

EFFECT OF COPPER SULFATE ON PYRITE FORMATION IN REDUCING SEDIMENTS

PHILIP G. MANNING, THOMAS P. MURPHY AND TATIANA MAYER

National Water Research Institute, P.O. Box 5050, Burlington, Ontario L7R 4A6

ELLIE E. PREPAS

Department of Zoology, University of Alberta, Edmonton, Alberta T6G 2E9

ABSTRACT

⁵⁷Fe Mössbauer spectrometry has been used to determine the distribution of iron among chlorite (Fe²⁺), hydrated ferric oxides (Fe³⁺), and pyrite in the reducing sediments of Figure Eight Lake, Alberta. The lake was treated on three occasions with copper sulfate algicide between 1980 and 1984. In the north basin, over the top 4 cm of sediment, ~20% of total iron is in pyrite; at 4 to 5 cm, pyrite concentrations increase rapidly, so that by 8 to 9 cm depth, 64% of total iron is in pyrite. On the other hand, concentrations of total copper follow an inverse profile to those of pyrite and organic carbon, increasing from background levels (25 µg g⁻¹ Cu) at ~10 cm beneath the sediment-water interface to 50 µg g⁻¹ Cu at 1 to 3 cm. These trends, which also occur in the sediments of the south basin, suggest that the formation of pyrite in the surface sediments has been inhibited since copper sulfate treatment. This inhibition arises from the reduced deposition of organic matter or copper ion toxicity to sulfate-reducing bacteria (or both). Hence, small additions of available copper ion can significantly affect the sulfur cycle in the lake.

Keywords: pyrite, sediments, copper, algicide, sulfur cycle, lake, Alberta, Mössbauer spectrometry.

SOMMAIRE

Nous avons utilisé la spectrométrie de Mössbauer ⁵⁷Fe pour déterminer la distribution du fer parmi chlorite (Fe²⁺), oxydes ferriques hydratés (Fe³⁺), et pyrite dans les sédiments réduits du lac Figure Eight, en Alberta. Le lac a été traité au sulfate de cuivre, utilisé comme algicide, à trois occasions entre 1980 et 1984. Dans la couche supérieure (4 cm) du sédiment du bassin du nord, environ 20% du fer est sous forme de pyrite; entre 4 et 5 cm, la teneur en pyrite augmente de façon marquée, de sorte qu'entre 8 et 9 cm de profondeur, 64% du fer y est sous forme de pyrite. Par contre, la teneur en cuivre total définit un profil à l'inverse de ceux qui représentent la pyrite et le carbone organique, augmentant d'une valeur de fond (25 µg g⁻¹ Cu) à environ 10 cm au-dessous de l'interface sédiment-eau jusqu'à 50 µg g⁻¹ entre 1 et 3 cm. Ces variations, que nous retrouvons aussi dans le bassin du sud, résulteraient de l'inhibition de la formation de la pyrite dans les sédiments de surface suite au traitement au sulfate de cuivre. Cette inhibition est due soit à une réduction du taux de déposition de la matière organique, soit à la toxicité de l'ion de cuivre pour les bactéries réductrices du soufre. Nous proposons donc que de légères additions de cuivre dispo-

nible sous forme ionique peuvent exercer une influence importante sur le cycle du soufre dans le lac.

(Traduit par la Rédaction)

Mots-clés: pyrite, sédiments, cuivre, algicide, cycle du soufre, lac, Alberta, spectrométrie de Mössbauer.

INTRODUCTION

Copper sulfate is an effective algicide in the control of aquatic weeds in lakes (Effler *et al.* 1980). Drawbacks to the method include the suppression of bacterial populations (Effler *et al.* 1980) and of zooplankton biomass (Winner 1985), and frequent depletion in oxygen on decomposition of the algal bloom (Whitaker *et al.* 1978). Sulfate-reducing bacteria play an important role in the sulfur cycle of lakes with anoxic sediments (Berner 1984). The sulfide ion produced reacts with available iron to form amorphous FeS compounds, which then react with sulfur to form stable pyrite, FeS₂ (Berner 1984). The formation of pyrite effectively removes sulfate from the overlying waters and increases the alkalinity (Cook *et al.* 1986). The reaction of sulfide with ferric ions in hydrated oxides and clay minerals to form pyrite has been followed in the sediments of two Ontario lakes (Manning *et al.* 1979, Manning & Ash 1979), in one of which, Moira Lake, arsenic may inhibit pyrite formation. Some ferrous ions may be abstracted from chlorite to form pyrite (Manning *et al.* 1979).

Here, we report on the results of a Mössbauer spectrometric study of pyrite formation in Figure Eight Lake, Alberta. The lake is small (37 ha) and shallow (mean depth of 3.1 m). Stream flow into the lake is minimal and occurs only during snow melt. Figure Eight Lake lies in glacial till, in the Kaskapau Formation, 40 km northwest of Peace River, Alberta (long. 56°18'N, lat. 117°54'W). The two main basins are separated by a neck 3.5 m deep; the north basin has a maximum depth of 5 m, and that of the south basin is 6 m. The lake is thermally stratified in summer and in winter, inducing anoxia over the 1- to 2-m-thick hypolimnion.

