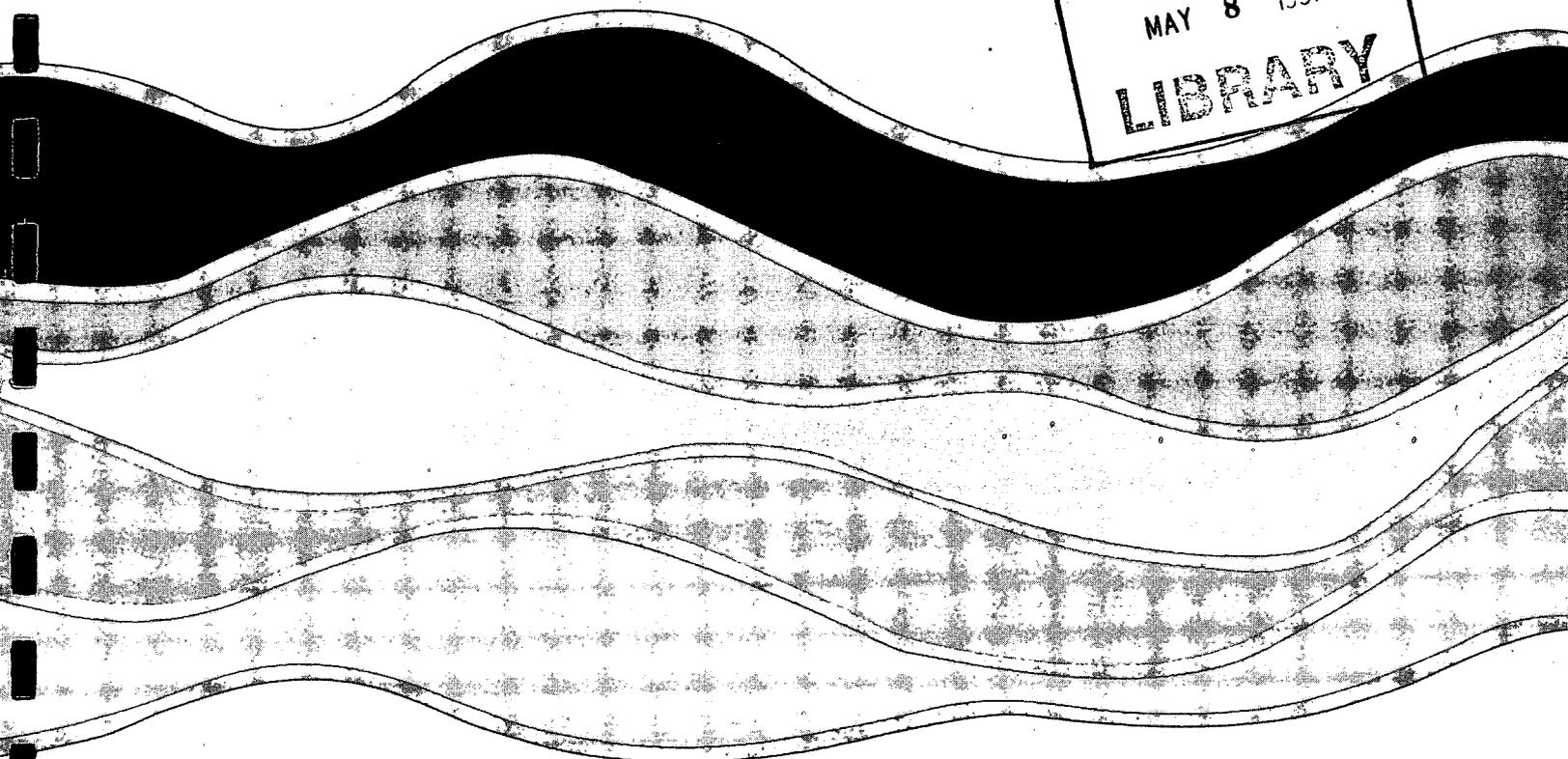
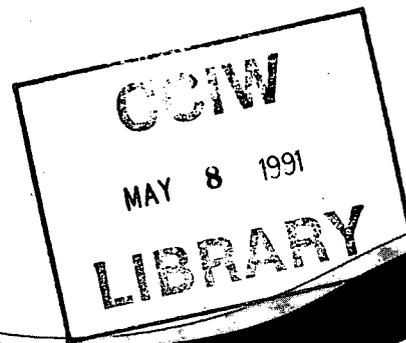
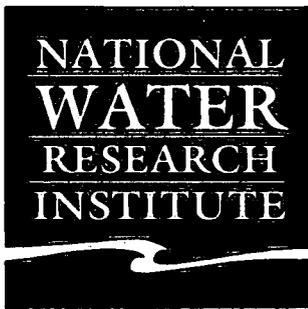


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**DIAGENETIC MANGANESE AND IRON  
 OXYHYDROXIDE PARTICLES  
 COLLECTED FROM A CANADIAN LAKE:  
 MORPHOLOGY AND CHEMICAL COMPOSITION**

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#### EXECUTIVE SUMMARY

Using a novel in situ collection technique, iron and manganese oxyhydroxides were isolated from the sediments of Brady Lake, Ontario, in a form amenable to chemical and microscopical analyses without the need to submit the material to degradative purification and concentration steps. The initial analyses indicate that one can now study such oxyhydroxides in their native state and carry out realistic experimental studies on their capacity to bind/redistribute/bury contaminants in lakes.

