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### On the Nature of Particulate Manganese in Simulated Lake Waters \*

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#### Abstract

The oxidation of simulated lake waters incipiently containing  $10^{-5}$  mol/l  $Mn^{2+}$  leads to the formation of a stable phase:  $\gamma$ -MnOOH. Because  $\gamma$ -MnOOH formed in most natural waters is of colloidal dimensions this phase will not be detected routinely. It is postulated that  $\gamma$ -MnOOH is the final product of an oxidation sequence with  $Mn_3O_4$  as intermediate.

#### 1. Introduction

Little seems to be known on the nature of particulate manganese in lake or sea waters. It has its origin in weathering processes of rocks and usually enters the exogenic cycle in the form of the  $[Mn(H_2O)_6]^{2+}$  ion. If exposed to air this ion will undergo oxidation. In the pH range of natural waters  $MnCO_3$  controls the solubility of  $Mn^{2+}$ .

We have prepared synthetic lake waters with manganese concentrations of the order of  $10^{-5}$  mol/l and followed the reactions until a precipitate appeared. The latter was investigated by means of electron microscopy, electron diffraction and X-ray diffraction.

#### 2. Experimental

«Duran 50» glass bottles of 10 l volume were cleaned with conc. HCl, rinsed with diluted HCl, and washed with  $H_2O$  bidest. For the solution  $H_2O$  bidest. was saturated with air. pH adjustment was made with  $NaHCO_3$ , NaOH or  $NH_4NO_3/NH_3$ . To some of the samples traces of silica (36 mg/l Ludox LS, an amorphous  $SiO_2$  with the specific surface area of  $200\text{ m}^2/\text{g}$ ) were added.  $Mn^{2+}$  was then added from a dilute solution of  $Mn(NO_3)_2 \cdot 4H_2O$ .

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The starting conditions of some representative experiments are listed in table 1.

Table 1: Starting conditions for the simulated lake waters

No.	$[NH_4NO_3]$ M	$[NaHCO_3]$ M	Ludox ml of dil. suspen- sion added	$[Mn(NO_3)_2]$ M	pH
1	$10^{-3}$			$10^{-5}$	8,80
2	$10^{-3}$		1	$10^{-5}$	8,82
3		$2 \cdot 10^{-3}$		$10^{-5}$	8,86
4		$2 \cdot 10^{-3}$	1	$10^{-5}$	8,65
5		$2 \cdot 10^{-3}$		$10^{-5}$	8,92
6		$2 \cdot 10^{-3}$	1	$10^{-5}$	8,99
7		$2 \cdot 10^{-3}$		$5 \cdot 10^{-6}$	8,82
8		$2 \cdot 10^{-3}$		$5 \cdot 10^{-6}$	8,78
11	Lake Greifensee water *			$5 \cdot 10^{-6}$	8,79
16		$2 \cdot 10^{-3}$		$10^{-5}$	8,06

\* (near Zurich, Switzerland) membrane filtered

The bottles were stored at  $20^\circ\text{C}$  in the dark and samples were taken periodically for the determination of residual soluble  $Mn^{2+}$  (AAS) and of pH. Some experiments lasted for more than a year. Precipitates collected from the samples were prepared on a carbon film and investigated in a Siemens Elmiskop and a Hitachi HU-12A electron microscope. For X-ray diffraction the sample was dried and exposed for ca. 3–8 hours, using monochromatic Fe and Mo radiation, in a focusing Guinier-de Wolff camera. Of some molybdenum patterns a densitometer trace was produced for easier evaluation.

#### 3. Results

A few representative examples of the time dependence of  $Mn^{2+}$  removal from solution are given in fig. 1.

