Abstract

The room-temperature Mössbauer spectra of freeze-dried, sulfide-rich sediments from Moira Lake, Ontario, comprise an outer high-spin ferrous doublet and an inner envelope made up mainly of pyrite and ferric doublets. In the upper 16 cm of sediment, iron is distributed between pyrite, ferrous, and ferric forms in the ratios 23:52:25. At greater depths, additional pyrite has formed at the expense of ferric ion, the ratios for the 28-30 cm fraction being 48:25:21. The lower pyrite and total-sulfide concentrations in the upper 30 cm of sediment may reflect higher dissolved-oxygen concentrations in the pore-waters, due to bioturbation processes. Alternatively, increased arsenic contamination in the upper 30 cm may be inhibiting the activity of sulfate-reducing bacteria.

Introduction

Mössbauer spectroscopy is a facile method of determining quantitatively the principal iron compounds in low-sulfide sediments (Coey et al., 1974, Coey 1975a, Readman et al. 1976, Perlow et al. 1974, Manning 1977). Some compounds are readily identified from their Mössbauer spectra alone, e.g., chlorite, siderite and magnetically-ordered oxides. In general, Mössbauer spectra are best interpreted with supportive X-ray diffraction and analytical data because the 0 to 0.8 mm s⁻¹ range, in particular, is dominated by broad absorptions comprising contributions from ferric ions in different sites and, in some cases, from low-spin ferrous ions in pyrite and mackinawite. Computer resolution of the Mössbauer spectra of sulfide-rich sediments (say, > 0.5% S) is likely to be complicated by the near-coincidence of the pyrite and ferric quadrupole doublets, as indicated by the isomer shifts and quadrupole splittings listed in Table 1.

This paper describes an interpretation of the Mössbauer spectra of the sulfide-rich reducing sediments from Moira Lake, Ontario. Moira Lake has a surface area of 4500 hectares and a mean depth of 5 m. Excessive algal blooms occur in summer, but bottom waters are always oxic. Elevated levels of As, Co and Ni in the upper 30 cm of sediment (Table 2) are caused

<p>|</p>
<table>
<thead>
<tr>
<th>Sediment fraction, cm</th>
<th>Inner Doublet</th>
<th>Outer Doublet</th>
<th>Area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS</td>
<td>QS</td>
<td>hW</td>
<td>IS</td>
</tr>
<tr>
<td>0-2</td>
<td>0.35</td>
<td>0.60</td>
<td>0.48</td>
</tr>
<tr>
<td>2-4</td>
<td>0.36</td>
<td>0.61</td>
<td>0.49</td>
</tr>
<tr>
<td>6-8</td>
<td>0.34</td>
<td>0.69</td>
<td>0.46</td>
</tr>
<tr>
<td>8-10</td>
<td>0.32</td>
<td>0.63</td>
<td>0.46</td>
</tr>
<tr>
<td>12-14</td>
<td>0.32</td>
<td>0.63</td>
<td>0.39</td>
</tr>
</tbody>
</table>

lower pyrite and total-sulfide concentrations in the upper 30 cm of sediment may reflect higher dissolved-oxygen concentrations in the pore-waters, due to bioturbation processes. Alternatively, increased arsenic contamination in the upper 30 cm may be inhibiting the activity of sulfate-reducing bacteria.

(Traduit par la Rédaction)
TABLE 2. TOTAL-Fe, IRON, AND ARSENIC CONCENTRATIONS IN MOIRA LAKE SEDIMENTS†

<table>
<thead>
<tr>
<th>Fraction</th>
<th>1-3 cm</th>
<th>9-12</th>
<th>12-15</th>
<th>15-18</th>
<th>20-24</th>
<th>25-35</th>
<th>35-40</th>
<th>45-50 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1.7</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>2.1</td>
<td>2.0</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe</td>
<td>4.3</td>
<td>4.2</td>
<td>4.4</td>
<td>4.1</td>
<td>4.6</td>
<td>4.5</td>
<td>4.6</td>
<td>4.5</td>
</tr>
<tr>
<td>As</td>
<td>0.15</td>
<td>0.08</td>
<td>0.07</td>
<td>0.07</td>
<td>0.025</td>
<td>0.003*</td>
<td>0.003*</td>
<td>0.003*</td>
</tr>
</tbody>
</table>

For Bend Bay surficial sediments: S = 0.8%, Fe = 4.9%, and As = 0.17%.