## RESUME POUR LA DIRECTION

Un nouvelle technique de prélèvement in situ a permis d'isoler des oxyhydroxydes de fer et de manganèse provenant de sédiments du lac Brady, en Ontario, sous une forme qui se prête à des analyses chimiques et microscopiques sans qu'il soit nécessaire de soumettre les matériaux aux étapes de la purification et de la concentration destructives. Les premières analyses révèlent qu'il est maintenant possible d'étudier ces oxyhydroxydes dans leur état naturel et d'effectuer des études expérimentales réalistes sur leur capacité de fixer/redistribuer/enfouir les contaminants dans les lacs.

## RÉSUMÉ

L'ultrastructure et la composition chimique des oxyhydroxydes diagénétiques naturels de manganèse et de fer ont été étudiées. Une technique de prélèvement et de séparation in situ, combinée à l'analyse chimique et à la microscopie électronique classiques, a permis d'étudier le partage des métaux traces entre les deux phases oxydes et la morphologie des oxyhydroxydes diagénétiques.

DIAGENETIC MANGANESE AND IRON OXYHYDROXIDE PARTICLES COLLECTED FROM A  
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ABSTRACT

The ultrastructure and chemical composition of natural diagenetic manganese and iron oxyhydroxides has been investigated. Using an *in situ* collection and separation technique combined with both conventional chemical analysis and electron microscopy we have studied trace metal partitioning between the two oxide phases and the morphology of the diagenetic oxyhydroxides.

INTRODUCTION

Both manganese and iron oxyhydroxides are thought to play an important role in the regulation of trace metal concentrations in natural aquatic systems. Very little physico-chemical data is at present available on Fe and Mn oxyhydroxides formed in sediments since direct measurement of their intrinsic properties is hindered by their considerable dilution in the sedimentary matrix (1-3% by weight of bottom sediments) and the lack of an appropriate separation technique. *In situ* collection and separation of diagenetic Mn and Fe oxyhydroxides from sediments is now possible using a simple technique which has recently been developed (ref 1). Using this approach, we have studied the physical nature and chemical composition of these diagenetic compounds.

METHODOLOGY

Teflon<sup>R</sup> sheets (8x15 cm, thickness 1.5 mm) were inserted vertically into the sediment of Brady lake by a diver and were left *in situ* for ten weeks to collect diagenetic Mn and Fe oxyhydroxides. The sheets were then retrieved and stored in sealed humidified Plexiglass containers. Sample preparation for electron microscopy was performed in the field within 6 hours of sampling by direct embedding (no prior steps) in a water soluble melamine resin (ref. 2). This approach which avoids sample dehydration has been shown to be minimally perturbing for natural iron colloids and preserves the ultrastructure of the particles (ref.3). Transmission Electron Microscopy (TEM) observations and micrographs were done with a Philips 300 TEM using ultrathin sections (ca. 70 nm). Energy dispersive spectroscopy (EDS) was done on ca. 140 nm sections using an I.S.I. DS-130 scanning transmission electron microscope (STEM) equipped with an EDS X-ray analyzer (γ-PGT/System 4). The microtomy was done according to Leppard et al. (ref. 4) and all sections were mounted on copper grids. Low resolution scanning electron microscopy (SEM) was done on a 2x1 cm slice of a Teflon sheet covered with both the Mn and Fe oxyhydroxide deposits, which was graphite coated, and analysed using a JEOL Model 330 SEM equipped with a Kevex 7000 EDS microprobe system.

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pH and concentration profiles for dissolved Fe, Mn and trace metals (As, Cd, Cu, Ni, Pb, Zn) were measured at the sediment water interface using porewater peepers (ref 5). Trace metal content of the Mn and Fe deposits were determined by Furnace Atomic Absorption Spectrometry after dissolving the oxyhydroxide deposits.

## RESULTS AND DISCUSSION

### Low resolution SEM

Once removed from the sediments, spatially resolved deposits of manganese and iron oxyhydroxides were observed on the Teflon<sup>R</sup> surface. They could be readily distinguished since the manganese rich layer was dark brown and laid above an iron rich layer which was light yellow. This sequence would be predicted from thermodynamic and kinetic considerations (ref 6). Chemical composition of the deposits was studied with the SEM using an EDS microprobe. A 3 mm transect across the Mn and Fe layers was analysed by successively measuring 250 x 250  $\mu\text{m}$  surfaces. Figure 1 shows three distinct zones: i) a Mn rich layer characterized by an Mn/Fe peak intensity ratio of ca. 7.5, ii) an intermediate transition zone which occurs within a vertical distance in the sediments of 500  $\mu\text{m}$  (+/- 100  $\mu\text{m}$ ) and iii) a Fe rich layer with a Fe/Mn peak intensity ratio of about 40. Ca and Si peaks were minor and appeared to have a random distribution across the transect suggesting slight contamination by other inorganic sediment constituents. In the Fe layer, the Ca and Si peak intensities were about 30 and 10 times smaller than the Fe peak. This contrasts with the findings of Buffle et al 1989, (ref. 7) who reported a much higher (ca. 3.3) Fe/Ca peak intensity ratio in iron oxyhydroxides isolated from the water column of a hardwater lake.