While in some samples  $Mn^{2+}$  was removed from the solution rather fast (7, 8, 9), in other samples a delayed reaction was observed (16). Especially in the presence

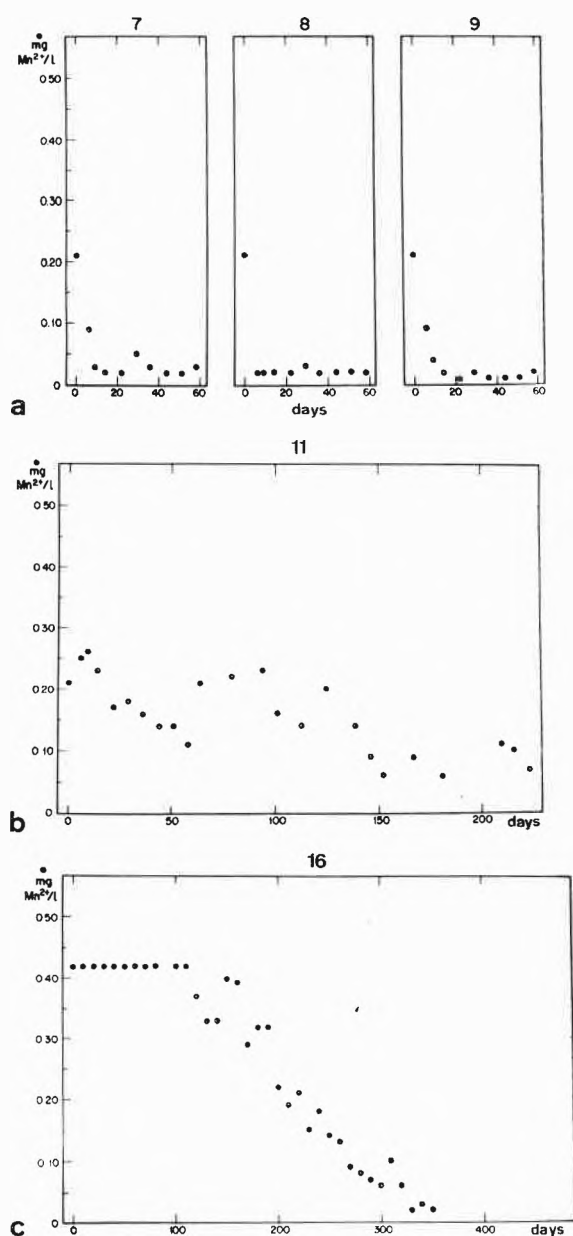


Fig. 1: Soluble  $[Mn^{2+}]$  as a function of time for five representative batches: a) No. 7, No. 8, No. 9; b) No. 11; c) No. 16

of solid silica, oxidation and precipitation are delayed for more than a year. Significantly the lake water of Greifensee produced a somewhat erratic curve.

The precipitates investigated resemble each other, with exception of that collected from natural lake water. The electron micrographs (e.g. fig. 3a) show long and thin needles and some equant particles.

Surprisingly, the Fe X-ray diffraction patterns for all these samples were entirely blank. By using Mo radiation a  $\frac{\text{signal}}{\text{noise}}$  ratio was reached that gave a recognizable densitometer trace. This trace can be explained unambiguously as being produced by very small, long needles of  $\gamma$ -MnOOH (fig. 2). All Mn phases known

to us, except  $\gamma$ -MnOOH, can be ruled out, and also the sample carrier film does not have its very broad additional reflection at the place of the 210 reflection of  $\gamma$ -MnOOH.

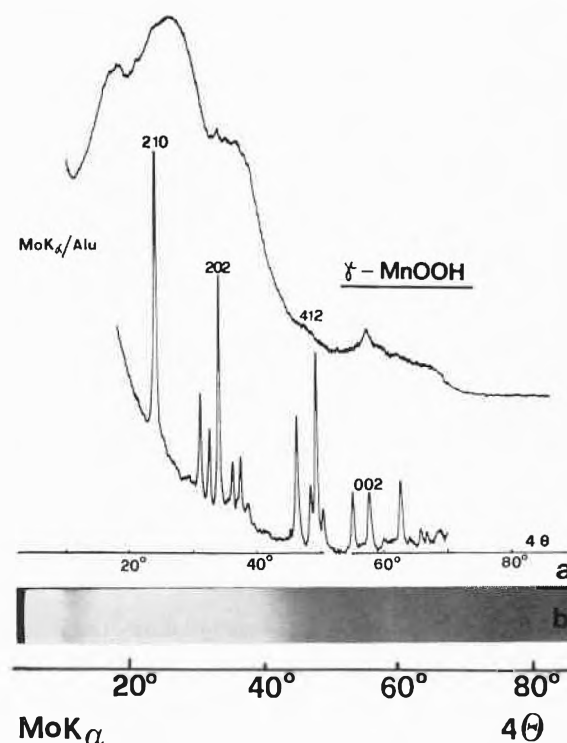


Fig. 2: X-ray diffraction,  $MoK_{\alpha}$  radiation, of a typical precipitate (No. 4)