To reduce algal production, the lake was treated

with copper sulfate in 1980, 1983, and 1984 at typical levels of 19 to 71 $\mu\text{g L}^{-1}$. The copper treatments increased the Secchi disc depth from 0.75 to 4.5 m in 1980, from 0.8 to 3.3 m in 1983, and from 1.6 to 4.0 m in 1984. Although the algal biomass was greatly reduced, each year had a period of algal turbidity that exceeded that found in the control lake, Amisk Lake. Amisk Lake typically has an algal bloom that produces a Secchi disc depth of about 1.0 m in late August, when the lake destratifies. Moreover, Figure Eight Lake was not treated in 1981 or 1982, and in these years algal blooms occurred; although no Secchi data were collected, fish kills occurred in winter. The aim of this work was to determine the effect of copper sulfate on formation of sedimentary pyrite.

EXPERIMENTAL DETAILS

Sediments were retrieved from Figure Eight Lake with a gravity corer on 30 July, 1985. Both basins were cored at close to maximum depth (5 m). The bottom waters were anoxic at the time of coring, and had been so for ~30 days, resulting in heavy release

little effect on the oxic regime. The surficial sediments are probably strongly reducing year-round. In October 1985, a core was retrieved from Amisk Lake, 150 km northwest of Edmonton, Alberta, for comparative studies of microbial assimilation. The cores were sectioned at 1-cm intervals within 0.5 h of retrieval and then frozen immediately. The samples were freeze-dried and stored in screw-capped vials at 4°C. The dried residuals were dark brown to black.

Room temperature ^{57}Fe Mössbauer spectra were recorded at the National Water Research Institute (NWRI) using a microprocessor-based spectrometer (Cryophysics Ltd. MS-103). Spectra were computed on a Cyber 171 computer using Stone's programs (Stone 1967). Values of chi-squared and visual fits were used as criteria of goodness of fit. Spectra were computed on the bases of two doublets (Fe^{2+} and " Fe^{3+} ") and of three doublets (Fe^{2+} , Fe^{3+} and FeS_2 ; Table 1 and Manning *et al.* 1979). The doublets of ferric iron and of pyrite are superimposable, hence the term " Fe^{3+} " encompasses absorptions of both forms of iron. Opaque pyrite spherules were seen under an optical microscope. Lorentzian line shapes were assumed. Areas and half-widths within a quadrupole doublet were constrained to be equal. In the first stages of computation of the three-doublet fits, the positions and half-widths of the pyrite peaks were constrained at values measured for crystalline pyrite (these agreed with those measured for pyrite framboids in deeper sections of Lake St. George muds; Manning *et al.* 1979); peak positions were released in the second stages of computation. The $\text{Fe}^{2+}:\text{Fe}^{3+}:\text{FeS}_2$ distributions were found to be similar in both stages, but for consistency the distributions reported here are the results of the first stage of computation. The estimated error in pyrite concentrations is $\pm 10\%$; much of this error runs consistently through all computations.

Mineralogical analyses were pursued by powder X-ray-diffraction methods using a Cu target and a Ni filter. Semiquantitative estimations were made using mixtures of standard materials. Minerals identified, in order of decreasing abundance, are quartz, illite, feldspar, chlorite and pyrite. The clay-mineral fraction in the Kaskapau Formation is composed of 5 to 35% kaolinite, 65 to 75% illite, and 10 to 20% chlorite (D. Scafe, Alberta Research Council, private comm.) Pyrite has not been observed in the Kaskapau Formation. Surface and deeper sections of sediment gave very similar X-ray-diffraction patterns.

The concentration of total iron was determined by acid dissolution followed by atomic absorption spectrometry (Desjardins 1978). Copper concentrations were determined by nitric-perchloric acid digestion and atomic absorption spectrometry. Inorganic and organic carbon concentrations were determined

