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# OCCURRENCE OF MANGANESE-RICH MICROPARTICLES IN THE EASTERN BASIN OF LAKE ERIE

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## ABSTRACT

Electron microscopy, combined with X-ray microanalysis, of suspended solids collected from the Eastern Basin of Lake Erie revealed a number of particles containing large concentrations of manganese and small quantities of Si, K, Ca, S, Cu and Zn. The particles were found, at one of the four sampling stations, in a fraction that passed a 3-μm-porosity membrane filter. The morphology of the particles shows characteristics similar to those of a manganese-precipitating organism known as *Metallogenium personatum*, which plays an important role in the formation of freshwater manganese deposits and may further serve as adsorption sites for heavy metals.

*Keywords*: suspended solids, Eastern Basin of Lake Erie, Ontario, manganese-rich particles, *Metallogenium personatum*.

## SOMMAIRE

Par microscopie électronique et microanalyse aux rayons X, on trouve que les particules en suspension dans le bassin Oriental du lac Erie contiennent de fortes teneurs en Mn et de faibles quantités de Si, K, Ca, S, Cu et Zn. Dans un des quatres sites d'échantillonnage, ces particules se trouvent dans la fraction qui passe un filtre à membrane de 3 μm de porosité. Par leur morphologie, ces particules rappellent l'organisme *Metallogenium personatum*, qui induit la précipitation du manganèse. Cet organisme, qui joue un rôle important dans la formation de gisements de Mn en eau douce, pourrait servir de site d'adsorption pour métaux lourds.

(Traduit par la Rédaction)

*Mots-clés*: particules en suspension, bassin Oriental du lac Erie, Ontario, manganèse, *Metallogenium personatum*.

## INTRODUCTION

Some of the Mn and Fe supplied to the freshwater system and to the oceans is deposited in the form of ferromanganese oxides or manganese nodules. The origin, occurrence and composition of these nodules have been studied intensively during recent years. The chemical concepts of formation and physicochemical characteristics of manganese nodules were reviewed by Marshall (1979). Several factors affecting the enrichment of marine and lacustrine nodules by various metals were discussed by Cronan (1977) and Calvert & Price (1977).

Allan (1979) found micronodules containing 4% Fe, 0.6% Mn and 383 μg/g Ni in Great Slave Lake, N.W.T. The occurrence and geochemistry of manganese nodules in the Great Lakes were described by Rossman & Callender (1968), Cronan & Thomas (1970, 1972) and Damiani *et al.* (1973). Marshall (1979) reviewed the present knowledge of microbial transformations of manganese in freshwater and marine systems, including the conditions necessary for microbial involvement in the formation of sedimentary manganese deposits.

This contribution describes the occurrence and morphology of manganese microparticles found in the water of the Eastern Basin of Lake Erie, as part of an ongoing investigation of the morphology of suspended particles and their association with metals in the Great Lakes.

## MATERIALS AND METHODS

Water samples were collected in August 1978 at four stations in the Eastern Basin of Lake Erie (Fig. 1) to investigate the chemical composition of suspended solids. About 600 l of water from 1 m below the surface and from 2 m above the bottom were collected and centrifuged to obtain a sufficient quantity of suspended solids for chemical analyses. Collected samples were then dried by lyophilization. Simultaneously, about 2 l of water were collected at the same depth and sampling stations using a Van Dorn bottle. About 100 ml of each of these water samples was filtered through a set of Unipore membranes (pore size 8, 3 and 0.45 μm) to separate the particles by size. The membranes were then dried in a desiccator and

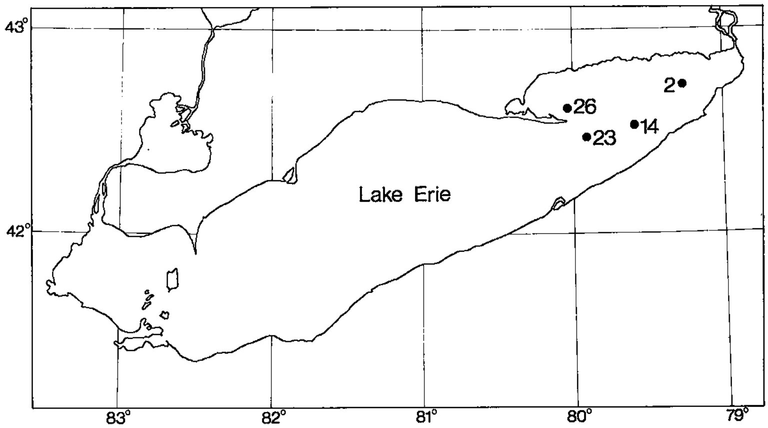


FIG. 1. Location of sampling stations in the Eastern Basin of Lake Erie.