- a) Densitometer trace of b) and of fully crystalline synthetic  $\gamma$ -MnOOH  
b) Original pattern

Obviously, there can be only few coherently scattering spacings along the [210] direction; there must be considerably more spacings along the [002] direction. Thus, the crystals must be thin and long. This is consistent with the electron micrographs.

It was more difficult to detect the morphology of the precipitates collected from the lake water. The apparently formless agglomerations had to be dispersed violently in order to make the actual crystals visible. These are extremely thin needles, only a few Å thick and about 100 to 500 Å long (fig. 3b).

#### 4. Discussion

The prevailing, and solely identified, phase in all these samples is  $\gamma$ -MnOOH. In some samples, however (e.g. fig. 3a), tiny equant crystals as remains of another phase can be detected. Because it is known that both  $Mn_3O_4$  and  $\beta$ -MnOOH transform into  $\gamma$ -MnOOH needles [1] we infer that these particles are  $Mn_3O_4$  cubes which are oxidation intermediates, apparently kinetically more stable than the transient  $\beta$ -MnOOH. Fig. 4 shows, for two crystallite sizes, the extent of

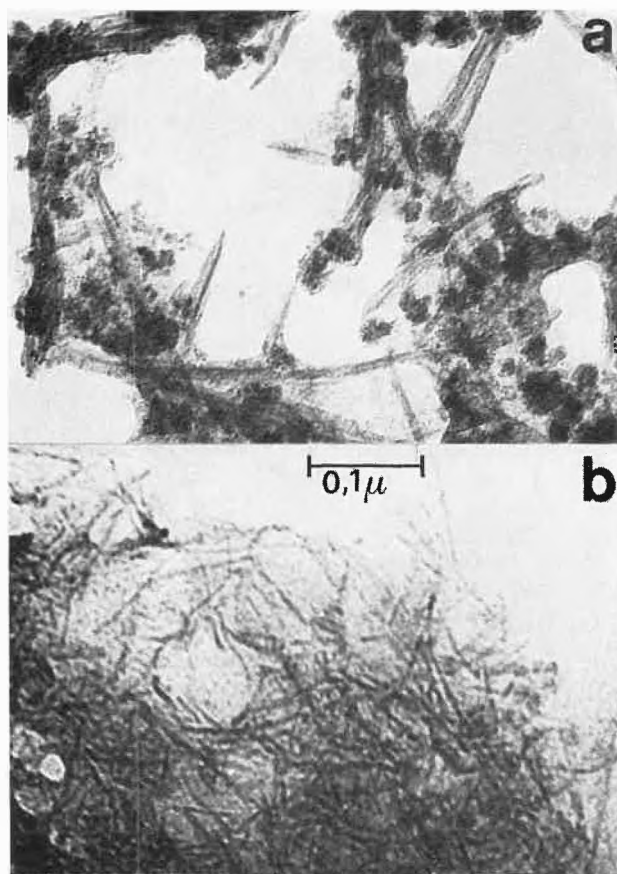


Fig. 3: Electron micrographs of two representative precipitates.  
a) No. 8 (H<sub>2</sub>O bidest.)  
b) No. 11 (lake water)

conversion, within a period of nine years, of dry Mn<sub>3</sub>O<sub>4</sub> into β-MnOOH or γ-MnOOH, respectively.

From these results and from Feitknechts experiments [1] we would expect that Mn<sup>2+</sup> precipitates initially as Mn(OH)<sub>2</sub> which then becomes oxidized very fast subsequently to a mixture of β-MnOOH and Mn<sub>3</sub>O<sub>4</sub>, and to γ-MnOOH.