TABLE 1. MÖSSBAUER PARAMETERS (mm s^{-1}) BASED ON THREE-DOUBLET COMPUTATIONS

Depth cm	Ferrous Ions			Ferric Ions		
	IS	QS	HW	IS	QS	HW
<u>North Basin</u>						
0-1	1.14	2.61	0.46	0.40	0.74	0.62
1-2	1.14	2.62	0.46	0.39	0.71	0.61
2-3	1.15	2.62	0.48	0.41	0.73	0.64
3-4	1.13	2.60	0.44	0.44	0.72	0.65
4-5	1.14	2.59	0.46	0.40	0.73	0.66
5-6	1.14	2.62	0.44	0.42	0.72	0.62
6-7	1.14	2.60	0.46	0.40	0.74	0.58
8-9	1.15	2.62	0.40	0.43	0.75	0.62
10-11	1.15	2.62	0.46	0.43	0.75	0.65
13-14	1.15	2.63	0.49	0.46	0.71	0.82
17-18	1.18	2.70	0.48	0.44	0.71	0.60
19-20	1.15	2.63	0.43	0.46	0.66	0.52
24-25	1.16	2.64	0.44	0.46	0.59	0.59
29-30	1.17	2.69	0.44	0.48	0.59	0.59
<u>South Basin</u>						
0-1	1.14	2.59	0.43	0.40	0.70	0.60
2-3	1.14	2.60	0.44	0.41	0.60	0.62
3-4	1.13	2.65	0.40	0.45	0.71	0.60
5-6	1.13	2.59	0.43	0.40	0.71	0.62
7-8	1.14	2.60	0.42	0.40	0.71	0.62
8-9	1.14	2.59	0.46	0.41	0.70	0.63
9-10	1.14	2.61	0.44	0.42	0.70	0.62
11-12	1.15	2.62	0.38	0.44	0.65	0.57
14-15	1.15	2.61	0.44	0.47	0.63	0.67
<u>North Basin, after exposure to air</u>						
1-2	1.14	2.63	0.43	0.41	0.70	0.60
5-6	1.12	2.59	0.42	0.44	0.72	0.61
<u>North Basin, after 0.1 M HCl treatment</u>						
5-6	1.15	2.62	0.56	0.42	0.66	0.62
12-13*	1.13	2.59	0.37	constrained		
FeS_2 (measured)				0.31	0.60	0.30

Pyrite peak positions and half-widths constrained at values determined for pyrite crystals.

* Ferric iron positions and half-widths constrained. All values good to $\pm 0.02 \text{ mm s}^{-1}$.

of iron and phosphorus from the sediments to the hypolimnion. Mixing occurred in mid-August, but by mid-December, under ice cover, the bottom waters were again rendered anoxic. In earlier years, including pre-treatment years, anoxia developed each summer and in most winters. Fish kills were common in winter. Copper treatment seems to have had with a Leco furnace, organic carbon being measured after removal of carbonate carbon with sulfurous acid (Kemp 1971). Total sulfur was measured with a semiautomatic Leco system with iodometric titration. All concentrations are expressed in weight percent or $\mu\text{g g}^{-1}$ of dry sediment. All analyses are good to $\pm 10\%$.

Microbial metabolic activities of sections of cores from the two basins of Figure Eight Lake and from Amisk Lake were measured, within 72 h of retrieval, with ^{14}C -acetate (Burnison *et al.* 1986). A concentration of 0.5 mL of wet sediment was mixed with either 15 or 75 mL of Chu-10 medium, resulting in $\sim 10\%$ utilization of the acetate. Two samples from each lake were incubated with four amounts of ^{14}C -acetate (39.5, 78.7, 155.8 and 449.7 nM) for Michaelis-Menten analysis, and the rest of the sediment sample was incubated with one concentration (449.7 nM). Control samples were treated with formalin. Incubations (0.5 h at 8°C) were terminated by filtration through 0.2 μm Sartorius cellulose

nitrate filters. The filters were dissolved in 10 mL of ACS-2 scintillation fluor with a sonicator and made into a gel by the addition of 4 mL of water, and then counted on a Seale Mark III scintillation counter.

RESULTS AND DISCUSSION

Mössbauer spectra assignments

The Mössbauer spectra (Figs. 1, 2) display, at first sight, two quadrupole doublets. The outer doublet, with calculated Mössbauer parameters IS , the isomer shift (relative to Fe foil), of $1.15 \pm 0.01 \text{ mm s}^{-1}$, QS , the quadrupole splitting, of $2.62 \pm 0.02 \text{ mm s}^{-1}$, and HW , the half width, of $0.41 \pm 0.04 \text{ mm s}^{-1}$, mainly marks ferrous ions in octahedral positions in chlorite and other silicates (Coe *et al.* 1974, Manning & Jones 1982). The presence of chlorite was confirmed by X-ray diffraction and mineralogical analyses. Absorptions of amorphous FeS may also be present under this envelope (Hilton *et al.* 1986). The two-doublet fits yield Mössbauer parameters for the inner "ferric" doublet which decrease steadily, for both north and south basins, with increasing depth of burial. Thus, the surficial muds yield parameters (IS $0.35 \pm 0.02 \text{ mm s}^{-1}$, QS $0.68 \pm 0.02 \text{ mm s}^{-1}$, and HW $0.51 \pm 0.02 \text{ mm s}^{-1}$) consis-

