Iron and sulfate reduction in the sediments of acidic mine lake 116 (Brandenburg, Germany): Rates and geochemical evaluation

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Abstract: A combination of rate measurements of iron(III)oxide and sulfate reduction, thermodynamic data, and pore water and solid phase analysis was used to evaluate the relative significance of iron and sulfate reduction in the sediments of an acidic strip mining lake (Lake 116, Brandenburg, Germany). The rate of sulfate reduction was determined using a ³⁵S radiotracer method. Rates of iron turnover were quantified by mass balances based on pore-water concentration profiles. The differences in Gibbs free energy yield from reduction of iron and sulfate and from methanogenesis were calculated from individual redox couples and concentrations of reactants in account for the influence of high Fe³⁺ concentrations and differing mineral phases. Integrated (0-20 cm) mean rates of sulfate reduction were 1.2 (pelagial), respectively 5.2 (littoral) mmol (m²d)⁻¹. Based on electron equivalents, the estimated iron reduction rates reached between about 50 % (pelagial) and 75 % (littoral) of the sulfate reduction rates. Compared to conditions usually assumed in the literature, in the sediments Gibbs free energy advantage of iron reduction over sulfate reduction was reduced from +11 KJeq⁻¹ to a range of about +7 KJeq⁻¹ (ferrihydrite, “reactive iron”) to −6 KJeq⁻¹ (goethite). This indicates that iron reduction was thermodynamically favored to sulfate reduction only if amorphous iron(III)oxides were available and is in accordance to the high competitiveness of sulfate reducers in the sediment. While total iron concentration in the sediments was high (up to 80% of the dryweight), reactive iron only accounted for 11-38% and was absolutely and relatively diminished in the zone of iron reduction. Pore-water concentration gradients and ¹²⁵⁷CS profiles indicated that little or no bioturbation occurred in the sediments, probably inhibiting the renewal of reactive iron. We further hypothesize that the reactivity of the iron oxide surfaces was reduced due to adsorption of DOM, suggested by IR spectra of the DOM and by a surface coverage estimate using literature data. Pelagial and littoral sediments displayed different dynamics. At the littoral relative iron reduction rate estimates were higher, iron sulfides were not accumulated and residence times of iron oxides were short compared to the pelagial. At the littoral site reoxidation of iron sulfides probably resulted in the renewal of reactive iron(III)oxides, possibly allowing for higher relative rates of iron reduction.

Key words: Sulfate reduction, iron reduction, iron oxides, Gibbs free energy, DOM, DRIFT-IR

1. Introduction

Sulfate and iron reduction in sediments have been investigated in numerous studies. A substantial knowledge about rates of and controls on sulfur and iron cycling in marine sediments has emerged from the application of solid phase extractions, radiotracer measurements and pore-water modeling (e.g. Chanton et al., 1987; Canfield, 1989; Water, Air, and Soil Pollution 108: 249-270, 1998. © 1998 Kluwer Academic Publishers, Printed in the Netherlands.)
Canfield et al., 1993b; Fossing and Jørgensen, 1989; Fossing and Jørgensen, 1990; Wang and van Cappellen, 1996). Sulfate and iron reduction in freshwater lakes have been studied less intensively, and studies often focused on the effects of atmospheric acidification (Urban et al. 1994; Kelly et al., 1995; Sass et al., 1997). While sulfate reduction in moderately acidic mine lakes and rivers has been investigated in few studies (Herlihy and Mills, 1985; Herlihy et al., 1987), to our knowledge no sulfate and iron reduction rates in highly acidic mine lakes (pH below 3) have been determined and evaluated. Acidic lakes differ from marine and freshwater sediments regarding the chemical composition of the sediments and the conditions of early diagenesis in several respects. Iron oxides and iron sulfides may predominantly constitute the solid phase (Peine and Peiffer, 1996). Concentrations of dissolved sulfate and iron can exceed freshwater concentrations by two or three orders of magnitude (Herlihy and Mills, 1985; Peine and Peiffer, 1996). The availability of organic substrates may limit reduction rates (Peine and Peiffer, 1996), and specific communities of benthic algae unknown to “natural” sediments may occur and control the geochemical conditions at the sediment-water interface (Kelly et al., 1995). Due to these differences the knowledge about rates of and controls on iron and sulfate reduction has to be adapted to the specific geochemical conditions of acidic mine lakes.

It was originally hypothesized that the sequence and dominance of terminal electron acceptor reactions in sediments is controlled on the basis of standard energy yields of the reactions (Berner 1980). Based on this hypothesis iron reduction precedes sulfate reduction (Berner, 1980; Canfield, 1993). More recent studies do not generally support this concept (Canfield et al., 1993b; Fossing and Jørgensen, 1990; Purrer and Wehrli 1996; Wang and Van Cappellen, 1996; Postma and Jakobsen, 1996). Researchers stress the importance of mineral phases and nutrient requirements for the occurrence of a certain diagenetic reaction. In particular, iron reducers preferentially reduce amorphous iron oxides (Lovley and Phillips, 1988) and outcompete sulfate reducers and methanogenic bacteria for organic matter in the presence of this type of iron oxide (Lovley, 1987). In analogy, it may be hypothesized that iron reduction can be disadvantageous if the solid iron oxide phase is highly crystalline. Similar effects by the adsorption of dissolved organic matter (DOM) and sulfate on oxide surfaces, which may reduce their reactivity due to a change in surface characteristics (Gu et al., 1994; McKnight et al., 1992) cannot be ruled out.