*Background As levels, based on values for uncontaminated lakes in the region and on deeper core analyses for Moira Lake muds.
† Dry wt. E. J. Capobianco, analyst.

by seepage from the now-defunct smelting complex at Deloro, located on the Moira River 12 km upstream. This river, the lake's only outlet, drains into the Bay of Quinte, Lake Ontario.

The main aims of the work are: (i) to determine the efficacy with which Mössbauer methods can distinguish ferric ions and low-spin ferrous ions; (ii) to determine the principal Fe compounds over a length of core embracing the period of mining and smelting activities at Deloro (1900 to 1961), and (iii) to seek evidence for amorphous or poorly crystallized iron sulfides.

EXPERIMENTAL DETAILS

A Kajak-Brinkhurst corer (Guelph Instruments Ltd.) was used to obtain 30 cm cores from beneath 4 m of water in a sheltered bay on the extreme western end of Moira Lake; the bay is separated from the inflow of the Moira River by a rocky promontory 800 m long. Cores were also collected from 3 m of water in Bend Bay, a small bay on the Moira River 3 km upstream of the lake and 9 km downstream from the former smelter. The cores were extruded and sectioned into 2 cm fractions on a convenient nearby dock, and the sample fractions frozen immediately. The sediments were placed in a freeze-drier, usually about five hours later; the dark grey dried residuals were then stored in a vacuum desiccator.

Mössbauer spectra of freeze-dried sediment residuals were run, as described earlier (Manning & Tricker 1975), using equipment at the University College of Wales, Aberystwyth. Spectra were fitted on the University of Manchester Regional Computer Centre CDC 6600 machine, using the fitting programs of Stone (1967). Lorentzian line-shapes were assumed and the area ratios of each peak of a quadrupole doublet were constrained to be equal. Orientation in the γ-ray beam of pyrite and of amorphous or poorly-crystallized ferric compounds was not anticipated; the high organic matter content (~30% by weight) would reduce any orientation of clay minerals.

RESULTS AND DISCUSSION

Representative spectra of freeze-dried residuals are shown in Figures 1 and 2; the presence of at least two doublets is apparent. The isolated high-energy absorption is undoubtedly caused by octahedrally-coordinated ferrous ions (Bancroft 1973), probably in a field of oxygen and OH ions. The broad envelope in the 0 to 0.8 mm s⁻¹ range contains absorptions from the same ferrous ions, from ferric ions, and from low-spin ferrous ions in pyrite and mackinawite (Vaughan & Ridout 1971, Morice et al. 1969). No black patches were observed in the sediment cores, suggesting that precursor sulfides (mackinawite, amorphous Fe–S compounds) are present in low concentrations.

Two-doublet fits of the Mössbauer spectra

Calculated values of isomer shift (IS), quadrupole splitting (QS) and half-width (HW) are listed in Table 1, and a computer-derived fit for one spectrum is shown in Figure 1. The IS and QS values derived for the outer doublet are similar to those reported for high-spin ferrous ions in chlorite (Coey et al. 1974, Coey 1975b, Manning 1977); the presence of chlorite was confirmed in an X-ray diffraction study. The peak half-width (Table 1) is rather large and reflects ferrous ions in a wide range of distorted octahedral sites. Illite and kaolinite are unlikely to make significant contributions to line broad-
Sediments from Moira Lake, Ontario

Fig. 2. Mössbauer spectra of Moira Lake sediment residuals. From top to bottom, the spectra mark the 0–2, 14–16 and 28–30 cm fractions. Continuous curve represents a computed fit using three doublets. Chi-squared values are, respectively, 260, 220 and 219, all with 239 degrees of freedom.

The Mössbauer parameters for the inner doublet (Table 1) for the 0–2, 2–4 and 6–8 cm fractions are in good agreement with corresponding values reported for amorphous hydrated ferric oxides in Bay of Quinte muds (Manning 1977) and in muds from several other lakes (Coey et al. 1974, Readman et al. 1976). In contrast, the Mössbauer parameters for the 24–26 and 28–30 cm fractions clearly approach values for low-spin ferrous ions in pyrite. This trend suggests that greater amounts of pyrite are formed in the deeper fractions at the expense of ferric ions. Significantly, the inner doublet:outer doublet area ratios remain unchanged with depth of sediment, confirming the ferric iron-to-pyrite conversion and suggesting further that the high-spin ferrous ions are in relatively inert sites, as would be the case in well-crystallized chlorite.