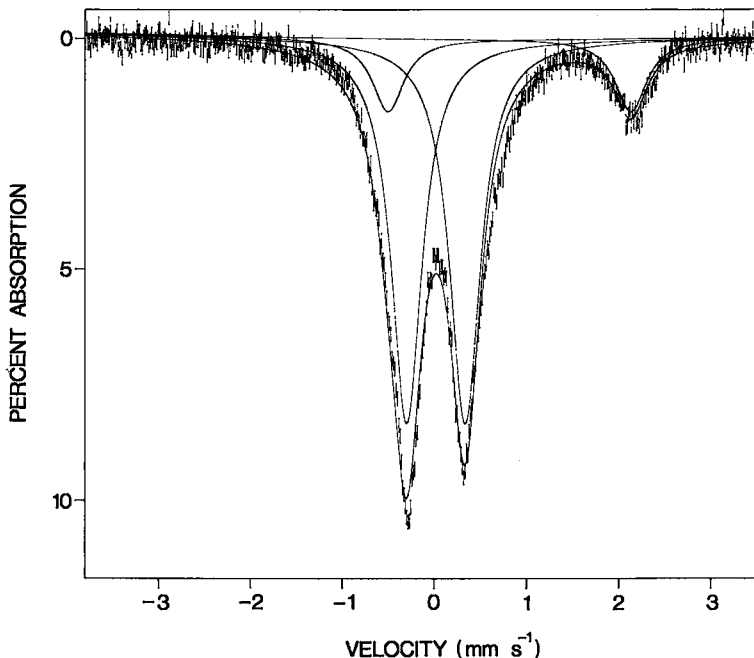


FIG. 1. Mössbauer spectrum of 5- to 6-cm section of north-basin core based on a two-doublet fit. Chi-squared is 1046 for 494 degrees of freedom. The spectrometer was calibrated against iron foil.

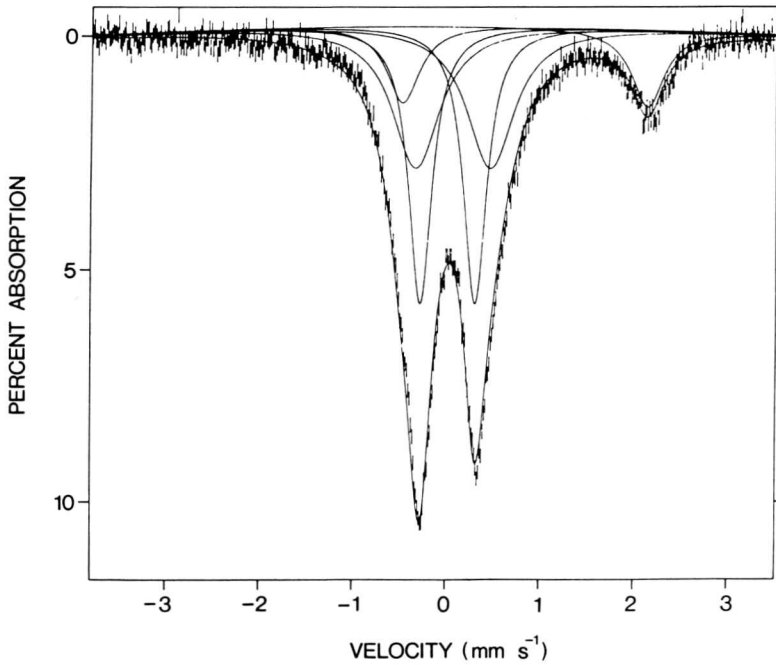


FIG. 2. Mössbauer spectrum of 5- to 6-cm section of north-basin core based on a three-doublet fit. Chi-squared is 533 for 494 degrees of freedom. Note improved fit in the $\sim 1.0 \text{ mm s}^{-1}$, region compared to the two-doublet fit in Figure 1.

TABLE 2. CONCENTRATIONS OF IRON, SULFUR, CARBON AND COPPER IN FIGURE EIGHT LAKE SEDIMENTS

Section cm	Fe _T	Fe ²⁺	Fe ³⁺	Fe(S ₂)	Fe ²⁺	Fe ³⁺	Fe(S ₂)	S _{reqd}	S _{meas}	C _{org}	Cu μg g ⁻¹
	wt%	% of Fe _T			wt%						
<u>North Basin</u>											
0-1	4.49	24.2	56.6	19.2	1.09	2.54	0.86	0.98	1.31	11.3	20
1-2	4.11	22.9	58.6	18.7	0.94	2.40	0.77	0.88	1.31	10.2	56
2-3	3.12	27.9	51.8	20.3	0.87	1.62	0.63	0.72	0.83	10.7	51
3-4	2.92	23.8	56.4	19.8	0.69	1.65	0.58	0.67	0.81	9.8	41
4-5	2.96	22.7	51.6	25.8	0.67	1.52	0.76	0.87	0.71	12.1	38
5-6	3.12	14.5	44.4	41.3	0.45	1.38	1.29	1.48	1.19	14.9	40
6-7	3.12	12.8	34.6	53.1	0.40	1.06	1.66	1.89	1.45	17.3	32
6-7	2.36	11.9	24.0	63.8	0.28	0.58	1.51	1.72	2.59	17.9	29
10-11	2.28	14.8	21.6	63.7	0.34	0.49	1.145	1.66	2.66	17.6	25
13-14	2.64	12.8	19.9	68.1	0.34	0.50	1.80	2.05	2.65	20.5	27
17-18	2.92	11.3	13.8	75.0	0.33	0.40	2.19	2.50	2.60	19.7	25
19-20	2.80	11.1	13.3	75.8	0.31	0.37	2.12	2.42	3.02	19.1	26
24-25	2.48	12.8	15.4	72.2	0.32	0.37	1.79	2.04	2.76	18.3	25
29-30	3.31	16.1	16.4	67.3	0.53	0.55	2.23	2.54	3.06	18.5	25
<u>South Basin</u>											
0-1	3.36	22.4	53.6	23.8	0.75	1.81	0.80	0.91	1.15	9.1	16
2-3	2.88	25.0	51.6	23.5	0.72	1.48	0.68	0.77	1.07	8.6	41
3-4	3.31	22.8	53.8	23.8	0.75	1.77	0.78	0.89	0.74	8.3	46
5-6	3.71	23.7	47.4	18.7	0.88	2.13	0.69	0.79	0.80	7.8	45
7-8	2.84	21.5	51.6	26.9	0.61	1.47	0.76	0.87	1.16	9.7	34
8-9	3.03	21.0	40.4	38.2	0.64	1.24	1.16	1.32	1.33	11.3	31
9-10	2.60	17.6	31.6	51.3	0.46	0.81	1.33	1.52	1.88	12.7	26
11-12	2.68	16.9	20.0	62.9	0.45	0.54	1.69	1.92	2.11	13.8	23
14-15	2.76	16.2	16.6	67.4	0.45	0.45	1.86	2.12	1.92	15.9	20
<u>North Basin, after exposure to air</u>											
1-2		19.2	58.6	22.2							
5-6		14.2	39.2	46.6							
<u>North Basin, after 0.1 M HCl treatment</u>											
5-6		16.7	34.4	48.9							
12-13		10.0	11.7	78.3							