The objective of this study is to quantify sulfate and iron reduction in the sediments of acidic mine drainage lake 116 (Brandenburg, Germany) and to develop hypotheses regarding the ratio of the estimated rates of the two pathways of carbon oxidation. Due to the specific conditions of early diagenesis in acidic mine lakes, we assumed that a change in energy yields from sulfate and iron reduction, the dynamics of solid phase sulfur and iron and the interaction between DOM and the solid iron phase are of importance.

2. Methods and Materials

2.1 STUDY SITE

Lake 116 is part of a interconnected chain of strip mining lakes located in Brandenburg (Germany). The surface area is 27.3 ha, with a maximum depth of 11 m (Figure 1). The former strip mines are cut into tertiary and quaternary clastic sediments containing lignite seams of 5 to 10 meters thickness on average (Laubag, 1996). Groundwater flooding of the mining area started in 1968 and was completed some years later. The sediment formed by sedimentation after flooding, Measurements and model calculations suggests...
that the lake receives most of its inflow by surface water from a little creek connecting the lakes (Weber, pers. communication). The outflow proceeds via surface water. In 1996 lake 116 showed a dimictic regime with an anoxic hypolimnion during summer stratification (sampling: May and August). In early November the water column was completely mixed. Sampling was done at maximum depth, in the following called „pelagial“ and close to the shoreline at depths of 3-4 m, subsequently called „littoral“.

Fig. 1. Lake 116 The area west of the lake consists of mining deposits (fine and medium sands and coal like substances), while the eastern shore is cut into sandy quaternary and tertiary deposits. The shallow littoral is overgrown with Phragmites communis. The adjacent slopes are covered by pioneer vegetation or birch and pine forest stands. The sampling locations are marked.

2.2 SAMPLING

Samples were taken with a gravity corer (diameter: 6 cm) from the sampling locations on several occasions (9/96-11/96) and transported in an isolating box to the laboratory within 10 hours. Sediment incubations began immediately after arrival. Table 1 displays which analyses were done in the individual cores. For the solid phase analyses the cores were cut into segments after visual separation into zones of changing structure and color. Diffusion chambers (cellulose acetate membrane; 0.45 µm pore diameter; 7 ml cell volume; Hesslein, 1976) were used for sampling the pore-water of the sediments in December 1996. They were filled with deionized and deaerated (nitrogen flux) water at the laboratory, transported to the lake and vertically inserted into the sediments by scuba divers and allowed to equilibrate for two weeks. Recovered from the sediment, the sealed chambers were transported in a water-filled box and subsequently sampled in the field by stinging syringes through the rubber seal of the cells. Each cell volume was divided in subsamples. Fe\textsuperscript{2+} concentrations and pH were determined immediately, while the other subsamples were frozen (-18°C) and stored until analyzed.
TABLE 1

<table>
<thead>
<tr>
<th>Core</th>
<th>Solid δ13S 13C</th>
<th>pe-values</th>
<th>sulfate reduction rates</th>
<th>IR</th>
<th>DOC, dissolved inorganics, iron reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymetal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td></td>
<td>X</td>
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<tr>
<td>P2</td>
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<tr>
<td>P3</td>
<td></td>
<td>X</td>
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<tr>
<td>P4</td>
<td></td>
<td>X</td>
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<tr>
<td>P5, P19</td>
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<tr>
<td>P20-P23</td>
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<td>X</td>
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<td>Dialysis chamber</td>
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<td>Littoral</td>
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<td>X</td>
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<tr>
<td>L1</td>
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<td>L2</td>
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<td>X</td>
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<td>L12-L15</td>
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<td>X</td>
</tr>
<tr>
<td>Dialysis chamber</td>
<td></td>
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</tr>
</tbody>
</table>

2.3 ANALYTICAL METHODS

SO4^2-, Cl, Ca^{2+}, Mg^{2+}, K^+, and NH4^+ were determined by ion chromatography (Metrohm 690), Fe^{2+} by the phenanthroline method (Frevert, 1983), methane and DIC by headspace gas chromatography, DOC by a total organic carbon analyzer (TOC5050, Shimadzu) and pH using an electrode (WTW E50, pH 7 and pH 3 buffers). No replicates were determined due to the small sample volumes. E_o values were determined by horizontally inserting an E_e-microelectrode into sediment cores, pe-values were calculated without correcting for differing pH (Equation 1; Sigg and Stumm, 1991).

\[ pe = F \left( \frac{2.303 R T}{I (E_{h}-E_{0})} \right) \]  

where: \( F \) is the Faraday constant = 96487 C mol\(^{-1}\); \( R \) is the gas constant = 8.314 J (K mol\(^{-1}\)); \( T \) is temperature in Kelvin; \( E_{h} \) is measured potential [mV] and \( E_{0} \) is potential of the reference electrode [mV].