Bend Bay spectra (Table 1) reveal a higher proportion of the high-spin ferrous ion than do those of the Moira Lake sediments. The Mössbauer parameters for the inner doublet are closer to those of ferric hydroxides than of pyrite. Lesser amounts of pyrite are anticipated because Fe:S ratios (Table 2) are considerably greater in the Bend Bay muds.

The two-doublet fits have several disadvantages. Firstly, the trends in the Mössbauer parameters are strongly indicative of ferric ion–pyrite admixtures. Secondly, optical microscopy shows clear evidence in all fractions of opaque pyrite framboids (Vallentyne 1963, Sweeney & Kaplan 1973). Thirdly, the computed fit on the high-energy limb of the main absorption envelope is rather poor; this is shown quite dramatically in the Moira Lake 0–2 cm spectrum (Fig. 1).

Three-doublet fits

With no constraints except for the equalizing of area ratios and of half-widths for the two peaks of a given doublet, all computer fits converged; however, the calculated Mössbauer parameters and the doublet:doublet area ratios were erratic from one spectrum to another. Because of good optical microscopic evidence for pyrite framboids, we decided to constrain the energies and half-widths of the pyrite absorptions. Peak positions were measured accurately for pyrite crystals and for pyrite in some modern sediments. Half-widths ranged from 0.275 to 0.30 mm s⁻¹; a value of 0.285 mm s⁻¹ has been assumed. Calculated values of IS, QS and HW
TABLE 3. MöSSBAUER PARAMETERS AND IRON DISTRIBUTIONS* FOR COMPOUNDS IN MOIRA LAKE SEDIMENTS. PYRITE PEAK POSITIONS AND HALF-WIDTHS CONSTRAINED

<table>
<thead>
<tr>
<th>Sediment fraction, cm</th>
<th>Inner Doublet (Fe²⁺) IS</th>
<th>QS</th>
<th>HM</th>
<th>Outer Doublet (Fe³⁺) IS</th>
<th>QS</th>
<th>HM</th>
<th>Feš² Fe²⁺ Fe³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-2</td>
<td>0.41</td>
<td>0.76</td>
<td>0.60</td>
<td>1.11</td>
<td>2.63</td>
<td>0.41</td>
<td>24</td>
</tr>
<tr>
<td>2-4</td>
<td>0.40</td>
<td>0.76</td>
<td>0.54</td>
<td>1.10</td>
<td>2.61</td>
<td>0.45</td>
<td>24</td>
</tr>
<tr>
<td>6-8</td>
<td>0.39</td>
<td>0.78</td>
<td>0.57</td>
<td>1.12</td>
<td>2.60</td>
<td>0.56</td>
<td>23</td>
</tr>
<tr>
<td>14-16</td>
<td>0.36</td>
<td>0.64</td>
<td>0.60</td>
<td>1.14</td>
<td>2.59</td>
<td>0.49</td>
<td>20</td>
</tr>
<tr>
<td>24-26</td>
<td>0.40</td>
<td>0.67</td>
<td>0.65</td>
<td>1.13</td>
<td>2.59</td>
<td>0.32</td>
<td>38</td>
</tr>
<tr>
<td>28-30</td>
<td>0.43</td>
<td>0.72</td>
<td>0.51</td>
<td>1.13</td>
<td>2.64</td>
<td>0.42</td>
<td>48</td>
</tr>
<tr>
<td>BB0-2**</td>
<td>0.39</td>
<td>0.71</td>
<td>0.62</td>
<td>1.13</td>
<td>2.59</td>
<td>0.47</td>
<td>11</td>
</tr>
<tr>
<td>BB22-24**</td>
<td>0.39</td>
<td>0.64</td>
<td>0.66</td>
<td>1.14</td>
<td>2.60</td>
<td>0.44</td>
<td>13</td>
</tr>
</tbody>
</table>

* Assumes equal recoil-free fractions for all compounds
**BB Bend-Bay sediments

for the high-spin ferrous and ferric ions, using these constraints on the pyrite absorptions, are listed in Table 3. Chi-squared values are slightly smaller than for the two-doublet fits, e.g., 257 vs. 291 for the 2-4 cm Moira Lake computation.