Pyrite positions and half-widths constrained at values determined for pyrite crystals. Deeper sections of South Basin core contain $\sim 2.2 \text{ wt} \% \text{ S}$. Estimated error in concentrations $\pm 10\%$. For the 1 to 2 cm section of North Basin sediment, the $S_{\text{meas}}:S(\text{of CuS})$ is $\sim 400:1$.

tent with ferric ions in amorphous hydrated oxides and in clays, e.g., illite (Coey *et al.* 1974). The X-ray-diffraction patterns show no evidence of crystalline ferric oxides. The deeper sections ($\sim 10 \text{ cm}$ burial) yield parameters for the inner doublet (correspondingly, 0.31 mm s^{-1} , 0.60 mm s^{-1} and 0.32 mm s^{-1} ; all ± 0.02) that are more consistent with those measured for pyrite crystals (0.31 mm s^{-1} , 0.60 mm s^{-1} and 0.30 mm s^{-1} ; Manning *et al.* 1979). The ferric iron and pyrite doublets are superimposable; consequently, the measured Mössbauer parameters for the inner doublet suggest a $\text{Fe}^{3+} \rightarrow \text{FeS}_2$ conversion on burial. Such a reaction occurs in other lake sediments (Manning & Ash 1979, Manning *et al.* 1979).

Four additional points argue against a simple two-doublet $\text{Fe}^{2+} - \text{Fe}^{3+}$ system: (i) " $\text{Fe}^{3+}:\text{Fe}^{2+}$ " ratios increase with increasing depth of burial (note the decreasing Fe^{2+} concentrations with increasing depth, Table 2). This is inconsistent with the reduction of ferric ions in reducing sediments (Manning *et al.* 1979, Manning & Jones 1982); (ii) for several sections, and particularly for those with similar Fe^{3+} and FeS_2 concentrations, the computed fit on the high-energy limb of the main envelope is poor (Fig. 1), whereas the visual fit for the $\text{Fe}^{2+} - \text{Fe}^{3+}$

- FeS_2 scheme is considerably improved (Fig. 2); (iii) values of chi-squared are significantly lower for many three-doublet fits, e.g., 577 versus 1046 for the north-basin 5- to 6-cm section, 533 versus 851 for 6 to 7 cm, and 564 versus 860 for 8 to 9 cm; (iv) opaque pyrite spherules can be seen using an optical microscope. Calculated Mössbauer parameters and ferrous, ferric, and pyrite concentrations are listed in Tables 1 and 2, respectively. The trends in iron forms are consistent for both north- and south-basin cores, showing the conversion of ferric and possibly ferrous ions into pyrite (Figs. 3, 4). Concentrations of total S follow those of FeS_2 , and in general there is more than sufficient S to account for FeS_2 (Table 2, Figs. 3, 4). The S concentrations are the highest yet recorded for the sediments of a freshwater lake. Sulfur added as CuSO_4 contributes negligibly to the total S concentration in the sediments (Table 2).

The consistency in calculated values of IS , QS , and HW for Fe^{2+} and Fe^{3+} ions in the three-doublet fits is gratifying, considering the low concentrations of these ions present in the deeper sections. The relative proportions of $\text{Fe}^{2+}:\text{Fe}^{3+}:\text{FeS}_2$ may not be absolutely correct because of possible differences in recoil-free fractions for ions in oxide and sulfur environments. However, the trends in concentrations of iron forms with depth and the analytical and computational procedures are valid.