DOM was characterized by Diffuse Reflectance Fourier-Transformed Infrared Spectroscopy (DRIFT-IR, Bruker IFS 66v, spectral resolution 4 cm\(^{-1}\)). Gravity cores were cut into segments (0.5 cm and 10-15, 12-17 cm, respectively), the segments centrifuged (3000 rpm, 20 min), filtered (0.45 µm, cellulose-nitrate) and freeze-dried. Identification of DRIFT-IR bands was done according to Kaiser et al. (1997), McCarthy and Rice (1985), and Niemeyer et al. (1992).

Total iron was determined by flame atomic absorption spectrometry after digestion of dried sediment with concentrated nitric and hydrochloric acid (1:1 ratio) in a microwave digester. Reactive iron was extracted by treatment with HCl (c = 1 mol L\(^{-1}\), Wallmann et al., 1993) and concentrations of Fe(total) determined by flame atomic absorption spectrometry. The concentration of Fe(III) was calculated by the difference between Fe(total) and Fe(II) (AVS). Possible presence of FeCO\(_3\) may have caused an overestimate of Fe(III). The content of total inorganic reduced sulfur compounds (TRIS: FeS\(_2\), FeS, S\(_2\)) and FeS (AVS) was determined by the method of Fossing and Jørgensen (1989) and Moestlund et al. (1994), respectively. Frozen sediment samples were thawed under N\(_2\) and distilled with HCl (c = 5 mol L\(^{-1}\); AVS and TRIS) and Cr(II)Cl\(_2\) (c = 0.15 mol L\(^{-1}\), TRIS). The H\(_2\)S released into the nitrogen stream was trapped in 50 ml of NaOH (c = 0.15 mol L\(^{-1}\)) solution. The sulfide was precipitated by addition of zinc acetate and photometrically
determined with a Varian Cary 1E at 665 nm (Frevert, 1983). The analytical recovery of a pyrite standard was 86% (n = 4, sd = 3%) and of a ZnS standard 96% (A/S, n = 4, sd = 3). Elementary sulfur was determined by HPLC (Gilson Ahimed Holochrom, RP-18 column, UV-visible, 265 nm) after a batch extraction of sediment with methanol (6 hours), centrifuging and filtering (0.7 μm). Analytical recovery of a S²⁻ standard was 98% (n = 8, sd = 12%).

δ³⁴S-values of the inorganic sulfur fractions and total sulfur were determined by gas mass-spectrometry at the pelagic site. The sediment was distilled as described for TRIS. Trapped H₂S was precipitated by adding zinc acetate (10 weight%), filtered, washed with aqua millipore and reacted with AgNO₃ (50 ml, 10 weight%) to Ag₂S, washed again and freeze dried before being measured. All radiols were determined by gamma spectrometry after freeze drying of sediment in order to date the sediments (Rowan et al., 1993; Wetland et al., 1993).

2.4 SULFATE REDUCTION

The δ³⁴S-radiotracer method was used (Jørgensen, 1978; Fossing and Jørgensen, 1989; Urban et al., 1994) to determine sulfate reduction rates. Subcores syringes (60 ml plastic syringes, length: 12 cm, diameter: 2.6 cm, tip-end cut off, 3 mm ports) were vertically inserted into the undisturbed sediment-water interface of gravity cores to a maximum depth of 20 to 40 cm. The subcores were closed at both ends with rubber stoppers ensuring that no air was enclosed during incubation. 6-30 μl (50 KBq) δ³⁵SO₄²⁻ (Amersham) were horizonally injected through rubber stoppered ports at 2-cm depth intervals using a micro-syringe (Hamilton Corp.). Samples were incubated for 10 to 14 hours at temperatures of 7° and 20° C, respectively. Following incubation, the subcores were plunged into a bath of liquid nitrogen and then stored at −20°C until analyzed. The frozen subcores were sectioned into 2-cm increments, thawed in a solution of zine acetate (30 ml, 5 weight%), distilled under a constant nitrogen flux with 5 ml of HCL (c = 5 mol L⁻¹) and 15 ml Cr(ClO₃)₃ (c = 0.15 mol L⁻¹) for 1.5 h at boiling temperature to extract the CRS-fraction of total sulfur (Canfield et al., 1986). The H₂S released into the nitrogen stream was trapped in 50 ml of NaOH (c = 0.15 mol L⁻¹), a 10 ml fraction added to 10 ml of a scintillation cocktail (Ultima Gold XR, Beckmann) and counted in plastic vials on a Beckmann LS 6000 scintillation counter. Quench corrections were made from the H number measured for each sample and a quench curve measured separately. The rate R (μmol cm⁻³ d⁻¹) of sulfate reduction was then calculated according to