The three-doublet fits seem justified on the following grounds: (a) the area ratios are remarkably consistent for the 0-2, 2-4, 6-8 and 14-16 cm Moira Lake fractions; (b) the Mössbauer parameters derived for the ferric doublet are in good agreement with values reported for amorphous ferric compounds in sediments (Coey et al. 1974, Manning 1977, Coey 1975a, b); (c) less pyrite is present in the Bend Bay sediments, consistent with lower S concentrations; (d) the computed fit on the high-energy limb of the main envelope is considerably improved, as indeed is the fit for the whole curve generally (Fig. 2), and (e) the increase in pyrite concentration coincides with an increase in total S concentrations (at a depth below 14-16 cm).

**General discussion**

The concentrations of the principal Fe species as a function of sediment depth are plotted in Figure 3. Pyrite is formed at the expense of the amorphous or poorly-crystallized ferric compounds. These ferric ions are remarkably stable, bearing in mind the reducing nature of the sediments. Conceivably, ferric hydroxides are deposited in a wide range of polymerized forms containing adsorbed phosphate. In Moira Lake and in other lakes with reducing sediments, the very fine amorphous material is reduced rapidly, probably in a matter of days or weeks, with the phosphate released to the overlying water. It is this fine fraction that exists in the brown oxidized microzone, e.g., Lake Erie sediments, and that is easily reduced (Burns & Ross 1972, Lean & Charlton 1976). The coarser-grained (more polymerized) ferric hydroxides take adsorbed phosphate to greater depths where, on reduction of iron, ferric phosphate would be converted to vivianite.

In the upper 14-16 cm of sediment, ~ 25% of total iron is present in Feš², corresponding to...
SEDIMENTS FROM MOIRA LAKE, ONTARIO

115

to an estimated 1.1% Fe and 1.25% S by weight; the total S content of the sediments is ~ 1.6%. At the 28–30 cm level, the pyrite fraction contains 2.1% Fe and 2.4% S, but the total S content is ~ 2.1%. This discrepancy may arise from a systematic error in the XRF analysis or, more likely, from differences in recoil-free fractions, from the use of a slightly incorrect value for the pyrite half-width, and from absorption by minor Fe compounds, e.g., mackinawite. Nevertheless, the trends demonstrated in Figure 3 are probably valid, except that the pyrite component may be overestimated by ~ 10%. Total S concentrations below 30 cm are not significantly greater than 2.1%, (Table 2); hence, it would seem that the Fe distributions in deeper sediments are similar to those for the 28–30 cm fraction. Approximately 90% of the sulfide in Bend Bay sediments is bound up in pyrite.

The decreasing pyrite production in the upper 30 cm of sediment may be caused by one, or both, of two processes. Firstly, diffusion of oxygen from the oxic surficial waters, possibly periodically, and promoted by bioturbation, may occur to a depth of ~ 30 cm. Alternatively, decreasing pyrite production may be caused by arsenic inhibition of sulfate-reducing bacteria; arsenic concentrations build up rapidly above the 30 cm level (Fig. 3, Table 2). There is insufficient organic matter in Moira Lake sediments to account for the high sulfide content; most of the sulfide is undoubtedly produced by sulfate-reducing bacteria (Berner 1970).

The mackinawite spectrum is a single peak with IS = 0.2 mm s⁻¹ (Vaughan & Ridout 1971); hence, any mackinawite in the Moira Lake sediments will absorb in the absorption “valley”. Our computed fits in the inner spectral region, based on high-spin ferrous, ferric, and pyrite doublets, seem satisfactory; thus, it is unlikely that > 10% of total Fe is in mackinawite.

ACKNOWLEDGMENTS

We thank Professor J.M. Thomas and Dr. W.J. Jones for the use of the Mössbauer equipment, Mr. G.E. Bengert for assistance in obtaining the core and Mr. J. Capobianco for the sediment analyses. Professor G.M. Bancroft ran some preliminary spectra.

REFERENCES


——— (1975b): The clay minerals: use of the Mössbauer effect to characterize them and study their transformation; Proc. Int. Conf. Mössbauer Effect (Cracow), 333-354.


Received May 1978; revised manuscript accepted August 1978.