To test for the presence of black amorphous Fe-S compounds, two sections of north-basin core were exposed to air for five months. The measured $\text{Fe}^{2+}:\text{Fe}^{3+}:\text{FeS}_2$ distributions (Table 2) are not greatly different from those of the fresh sediment. Furthermore, the intensity of the outer (chlorite) doublet remained almost unchanged after reaction with 0.1 M HCl (Tables 1, 2). The decrease in the concentration of the outer (chlorite) doublet with increasing depth of burial (Tables 1, 2) indicates abstraction of ferrous ions by H_2S . FeS compounds may have Mössbauer signatures coincident with the chlorite peaks, but they seem relatively unimportant.

Copper profiles

Copper concentrations are maximum in both cores in the 1- to 2-cm section and, beneath this, decline to background values at ~8 cm in the north-basin core and at ~12 cm in the south core (Figs. 3, 4, Table 2). Increasing Cu concentrations in the sediment are reflected in decreasing FeS_2 and total S concentrations (Figs. 3, 4), suggesting the inhibition of sulfur production and pyrite formation by copper ions. Similar inhibition of pyrite, by arsenic, has been proposed in Moira Lake (Manning & Ash 1979).

The copper ions may be retained within the refractory organic component of the sediment (Lum &

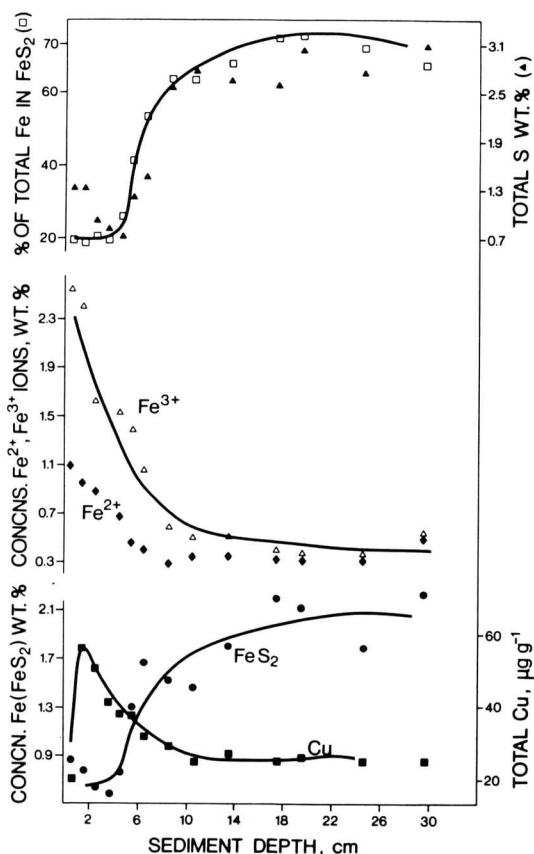


FIG. 3. Plots showing concentrations of Fe^{2+} , Fe^{3+} , FeS_2 , total Cu, total S, and % of total Fe in Fe^{2+} as functions of sediment depth beneath the sediment-water interface. North-basin core.

Gammon 1985). However, in view of the anoxic and sulfidic nature of the sediment and pore-waters, the copper ions are probably trapped in a Cu-S solid phase, e.g., chalcocite or covellite (CuS) (Carigan & Nriagu 1985). The ratio of total S to total Cu is ~300:1 by weight, hence insignificant amounts of S are bound in CuS .

The possibility of Cu migration in the sediment column, prior to entrapment in a solid phase, renders the Cu profile suspect for estimating rates of sedimentation. However, the Cu profile is approximately the inverse of that of organic carbon (Figs. 3, 4, Table 2), indicating a rate of sedimentation of 1 to 2 cm annually. ^{210}Pb dating was compromised by scatter and paucity of points over the pertinent time-interval. Rapid precipitation of CuS would support the Cu profile as a time scale.

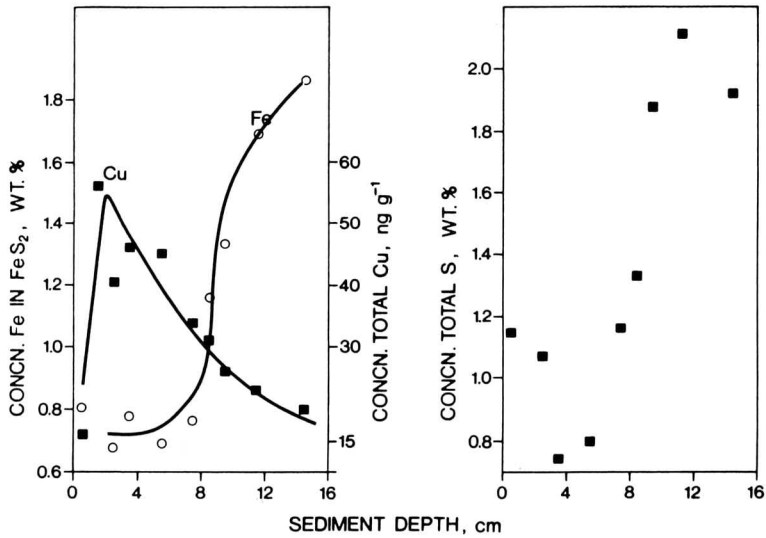


FIG. 4. Plots showing concentrations of Fe(S₂), total Cu, and total S as functions of sediment depth. South-basin core.