\[ R = \frac{\delta S_{\text{reduced}}^{\text{S}} \cdot [SO_4^{\text{a}}] \cdot \alpha \cdot t}{\delta \text{SO}_4^{\text{a}} \cdot [\text{S}] \cdot \text{injected}} \]

\[ \delta S_{\text{reduced}}^{\text{S}} \text{: sum of all reduced forms of } \delta^{34}\text{S recovered [Bq], } \delta\text{SO}_4^{\text{a}} \text{: amount of radiotracer injected [Bq], } [\text{SO}_4^{\text{a}}] \text{: sulfate concentration [μmol cm}^{-3}\text{] in the sample, } \alpha \text{: isotope fractionation factor (1.05) and } t \text{: incubation time [d].} \]

The analytical error of the CRS analysis was determined by measuring 8 duplicates of a Na₂S⁻³⁻ solution. The relative error of a sample was 5.7% based on the average of the recovered activity. To measure analytical recovery and to determine whether oxidation occurred during incubation, freezing or storage, subcores were injected with a Na₂S⁻³⁻ solution and immediately frozen. In each of three replicates, 70% of the injected Na₂S⁻³⁻ activity could be recovered. Recovery was not included into the rate calculations. To determine whether the availability of organic substrates limited the microbial turnover of
sulfate in the sediments, through the ports subcores were injected with sodium acetate (50 μl, 1M) and pre-incubated for 5 days at 20°C to allow for distribution of the acetate and for growth of the acetate consuming microbial population. In replicate subcores, taken from the same gravity core, no sodium acetate was injected. The influence of temperature on the sulfate reduction rates was examined by incubating 3 replicates of samples at temperatures of 4°C, 7°C, 15°C and 20°C for 4-5 hours. Before injecting the 35SO4 2- the samples were equilibrated at the incubation temperatures for 24 hours.

2.5 PORE-WATER MODELING

Rates of Fe2+ turnover in the sediment were determined by combining mass balances of sedimentary layers with the calculation of diffusive fluxes at the boundaries of the layers (Chanton et al., 1987; Sherman et al., 1994; Kuivila and Murray, 1984). Since H2S could not be detected by smell, it was assumed that all released H2S reacted with Fe2+. In order to correct for this precipitation reaction, the cumulative sediment surface based rate of sulfate reduction was added to the sediment surface based rate of iron reduction as determined by the mass balance calculation. This was not done for sediment volume based rates at different depths since iron and sulfate reduction were not determined in the same samples. At steady-state conditions, constant porosity and neglecting compaction and advective flow, the turnover rate in a layer can be calculated from equation (3).

\[
\frac{\Delta C_{\text{Fe}^{2+}}}{\Delta z_{\text{out}}} - \frac{\Delta C_{\text{Fe}^{2+}}}{\Delta z_{\text{in}}} = P
\]

with \((\Delta C/\Delta z)\) being the gradient at the layer boundary [nmol cm⁻²], \(P\) the net turnover rate [nmol cm⁻² day⁻¹] and \(D_{1,\text{Fe}^{2+}}\) the whole-sediment diffusion coefficient for Fe²⁺ [cm² day⁻¹].

Porosity differences between adjacent layers of the sediment above the former ground of the mine were below 10%. Data points indicating sampling errors were eliminated, and the profiles were smoothed by calculating the individual concentration value from the average of the measured value (weighted twice) and the neighboring values (weighted one time each). Segments of 2 or 3 cm were chosen for the calculations since data points were available at centimeter distances. The gradient at the boundaries was determined by linear regressions of 3 data points (generally \(R²=0.9\); 4 exceptions: \(R²=0.6\)).

From diffusion of a 35SO4 2- tracer in three replicate subcores of each sampling location (Jørgensen 1978) the whole-sediment diffusion coefficient \(D_{\text{sulfate}}\) was determined for SO4 2-. \(D_{1,\text{sulfate}}\) was compared to the molecular diffusion coefficient \(D_{\text{molecule}}\) taken from Li and Gregory (1973), allowing the calculation of a whole-sediment correction factor \(α\)

\[
α = \frac{D_{1,\text{sulfate}}}{D_{\text{sulfate}}}
\]

The diffusion coefficient of Fe²⁺ was calculated by \(D_{1,\text{Fe}^{2+}} = α \cdot D_{\text{Fe}^{2+}}\). \(D_{\text{Fe}^{2+}}\) was also taken from Li and Gregory (1973) and corrected for temperature effects by the Stokes-Einstein relation (Berner, 1980). Only Fe²⁺ and H⁺ displayed strong concentration gradients (Figure 2). Since H⁺ concentrations above 1 μmol L⁻¹ were restricted to the upper 2 cm of the sediment, we did not correct for electric effects in modeling Fe²⁺ turnover, as has be done elsewhere (Kuivila and Murray, 1984; McDuff and Ellis, 1979).
2.6 THERMODYNAMIC CALCULATIONS

To assess the thermodynamic conditions in the sediment, pH values for individual redox couples were calculated using the measured concentrations of Fe\(^{2+}\), SO\(_4^{2-}\), methane, DIC, and pH by equations 5-12 (Table 2).