used for our investigation of the morphology and chemistry of individual particles by electron microscopy. For this purpose, a section of about 1 $cm^2$ was cut out from each membrane, mounted on the specimen stub and carbon-coated. The suspended particles of sediment were investigated by SEM (AMR 1000) interfaced with an energy-dispersion X-ray spectrometer (TN–11). Several micrographs were obtained to document the morphology of the particles. To obtain a qualitative chemical analysis of the material, we focused the static beam of electrons on individual particles. The X-ray spectrum was accumulated for 60 seconds using 20 kV accelerating potential and $1 \times 10^{-9}$ A beam current. Chemical analyses of water samples were carried out according to the Analytical Methods Manual (1979).

## RESULTS

Abundant ring-shaped particles were found at station 2, 2 m above the bottom in the 3-$\mu$m-size fraction (Fig. 2). Figure 3 shows one of the manganese-containing rings at a magnification of 20,000, together with results of the X-ray microanalysis by energy dispersion. The ring dimensions are approximately 2.5 $\mu$m on the outside diameter and about 1.3 $\mu$m inside. The wall appears to be a biological structure, deformed by inadequate preparation for biological material (the specimen was not fixed to preserve micro-organisms and was air-dried after filtration). The major element detected in the particle is manganese. Small quantities of S, Cl, K and Ca also detected in the particle are usually associated with organic material. Si can originate

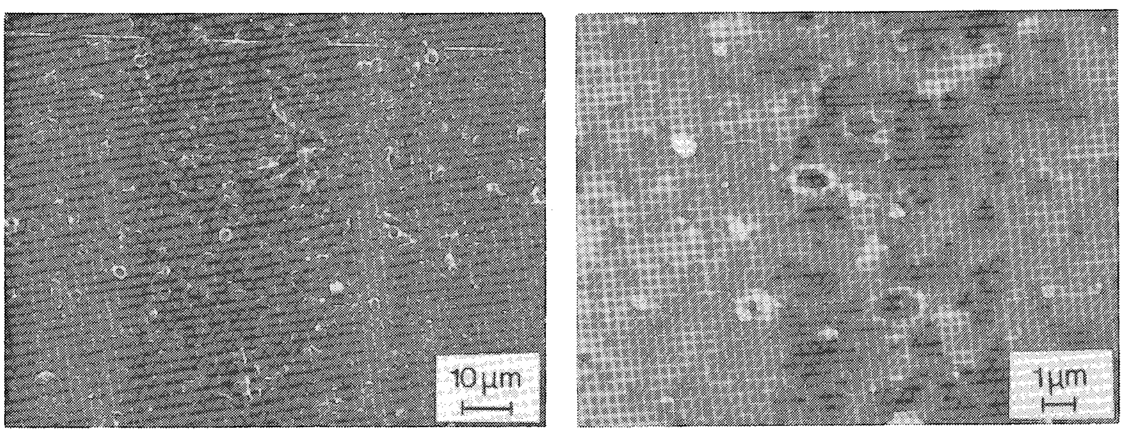


FIG. 2. Scanning-electron photomicrographs of the manganese-rich ring-shaped microparticles found at sampling station 2 in the Eastern Basin of Lake Erie.