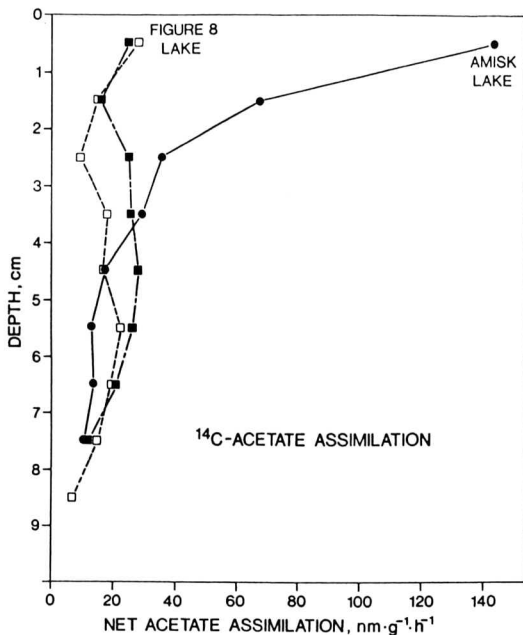


FIG. 5. ¹⁴C-acetate assimilation by freshly collected sediments from Figure Eight and Amisk Lakes. Open squares represent the south basin, and the filled squares, the north basin of Figure Eight Lake.

Organic carbon profiles

The elevated concentrations of copper in Figure Eight Lake sediments are closely and inversely linked to relatively low concentrations of organic carbon (Table 2). The carbon values clearly reflect the suppression of algal productivity and the lower deposition of organic matter following applications of copper sulfate. Concentrations of pyrite in sediments, and particularly in marine sediments, are controlled by the amounts of organic matter and of available sulfate and iron compounds (Berner 1984). In Figure Eight Lake, the marked decrease in deposition of organic matter to the sediments contributes to the decrease in pyrite formation.

Microbial assimilation

The microbial assimilation of ¹⁴C-acetate in the upper few cm of Figure Eight Lake sediments is considerably inhibited (Fig. 5); the plot profile for Amisk Lake sediments is representative of most temperate lakes (K. Burnison, pers. comm.). Microbial assimilation is lower for the 1- to 2-cm and 2- to 3-cm sections of Figure Eight Lake sediments than it is for deeper sections (Fig. 5), in good correspondence with elevated concentrations of copper (Figs. 3, 4). It seems reasonable to attribute the lower microbial assimilation decrease to decreased deposition of

organic matter or to copper ion toxicity to bacteria (or to both factors).

Most of the organic matter deposited to the sediments of Figure Eight Lake is easily metabolizable because the input of terrigenous organic matter is probably very low. Stream flow into the lake is minimal. Groundwaters are generally low in dissolved organic carbon (Thurman 1984). Calculations based on the increase in particulate and dissolved organic carbon during an algal bloom suggest that 97% of the organic matter is internally generated (*i.e.*, from CO₂).

GENERAL DISCUSSION

The toxicity of small amounts of Cu²⁺ ions to algae and to sediment bacteria and the lower deposition of organic matter have a marked effect on sulfide production and pyrite fixation. Amphipods disappeared from the water column after the first copper sulfate treatment (D. Walty, pers. comm.); consequently, the food chain in Figure Eight Lake was disrupted. The pyrite-depth profiles (Figs. 3, 4) do not correspond to the general understanding of the mechanisms of pyrite formation. Under normal conditions of sedimentation, the availabilities of sulfate, organic matter, and reactive iron compounds are highest at the sediment surface. The rate of pyrite formation, therefore, should be at a maximum at or near the surface. In Lake St. George sediments (Manning *et al.* 1979), 50% of total iron in the top 2 cm is present as FeS₂, the remainder of the iron being converted to pyrite over a few centuries. Ferrous ion is extracted from chlorite and clays in the sediments of Figure Eight Lake and Lake St. George.

Sulfate-ion concentrations in the overlying waters had pretreatment values of ~9 μg L⁻¹, SO₄; the values increased to ~32 μg L⁻¹, in August 1984 and to ~23 μg L⁻¹, SO₄ in November 1985, an increase of ~15 μg L⁻¹, SO₄. This increase in a 3.3-m column of water over 1 m² is equivalent to ~50 g SO₄ or 17 g S. The decrease in FeS₂ concentrations in the sediment since initial CuSO₄ treatment is ~1.5% S, which for the top cm of mud equates to a loss of ~15 g S. Hence, the lower concentrations of sulfide in the sediment are matched reasonably well by higher levels of SO₄ in the water. The calculation ignores the decreased production of pyrite over ~6 cm, but counterbalancing this is the likelihood that sediments in shallower water probably contain less pyrite. According to the formula $2\text{FeS}_2 + 15/2 \text{O}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_4^{2-} + 8\text{H}^+$, the release of 0.5 moles of S m⁻², is accompanied by the release of 1 mole H⁺ m⁻², or, over the whole lake, 3.5×10^4 , moles H⁺ L⁻¹.