<table>
<thead>
<tr>
<th>Used equations</th>
<th>Used functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5) SO(_4^{2-}) + 2H(^+) + 2e(^-) = H(_2)SO(_4)</td>
<td>(p_{\text{SO}} = 0.67 - 1.0 \log \left(\frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{SO}_4]}\right) - 0.09 \cdot \text{pH})</td>
</tr>
<tr>
<td>(6) FeS(s) + H(^+) = Fe(^{2+}) + HS</td>
<td>(p_{\text{pH}} = 2.95 - \log \left(\frac{[\text{Fe}^{2+}]}{[\text{HS}]}\right))</td>
</tr>
<tr>
<td>(7) HS(^-) + H(^+) = H(_2)S</td>
<td>(K_{\text{HHS}} = [\text{H}^+] \cdot [\text{H}_2\text{S}] = 10^{-7.3})</td>
</tr>
</tbody>
</table>

Iron

(8) Fe\(_2(OH)_3\)(hydrathoixite, s) + 3H\(^+\) + e\(^-\) = Fe\(^{3+}\) + 3OH\(^-\) + 3H\(^+\)

(9) Fe\(_3(OH)_4\)(goethite, s) + 4H\(^+\) + e\(^-\) = Fe\(_2\)O\(_2\) + 3H\(^+\) + 4H\(^-\)

(10) Fe\(_2\)O\(_3\)(schwertmannite, s) + 4H\(^+\) + e\(^-\) = Fe\(_2\)O\(_3\) + 3H\(^-\)

Carbon

(11) H\(_2\)CO\(_3\) = CO\(_2\) + H\(_2\)O

(12) CH\(_4\) + H\(^+\) + e\(^-\) = CH\(_4\) + 2H\(_2\)O

\[ ^1\text{HCO}_2^+ = C\text{a}^k + 0 = 1 + K_{\text{H}[\text{H}^+]} \]

\[ \text{pH} = -0.87 + 1.0 \log \left(\frac{\text{CO}_2}{\text{H}_2\text{O}}\right) \]

The protonysis coefficient \(k\) for the carbonate system was used (Stumm and Morgan 1996, p. 127f.)

Concentrations were corrected for ionic strength effects and transformed into activities by the extended law of Debye-Hückel (Stumm and Morgan, 1996). Since H\(_2\)S was not analytically determined, a concentration range determined by the solubility product of pyrite (10\(^{-36.6}\)) and FeS (10\(^{-29.5}\)) was assumed (Stumm and Morgan, 1996). Within this range, the absolute values of the sulfide concentration did not qualitatively influence the results. Gibbs free energy change (\(\Delta G\)) for a reaction is connected to pH values by equation (13) (Stumm and Morgan, 1996):

\[
\Delta G = -RTn (p_{e_1} \cdot p_{e_2}) \quad (13)
\]

with \(p_{e_1} = \text{ps of oxidation half-reaction}, p_{e_2} = \text{ps of reduction half-reaction}\)

We assume that the organic matter that is oxidized by iron, sulfate and dissolved carbon dioxide (methanogenesis) is identical (\(p_{e_1} = \text{constant}\)). Differences in energy yield from organic carbon oxidation were calculated by equation (14), following from equation (13):

\[
\Delta \text{G}_A - \Delta \text{G}_B = RT \ln \left(\frac{\text{p}_{eA}}{\text{p}_{eB}}\right) \quad (14)
\]

with \(p_{eA} = \text{ps of reduction half-reaction A}, p_{eB} = \text{ps of reduction half-reaction B}\)

3. Results

3.1 PORE-WATER DATA

The pH increased from below 3 at the sediment-water interface to above 6 at depths of 2 cm to 3 cm, while the pH decreased from above 7 to below 5. Fe\(^{3+}\), Ni\(^{2+}\), and DOC concentrations sharply increased below the sediment-water interface, while the concentration gradients of SO\(_4^{2-}\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\), and Cl\(^{-}\) were less pronounced (Figure 2).
The pore water was dominated by SO$_4^{2-}$, Fe$^{2+}$, and Ca$^{2+}$ with concentrations ranging from 2000 μmol L$^{-1}$ to 6000 μmol L$^{-1}$ (Figure 2). Below a depth of 2 cm no significant concentrations of Fe$^{3+}$ were expected, due to pH values above 6. NH$_4^+$, Na$^+$, K$^+$ ranged from 50 μmol L$^{-1}$ to 800 μmol L$^{-1}$. Total DIC increased from about 200 μmol L$^{-1}$ at the interface to 600 μmol L$^{-1}$ (pelagial), respectively 1200 (littoral) μmol L$^{-1}$ at a depth of 1 cm. DOC concentrations increased from below 6 mg L$^{-1}$ at the sediment-water interface to about 40 mg L$^{-1}$ (pelagial), respectively 80 mg L$^{-1}$ (littoral) at a depth of 8 cm (Figure 3). Methane concentrations ranged between 10 to 60 μmol L$^{-1}$.

