drop in Eh is the result of microbial reduction processes and not a mechanism of relevant chemical transformations. Its significant role is restricted to the creation of a certain redox level that may support the stability of Mn (II) or Fe (II) compounds.

Beyond a transitional area (with minor or moderate organic supply and thus relatively low microbiological activity) we usually find the central pelagic zone (red oozes) with extremely low organic sedimentation rates (Volkov et al., 1975). These areas with extended fields of manganese nodules are relatively poor in organic matter (0.1–0.3% organic carbon) (Müller, 1977), strictly aerobic and characterized by extremely low oxygen-consumption rates. The restricted microbial activity is supported by low temperatures (nearly ± 1 °C) and the enormous hydrostatic pressure (5000-m depth corresponds to 500 bar). Due to the low bacterial activity, the redox potential remains at levels of +400 and +565 mV (Müller, 1977). Such conditions should be considered as the main prerequisite for nodule formation.

The equator region, however, is characterized by relatively high primary production and thus higher sedimentation rates of organic matter which result in enhanced microbial activity and reduction processes. Consequently no nodules may be generated in this particular area of the central ocean.

NODULE LYSIS AS AN ENVIRONMENTAL IMPACT

In Figure 2 the original deep-sea situation (A) is compared with the conditions (B) that may result from deep-sea mining. Apart from the direct influence of discharged by-products, prolonged deep-sea mining may induce at least two side effects. Firstly, the disturbed sediments may pollute the upper water column with clays and particulate organic matter (POM), which settle again only very slowly. The turbidity will destroy marine phyto- and zooplankton as well as the sessile fauna in the area close to the hauling plant (Thiel, 1975, 1978; Amos et al., 1977). However, there may be a second problem that should be outlined here. Once disturbed, the suspended organic matter will be mineralized rapidly and the liberated nutrients will probably support a plankton

bloom in the surface regions (increased primary production). Unmined manganese nodules will be buried by settling of the suspended material, which is significantly enriched by phytoplanktonic debris. This additional energy supply will increase the activity of the microorganisms and the rate of oxygen consumption. Because of oxygen depletion, the bacteria will switch to other electron acceptors such as NO_3^- , Mn (IV) and Fe (III) causing denitrification as well as the reductive dissolution of manganese nodules (Fig. 2B). The higher the amount of decomposable organic debris, the more intensive and complete is the lysis of buried manganese nodules in the sediment. These intensive mineralization processes cause the Eh to drop rapidly. At this stage, the processes and conditions in the upper layers of the disturbed sediments are comparable with the neritic situation at the continental slope. Although the mobilized Mn (II) and Fe (II) compounds may be reprecipitated in the aerobic area near the hauling plant, the fate of the liberated trace elements is unknown.

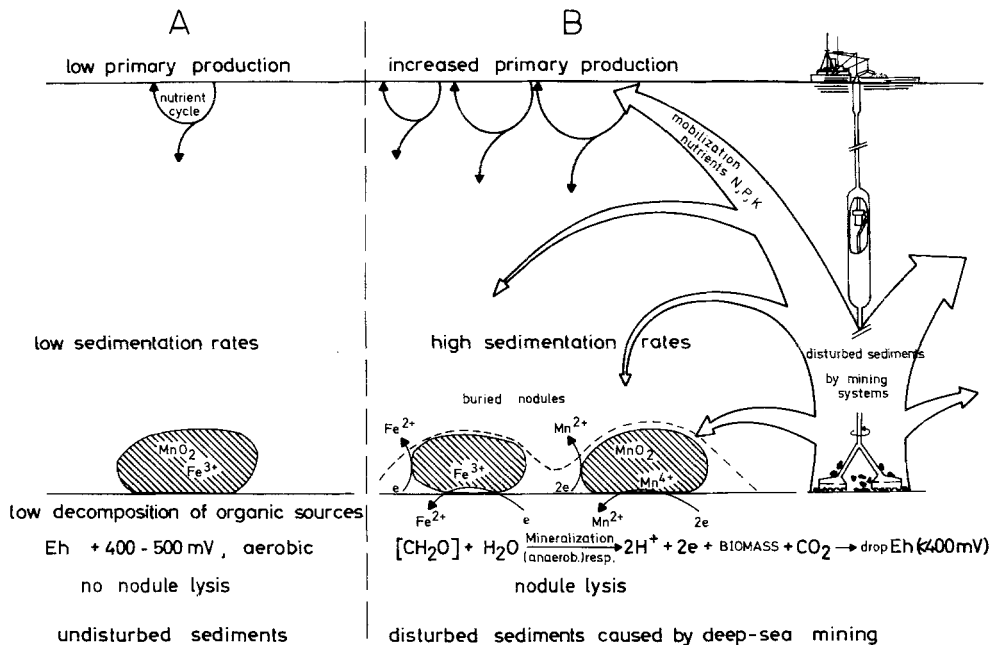


Fig. 2. The lysis of manganese nodules as a possible result of deep-sea mining. Because of mining activity (B), sediments are disturbed, nutrients become mobilized and primary production will occur. Nodules next to the hauling plant are buried by resettled sediments enriched with organic debris. In the following intensive mineralization processes oxygen may become exhausted, and microorganisms will switch to Mn (IV) and Fe (III) oxides as alternative electron acceptors in order to continue their energy-conserving reactions (ATP synthesis by anaerobic respiration)

Although our hazardous interpretation is largely hypothetical, its ecophysiological background is derived from well established processes that occur in organic-rich, hydromorphic soils (Ottow & Glathe, 1973; Munch & Ottow, 1977). We therefore wish to attract attention to the possible economical and ecological risks that may arise from deep-sea mining performed on a large scale. The risks outlined here should be experi-

mentally examined before deep-sea mining is started. The "water desert" of the central Pacific is – like most other living systems – the result of a sensitive biological balance. We should learn in future to consider ecological knowledge as an essential prerequisite for responsible environmental management.

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