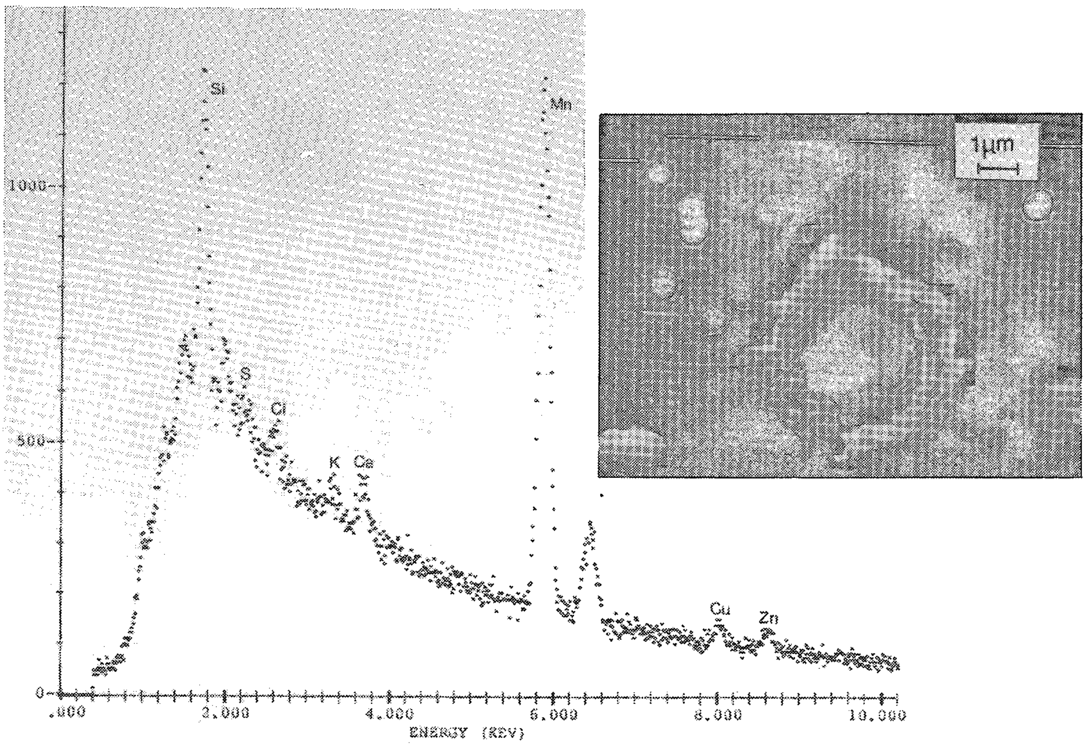


FIG. 3. Scanning-electron photomicrographs of the manganese-rich ring-shaped microparticles at a higher magnification (x20,000) with results of X-ray analyses by energy dispersion. Specimen collected in August 1978 at station 2, 1 m from bottom.

either from the organic material or from a quartz microparticle incorporated in the structure. Allan (1979) demonstrated the presence of quartz in ferromanganese nodules from Great Slave Lake. He suggested that the small nodules are quartz grains with amorphous coatings rich in Mn, Ni and Pb. The EDX spectrum in Figure 3 shows the presence of Cu and Zn in the ring-shaped particle from Lake Erie.

A star-shaped particle about 2 μm in diameter also was found to contain manganese (Fig. 4). It includes a number of flagellae protruding from a central ring. The EDX spectrum shows a composition similar to that of the ring-shaped manganese particle. No similar particles were found at the other sampling stations investigated.

The environmental conditions at each station during the sampling time are outlined in Table 1, together with concentrations of Mn and Eh values measured in the 3-cm surface-sediment layer, as given by Thomas & Mudroch (1979).

As shown in Table 1, at station 2, the concentration of dissolved oxygen at a depth of 20 m was slightly lower than at the other stations; the concentration of dissolved manganese was 1.5 μg/l compared with 3.90 and 1.80 μg/l at stations 14 and 26, respectively. MnO concentration in the surface sediment was similar at all four stations, and the redox potential was lowest at station 2. However, except for the large difference in the bottom temperature, the measured parameters did not differ very much from station to station.