Spectra of the DOM (P 20-23, L 12-15) are dominated by the bands of aromatic, phenol, and carboxylic groups, and in case of the littoral samples by carbohydrate groups (Figure 4). The band at 1620 cm$^{-1}$ refers to the C=O vibration of aromatic and aliphatic structure and carboxylate. The shoulder at 1580 cm$^{-1}$ is another indicator of aromatic structures. The band of the pelagial samples at 1250 cm$^{-1}$ can be assigned to C—O stretching or phenolic groups that is usually reported at 1270 cm$^{-1}$. Alternatively it can be assigned to carboxyl groups (C—O stretching and/or O—H deformation) reported at 1200-1230 cm$^{-1}$. A shift of the carboxyl bands towards higher wavenumbers (1250 cm$^{-1}$) has been reported for DOM that interacted with ferricydrite and goethite (Kaiser et al., 1997). The band at 1210 cm$^{-1}$ of the upper littoral and the corresponding shoulder of the large peak of the lower littoral sample can be assigned to carboxyl groups, too. The signals between 1000 cm$^{-1}$ and 1170 cm$^{-1}$ indicate carbohydrates (C—O stretching).
Fig. 3. D2C concentrations in the pore waters of the sediments and above the sediment-water interface.

Fig. 4. IR spectra of pore water DOM: F20-23. L12-15
3.2 SOLID PHASES

The sediment cores were layered regarding structure and color (visual examination). The pelagial cores displayed similar layering and a darkish grey-brown to black color, the littoral cores a more heterogeneous or missing layering and an intense reddish-orange (top) to grey-brown color (bottom). At the littoral (rarely, but not always, a dense layer of green algae was observed above the sediment-water interface of individual cores.

Finely sectioned core P-1 and P-2 displayed an incremental increase of compactness with depth, followed by a rapid increase at 18 cm and 13.5 cm, respectively (Figure 3). This was qualitatively confirmed by the coarsely sectioned cores P-3 and L-1 (Table 3). Concentration of $^{137}$Cs in P-2 peaked at −4 cm and −13.5 cm (Figure 5). At the pelagial (P-3) total, oxalate, and HCl dissolvable iron concentrations peaked at 6-13.5 cm (Table 3). At this depth the sediments mainly consisted of iron oxides. Reactive iron(III)oxides (HCl dissolvable) displayed lowest absolute and relative concentrations at 2-6 cm depth. At the littoral (L-1) the maximum of iron concentrations was found in the uppermost layer. Compared to the pelagial, the relative amount of reactive iron was higher and showed a minimum at 4.5-9 cm. TRIS (Fe$^{II}$, Fe$^{III}$, and $S^{2-}$) was found in concentrations of 0.1 to 7.0 mmol g$^{-1}$ in P-3 and 0.005 to 0.023 mmol g$^{-1}$ in L-1 (Table 3). $\delta^{34}$S values of the TRIS fraction in P-1 decreased from −9.3% (0 cm) to −45.5% (12.5 cm), while the values for total sulfur only decreased from −8.1% to −9.3% below a depth of 6 cm (Figure 6). The $\delta^{34}$S value of lignite and of the water column (20/8/1996) were −18.7% and 4.3-8.3%, respectively.

**TABLE 3**

<table>
<thead>
<tr>
<th>Core</th>
<th>Compactness (g/cm$^3$)</th>
<th>$Fe_{ox}$</th>
<th>% of total mass</th>
<th>Fe(III) (HCl)$^{-}$</th>
<th>% of $Fe_{ox}$</th>
<th>TRIS</th>
<th>$FeS$</th>
<th>$S^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-3</td>
<td>0.95</td>
<td>2.00</td>
<td>0.25</td>
<td>37.4</td>
<td>1.06</td>
<td>24</td>
<td>2.04</td>
<td>0.41 + 0.03</td>
</tr>
<tr>
<td>6-6</td>
<td>0.17</td>
<td>3.74 +</td>
<td>0.13</td>
<td>32.2</td>
<td>0.43</td>
<td>11</td>
<td>0.26</td>
<td>0.06 + 0.00</td>
</tr>
<tr>
<td>6-13.5</td>
<td>0.16</td>
<td>9.30 +</td>
<td>0.26</td>
<td>82.0</td>
<td>2.55</td>
<td>155</td>
<td>0.92</td>
<td>0.07 + 0.04</td>
</tr>
<tr>
<td>&gt;13.5</td>
<td>0.46</td>
<td>1.01 +</td>
<td>0.02</td>
<td>9</td>
<td>0.29</td>
<td>29</td>
<td>0.09</td>
<td>0.00 + 0.00</td>
</tr>
<tr>
<td>L-1</td>
<td>0.13</td>
<td>7.55 +</td>
<td>0.83</td>
<td>67.1</td>
<td>2.98</td>
<td>39</td>
<td>0.02</td>
<td>0.003 + 0.00</td>
</tr>
<tr>
<td>4.5-9</td>
<td>0.65</td>
<td>1.08 +</td>
<td>0.04</td>
<td>9.5</td>
<td>0.18</td>
<td>17</td>
<td>0.01</td>
<td>0.000 + 0.00</td>
</tr>
<tr>
<td>&gt;9</td>
<td>0.98</td>
<td>0.13 +</td>
<td>0.01</td>
<td>1.1</td>
<td>0.05</td>
<td>38</td>
<td>0.01</td>
<td>0.000 + 0.00</td>
</tr>
</tbody>
</table>