The pH of the surface waters of Figure Eight Lake in summer is 8 to 9, which high value reflects the high productivity of the lake: photosynthesis con-

sumes carbon dioxide. Consequently, in hypertrophic hard-water lakes, the presence of Cu²⁺ ions may drastically inhibit sulfate reduction and pyrite formation, but have a minor effect on water acidity. The effect of copper treatment on the acidity of a eutrophic soft-water lake may be more important. In lakes of low productivity (low trophic character), sulfate reduction and pyrite formation are relatively unimportant. Nevertheless, copper ion toxicity to bacteria and to amphipods is significant and undesirable because of damage to the food chain, leading ultimately to poorer-quality fish. The copper ions contained within minerals such as chalcopyrite and nickel sulfides, deposited to the sediments from mining activities, are mainly unavailable, provided the sediments remain anoxic.

The use of copper sulfate as an algicide should be carefully reconsidered. The method is inexpensive, but the small concentrations of copper required significantly affect the sulfur cycle. Furthermore, algal suppression is temporary, lasting a few months, possibly because the precipitation of copper as a solid sulfide phase renders the copper unavailable.

ACKNOWLEDGEMENTS

The authors thank A. Mudroch, J. Nriagu, D. Scafe and D. Walty for much assistance. The referees proposed several improvements to the manuscript.

REFERENCES

- BERNER, R.A. (1984): Sedimentary pyrite formation: an update. *Geochim. Cosmochim. Acta* **48**, 605-615.
- BURNISON, B.K., RAO, S.S., JURKOVIC, A.A. & NUTTLEY, D.J. (1986): Sediment microbial activity in acidic and non-acidic lakes. *Water Poll. Res. J. Can.* **21**, 560-571.
- CARIGNAN, R. & NRIAGU, J.O. (1985): Trace metal deposition and mobility in the sediments of two lakes near Sudbury, Ontario. *Geochim. Cosmochim. Acta* **49**, 1753-1764.
- COEY, J.M.D., SCHINDLER, D.W. & WEBER, F. (1974): Iron compounds in lake sediments. *Can. J. Earth Sci.* **11**, 1489-1493.
- COOK, R.B., KELLY, C.A., SCHINDLER, D.W. & TURNER, M.A. (1986): Mechanisms of hydrogen ion neutralization in an experimentally acidified lake. *Limnol. Oceanogr.* **31**, 134-148.
- DESJARDINS, J.F. (1978): Acid dissolution. In *Manual on Soil Sampling and Methods of Analysis* (J.A. McKeague, ed.). Can. Soc. Soil Sci., Ottawa, Ontario.

- EFFLER, S.W., LITTEN, S., FIELD, S.F., TON-NGORK, T., HALE, F., MEYER, M. & QUIRK, M. (1980): Whole lake responses to low level copper sulfate treatment. *Water Res.* **14**, 1489-1499.
- HILTON, J., LONG, G.J., CHAPMAN, J.S. & LISHMAN, J.P. (1986): Iron mineralogy in sediments. A Mössbauer study. *Geochim. Cosmochim. Acta* **50**, 2147-2151.
- KEMP, A.L.W. (1971): Organic carbon in the surface sediments of Lakes Ontario, Erie and Huron. *J. Sed. Petrology* **41**, 537-548.
- LUM, K.R. & GAMMON, K.L. (1985): Geochemical availability of some trace and major elements in surficial sediments of the Detroit River and western Lake Erie. *J. Great Lakes Res.* **11**, 328-338.
- MANNING, P.G. & ASH, L.A. (1979): Mössbauer spectral studies of pyrite, ferric and high-spin ferrous distributions in sulfide-rich sediments from Moira Lake, Ontario. *Can. Mineral.* **17**, 111-115.
- _____, & JONES, W. (1982): The binding capacity of ferric hydroxides for non-apatite inorganic phosphorus in sediments of the depositional basins of Lakes Erie and Ontario. *Can. Mineral.* **20**, 169-176.
- _____, WILLIAMS, J.D.H., CHARLTON, M.N., ASH, L.A. & BIRCHALL, T. (1979): Mössbauer spectral studies of the diagenesis of iron in a sulfide-rich sediment core. *Nature* **280**, 134-136.
- STONE, A.J. (1967): Least-squares fitting of Mössbauer spectra. Appendix to Bancroft, G.M., Maddock, A.G., Ong, W.K., Prince, R.H. & Stone, A.J. (1967): Mössbauer spectra of iron (III) diketone complexes. *J. Chem. Soc.* **A1967**, 1966-1971.
- THURMAN, E.M. (1984): *Organic Geochemistry of Natural Waters*. Nijhoff & Junk, Dordrecht, Netherlands.
- WHITAKER, J., BARICA, J., KLING, H. & BUCKLEY, M. (1978): efficacy of copper sulfate in the suppression of *Aphenezomenon flos-aquae* blooms in prairie lakes. *Environ. Pollut.* **15**, 185-194.
- WINNER, R.S. (1985): Bioaccumulation and toxicity of copper as affected by interactions between humic acid and water hardness. *Water Res.* **4**, 449-455.

Received January 24, 1987, revised manuscript accepted November 21, 1987.