## DISCUSSION

Certain aspects of abiotic formation of manganese deposits in the Great Lakes environment are supported by many studies. Rossman & Callender (1968) found manganese coatings and crust on sand grains, pebbles, cobbles and as part of the bulk sedimentary material in Lake Michigan. They found enrichment in manganese in the upper 10 cm of several sediment cores as compared with the lower parts of the cores. The manganese content of interstitial water from Green Bay and northern Lake

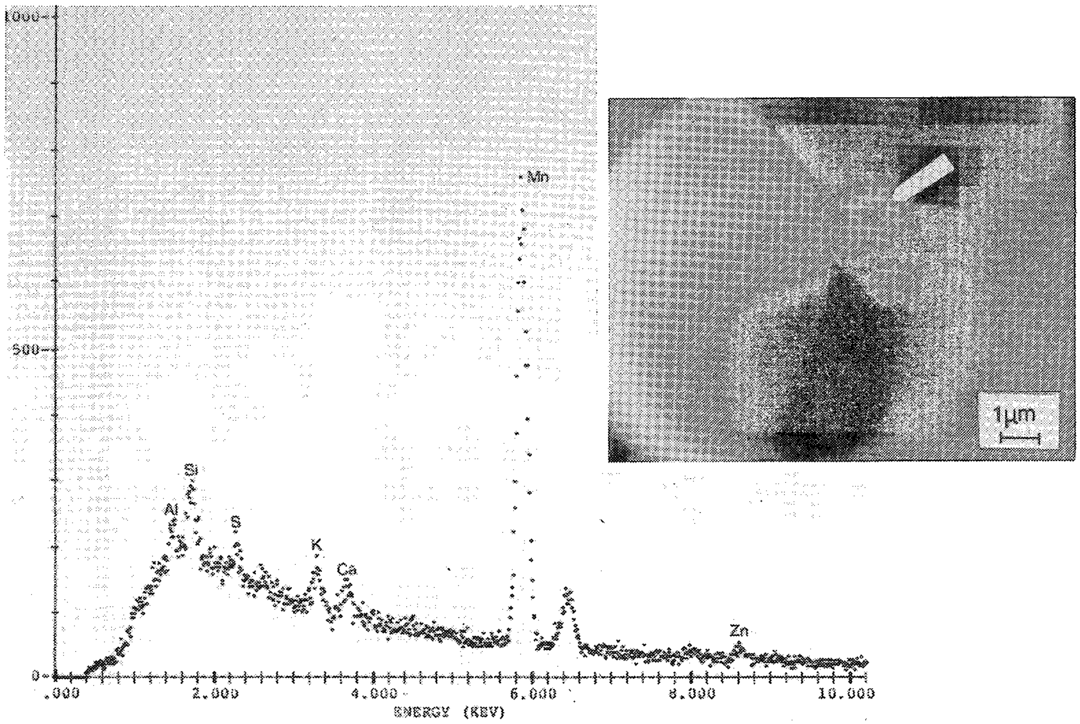


FIG. 4. Scanning-electron micrograph with EDX spectrum of a star-shaped microparticle found at sampling station 2 in the Eastern Basin of Lake Erie. Specimen collected in August 1978 at station 2, 2 m from bottom.

Michigan sediments was found to be enriched over lake water (< 1 to 25 ppb Mn) as much as 2500 and 4000 times, respectively. In addition, the manganese content of rivers entering Green Bay is up to 20 times higher than that of the lake. Cronan & Thomas (1972) found large deposits both of sands coated with ferromanganese oxide and of scattered manganese nodules in the northern part of Lake Ontario. Mn is present, in the interstitial waters of the sediments underlying the deposit, in higher concentrations than in the overlying lake waters. The origin of these deposits is thought to be related (1) to the upward diffusion of Mn and

TABLE 1. PARAMETERS MEASURED AT THE SAMPLING STATIONS

| Station No. | Depth m | Water Column: Dissolved $O_2$ mg/l | Dissolved Mn ug/l | Temperature °C | Surface Sediment[a]: MnO % | Eh mV |
|---|---|---|---|---|---|---|
| 2 | 2.0 | 8.8 | 0.45 | 23.4 | 0.2 | -100-0 |
| | 20.0 | 8.3 | 1.50 | 22.9 | | |
| 14 | 2.0 | 8.7 | 0.68 | 22.6 | 0.2 | 0-100 |
| | 43.0 | 9.8 | 3.90 | 4.5 | | |
| 23 | 2.0 | 8.6 | n.a. | 15.8 | 0.2 | 0-100 |
| | 60.5 | 9.8 | n.a. | 4.2 | | |
| 26 | 2.0 | 9.9 | 0.40 | 21.3 | 0.2 | 0-100 |
| | 40.5 | 11.4 | 1.80 | 4.6 | | |

[a] Data of Thomas & Mudroch (1979)
n.a. = not analysed
pH range of water = 8.3-8.5

Fe from the underlying sediments and (2) to the movement of manganese-enriched bottom waters of the Central Basin towards the northern shore, where the redox potential of the surface sediments ranges between 300 and 400 mV.