Three replicates. Two replicates.$^{2}$FeCO$_3$ assumed.

3.3 REDUCTION RATES

Sulfate reduction rates in individual cores ranged from 0 to 41.4 mmol cm$^{-3}$ d$^{-1}$ at the pelagial and 128.4 mmol cm$^{-3}$ d$^{-1}$ at the littoral (Figure 7). At the littoral site the depth-integrated mean of the rates (0-20 cm, based on the sediment surface area) was about <
Fig. 5. Mass of solids per volume of sediment (P-1 and P-2) and activity of $^{137}$Cs in the core F-2. Peaks of $^{137}$Cs are assigned to fallout periods.

Fig. 6. $\delta^{34}S$ of the total sulfur and the TRIS fraction in the pelagic sediment (P-1). $\delta^{34}S$ of sulfate at the sediment-water interface was -4%. Of organic light-sulfur, -8.7%.
times the rate of the pelagial site. The littoral rate was 5.20 mmol m$^2$ d$^{-1}$, the pelagial 1.25 mmol m$^2$ d$^{-1}$. Note that the incubation temperature of the littoral sediment was 20°C compared to 7°C for the pelagial one. From 4°C to 20°C the $Q_{10}$ value (factor of rate increase per 10°C) was determined to be 2.6, being identical with a $Q_{10}$ value determined by Urban et al., 1994. For a comparison of sediment surface based iron and sulfate reduction rates we therefore corrected the littoral rates by using the $Q_{10}$ value (Table 4). While in the pelagial cores the rates peaked close to the sediment-water interface, at the littoral site a more heterogeneous depth distribution of rates could be observed (Figure 7). By adding acetate as an additional carbon source for acetate consuming heterotrophic sulfate reducing bacteria, reduction rates substantially increased across most of the profile of 116 pelagial (Figure 8). Between −1 cm and −13 cm the rates in the acetate spiked subcore exceeded the rates in the reference subcore by a factor of 3 to 10.

Iron was released and consumed at both sites at maximal rates above 50 nmol cm$^{-3}$ d$^{-1}$ (pelagial) and 150 nmol cm$^{-3}$ d$^{-1}$ (littoral). The maximum of Fe$^{2+}$ release was estimated to occur at a depth of 1 cm to 5 cm in the pelagial and at 6 cm in the littoral (Figure 9). The estimated rates indicate that the reduction of sulfate consumed at least a similar (littoral) or higher (pelagial) amount of electron equivalents than the reduction of iron(III)oxides (Table 4).

![Pelagial Reduction Rate](image1)

![Littoral Reduction Rate](image2)

**Fig. 7.** Sulfate reduction rates in the sediments of lake 116 for individual cores.
Fig. 8. Pelagic sulfate reduction rates with and without addition of acetate.

Fig. 9. Calculated release (values >0) or consumption of Fe$^{2+}$ in the pelagic and the littoral sediment and above the sediment-water interface of lake 116.
TABLE 4

Depth-integrated consumption of electron equivalents by sulfate and iron reduction (mEq/m²/yr) rates of sulfate reduction are mean values

<table>
<thead>
<tr>
<th></th>
<th>116 pelagial</th>
<th>116 littoral</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma$ sulfate</td>
<td>9.0</td>
<td>10.8 ($\pm$1.0)$^1$</td>
</tr>
<tr>
<td>$\Sigma$ net reduction iron (III)</td>
<td>3.8</td>
<td>6.9</td>
</tr>
<tr>
<td>$\Sigma$ gross reduction iron (II)</td>
<td>5.0</td>
<td>8.2 ($\pm$1.0)$^1$</td>
</tr>
</tbody>
</table>

$^1$ Determined at 7°C (pelagial) and 20°C (littoral); $^*$ Pure water temperature was 7°C $^{-1}$ corrected to 7°C by a QM value of 2.6; $^1$ Original data