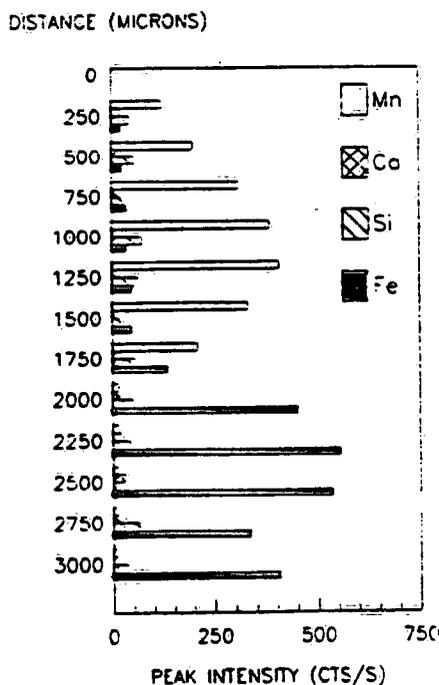


FIGURE 1. EDS transect analysis across the Mn/Fe layers. Peak heights (in counts per sec) were obtained after counting for 50 s. for a surface of 250 x 250 microns.

## High resolution TEM and EDS

*Iron rich layer*--Within the iron rich zone a diverse and morphologically distinctive range of colloidal sized structures was observed. There was a discontinuous film<sub>R</sub> of extremely variable thickness (up to 5  $\mu$ m) close to the Teflon<sup>R</sup> surface. Within a film both structural and chemical differentiation was documented. Two distinct types of films were observed: i) a single or multiple amorphous layer, rich in iron, which sometimes included fracture planes. ii) films which contained electron translucent fibrous structures which were also rich in iron. Diverse electron opaque colloids were on occasion seen occluded within the loosely packed fibrous mass of a thick film. At least three morphological types of iron rich large colloids were observed, a fourth type of occluded colloid was impoverished in iron but rich in both Si and Al. Heterogeneous aggregates adhering to the outer side of the film were uncommon; however, many of the outer colloids were not rich in Fe but were rich in S, Ca, P, Al and Si in various combinations.

*Manganese rich layer*-- A discontinuous film of variable thickness adhering to the Teflon<sup>R</sup> surface was found. In places the film thickness was uniform (ca. 1.5  $\mu$ m) and its substructure was regular. It consisted of an amorphous electron translucent central band, of about one half the total thickness, with on either side an electron opaque layer from which projected irregular electron opaque colloids. Both the central band and the electron opaque layer and colloids were rich in Mn, but only rarely was a Fe peak found. As in the case of the iron rich layer, heterogeneous aggregates of colloids could sometimes be seen projecting from one side of the Mn film; these were found to be varied in type and contained various combinations of S, Si, Al, P, K and Ca but impoverished in Mn. P was frequently encountered in the Mn film and in the external heteroaggregates.

### Macroscopic chemical composition

The vertical resolution of the Mn and Fe deposits enabled their physical separation by scraping off each deposit and then, after dissolution, analysing their chemical makeup by AAS. The amount of Fe, Mn and the associated trace elements are given in Table 1.

TABLE 1. Trace element concentrations in iron and manganese deposits separated from Brady Lake. Quantities given are the total amount collected on two Teflon<sup>R</sup> collectors installed in the same location.

|         | Fe   | Mn  | As   | Cd  | Cu | Ni  | Pb  | Zn   |
|---------|------|-----|------|-----|----|-----|-----|------|
|         | (ug) |     | (ng) |     |    |     |     |      |
| Mn rich |      |     |      |     |    |     |     |      |
| layer   | 45   | 173 | 25   | 2.2 | 34 | 206 | 131 | 1090 |
| Fe rich |      |     |      |     |    |     |     |      |
| layer   | 860  | 51  | 80   | 1.5 | 58 | 70  | 326 | 790  |

Within the manganese layer, a Mn/Fe ratio of 3.8 was found whereas within the Fe layer, the Fe/Mn ratio was 16.9. These ratios are much higher than the peak intensity ratios found by low resolution SEM (7.4 and 40, respectively) Obviously, the analytical resolution (250  $\mu\text{m}$ ) between the two layers is better in the latter case. Combining this data with the EDS analysis done on thin sections we have found that : (i) No or very little Mn is found in the Fe rich layer and (ii) within the Mn rich layer there were pure Mn oxyhydroxide deposits but in some cases a small Fe peak was found associated to a large Mn peak. Finally, it is interesting to note that the data in Table 1 show that Zn and Ni are preferentially retained by the Mn oxyhydroxide whereas As and Cu are mostly associated with Fe oxides.

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