Damiani *et al.* (1973) found manganese nodules in the Bay of Quinte, Lake Ontario, both in association with thin lag sand or gravel derived by erosive action on glacial deposits, and directly upon a glaciolacustrine clay surface. X-ray-diffraction results revealed the presence of goethite in all the Bay of Quinte nodules and rhodochrosite in one. The nodules collected from the other parts of Lake Ontario were reported to be of amorphous character.

Conditions necessary for microbial involvement in the formation of manganese deposits in a freshwater environment have been reported by many authors and were summarized by Ehrlich (1976). Perfil'ev & Gabe (1965) discovered a new genus of the manganese-oxidizing and -depositing microbe *Metallogenium personatum* in the upper layer of the bottom sediments of a number of lakes in Karelia (U.S.S.R.). In a meromictic lake, Dubinina *et al.* (1974) found the maximum population of the manganese-oxidizing micro-organisms *Metallogenium personatum* at a depth of 23 m, with an oxygen concentration of 0.05 mg/l.

Both teams of investigators mentioned above found a filamentous star-like structure of the organism at one stage of its development very similar to that which we observed in microparticles in Lake Erie at station 2 (Fig. 4). The abundant ring-shaped manganese particles also observed at this station at depths of 2 and 20 m may be a stage of the complex life-cycle of *Metallogenium* sp. in this specific environment.

No manganese-containing particles were detected at the other three sampling stations, and there was no stratification of water at station 2. However, the thermocline was observed at a depth of 21 to 25 m at the other sampling stations.

According to the abiotic theoretical model of Delfino & Lee (1968), manganese at a depth of 20 m at station 2 would be present mainly as $MnO_2(s)$ or as Mn(II) sorbed onto iron and manganese oxides. Ehrlich (1976) suggested that Mn(II) is oxidized rapidly to Mn(IV) by micro-organisms associated with the particulate oxides. According to Perfil'ev & Gabe (1965), the more highly reducing conditions in the surface sediment at station 2 would be suitable for multiplication of *Metallogenium personatum*, which may further migrate from the sediment to the overlying water. The low redox potential of the sediment would be the only explanation for the origin and growth of *Metallogenium* sp. So far, this organism has been found in water of low oxygen concentration and higher in manganese content than observed at station 2. Because the instrument used was not capable of detecting elements with atomic number $< 11$, *i.e.*, O, C and H, we were unable to determine if the microparticles were composed of manganese oxide or carbonate.

No manganese deposits have been reported in Lake Erie; however, Burns & Nriagu (1976) found that particles in the Lake Erie waters were relatively enriched in manganese, compared with the sediment. This was attributed to the solution and reprecipitation of manganese in the Lake Erie sediment. They suggested the transport of manganese extracted from sediment from the Western to Eastern Basin of Lake Erie. MnO concentration in surficial sediments at some localities in Lake Ontario exceeds 1% (Thomas & Mudroch 1979), and ferromanganese concretions have been found in the northern part of the Lake and in the Bay of Quinte. These concretions contain Ni, Cu, Co, Pb and Zn (Cronan & Thomas 1970, 1972, Damiani *et al.* 1973) and therefore play an important role in the transport and distribution of these metals in Lake Ontario.

Studies by Simons (1976) and Lam & Simons (1976) showed that water is transported from Lake Erie into Lake Ontario. The manganese microparticles may then be transported in the water; they may either settle at a depositional basin or be further transported into an area with optimal conditions for manganese deposition, where they may provide nucleation sites or adsorbing surfaces for manganese and iron, as well as for other metals.

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