In our solutions, however, solid Mn(OH)<sub>2</sub> cannot be formed. In the HCO<sub>3</sub><sup>-</sup> containing solutions, on the other hand, the formation of solid MnCO<sub>3</sub> is possible; furthermore Mn<sup>2+</sup> may form adsorption adducts at silica and other surfaces.

The final precipitate becomes more crystalline, the slower the oxygenation reaction (e.g. in presence of suspended SiO<sub>2</sub>).

In natural water, γ-MnOOH crystals of almost untraceable dimensions are formed, presumably because rates of nucleation and crystal growth are sufficiently fast. Our observations explain why γ-MnOOH cannot be detected routinely in lake or ocean water or in their sediments because the crystals of colloidal dimensions cannot be detected in the presence of all the other solids prevailing.

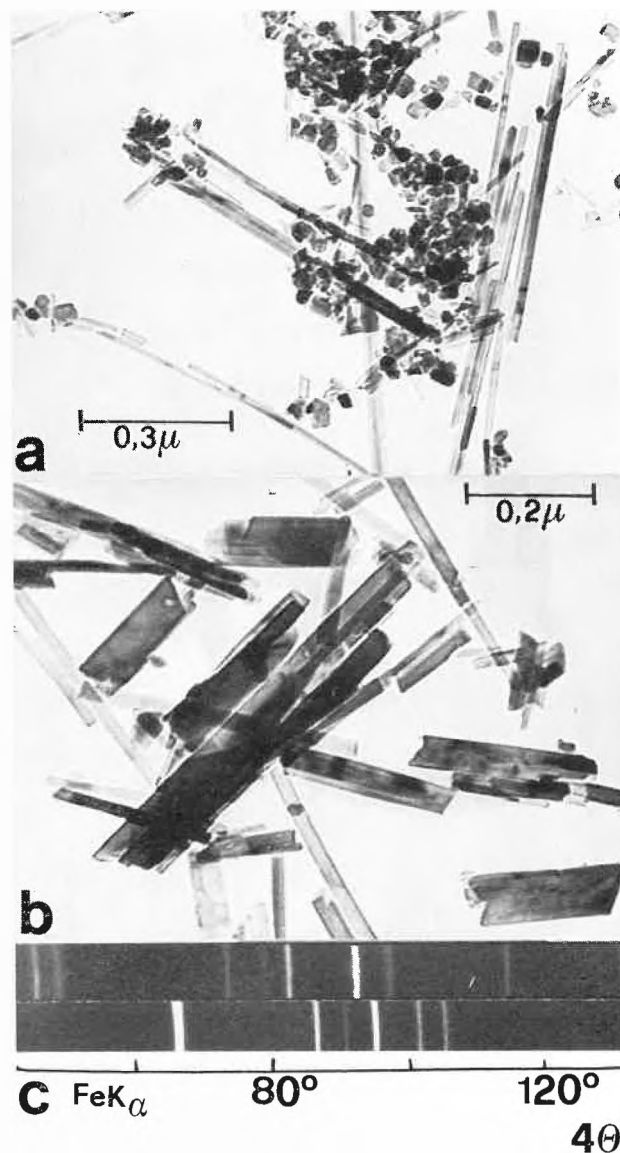


Fig. 4: Electron micrographs and X-ray diffraction patterns of the products of two Mn<sub>3</sub>O<sub>4</sub> samples after 9 years standing in air of 85% rel. humidity.

- a) Initial product of relatively large crystals:  
The reaction is slow and has only reached the stage Mn<sub>3</sub>O<sub>4</sub> + β-MnOOH
- b) Initial product of relatively small crystals:  
The reaction is faster, and the entire sample is converted to γ-MnOOH
- c) X-ray diffraction patterns corresponding to a (top) and b (bottom)

#### Acknowledgements

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#### Literature

- 1 W. Feitknecht, P. Brunner and H. R. Oswald: Z. anorg. allg. Chemie 316 (1962) 154.