3.4 THERMODYNAMICS

Calculated differences in energy yield from iron and sulfate reduction changed with depth and depended on the type of the iron oxide used in the calculations. They did not substantially differ between the two sites, except that at the pelagial the energy yield gradient close to the sediment-water interface was more pronounced. At the sediment-water interface of the pelagial iron reduction provided an energy yield that exceeded the energy yield of sulfate reduction by 12 KJ(eq)$^{-1}$ to 24 KJ(eq)$^{-1}$, depending on the type of iron oxide (Figure 10). At the littoral site this energy yield advantage was within 1 KJ(eq)$^{-1}$ and 25 KJ(eq)$^{-1}$. At a depth of 6 cm, values within -6 KJ(eq)$^{-1}$ and 10 KJ(eq)$^{-1}$ were attained. Below a depth of 1 cm at the pelagial and 2 cm at the littoral the reduction of the highly crystallized iron oxides goethite and jaroite provided a lower energy yield than the reduction of sulfate. Compared to the reduction of dissolved carbon dioxide, iron reduction of ferricydrite provided an energy yield advantage that was 26 KJ(eq)$^{-1}$ at the pelagial and 34 KJ(eq)$^{-1}$ at the littoral sediment-water interface and decreased to 10 KJ(eq)$^{-1}$ and 8 KJ(eq)$^{-1}$ respectively (Figure 10). Sulfate reduction provided a slightly higher energy yield than carbon dioxide reduction to methane (2-10 KJ(eq)$^{-1}$) at all depths.
Figure 10. Gibbs free energy change (G) of iron reduction compared to sulfate reduction (different iron oxides) and compared to the reduction of dissolved CO₂ (iron oxide: ferrihydrite).
4. Discussion

4.1 RATES

No clearly separated reaction zones of sulfate and iron reduction could be observed on intact cores of 2 cm segments (Figures 7 and 9). This was in accordance to measurements in and modeling results for marine and freshwater sediments (Canfield et al., 1993b; Furrer and Wehrlı, 1996; Wang and Van Cappellen, 1996). The rates of sulfate and iron reduction in Lake 116 are in the wide range of rates that are reported in the literature (Table 5). Differences in rates may be caused by seasonal variations, since the rates were determined at different seasons and temperature conditions. In Lake Anna, the only lake that was to some extent influenced by acidic mine drainage and where sulfate reduction rates were determined (lake water; pH 4.3 and higher; Herlihy and Mills, 1985), the sulfate reduction rates exceeded the rates of lake 116 by one or two magnitudes. In contrast, rates in hypersaline Little Rock Lake (Urban et al., 1995) and in the continental margin sediments of eastern Skagerrak were similar (Canfield et al., 1993b).

| TABLE 5 |

<table>
<thead>
<tr>
<th>Sulphate reduction</th>
<th>Sulfate concentration in pore waters [µM]</th>
<th>Reduction rate [µmol/(m² d)]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater sediments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake 116 Pelagial</td>
<td>70-9000</td>
<td>1.2</td>
<td>this study</td>
</tr>
<tr>
<td>Lake 116 Littoral</td>
<td>2900-5800</td>
<td>5.2</td>
<td>this study</td>
</tr>
<tr>
<td>Lake 76 Pelagial</td>
<td>12000-14000</td>
<td>2.4</td>
<td>Blodau, unpublished</td>
</tr>
<tr>
<td>Lake 76 Littoral</td>
<td>19000-22000</td>
<td>4.6</td>
<td>Blodau, unpublished</td>
</tr>
<tr>
<td>Little Rock Littoral</td>
<td>6-62</td>
<td>1.8-2.1</td>
<td>Urban et al. 1995</td>
</tr>
<tr>
<td>Little Rock Pelagial</td>
<td>6-62</td>
<td>1.5-5.2 (5 m depth)</td>
<td>Urban et al. 1995</td>
</tr>
<tr>
<td>Wisteregreen</td>
<td>100</td>
<td>1.5</td>
<td>Smith and Kugl 1981</td>
</tr>
<tr>
<td>Mendota</td>
<td>83-2200</td>
<td>100-220</td>
<td>Ingvorsen et al. 1981</td>
</tr>
<tr>
<td>Washington</td>
<td>105</td>
<td>0.12</td>
<td>Kuijila et al. 1989</td>
</tr>
<tr>
<td>Lake Anna</td>
<td>510</td>
<td>1.71-226</td>
<td>Herlihy and Mills, 1985</td>
</tr>
<tr>
<td>Marine sediments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limfjorden</td>
<td>13</td>
<td>13</td>
<td>Jürgensena 1977</td>
</tr>
<tr>
<td>Skagerrak</td>
<td>0.1-8.1</td>
<td>0.1-8.1</td>
<td>Canfield et al. 1993b</td>
</tr>
<tr>
<td>Cape Lookout Light</td>
<td>18.2</td>
<td>18.2</td>
<td>Chanon et al. 1987</td>
</tr>
<tr>
<td>Iron(III) reduction</td>
<td>Fe(III)oxide concentration [µmol/cm²]</td>
<td>Reduction rate [µmol/(m² d)]</td>
<td></td>
</tr>
<tr>
<td>Lake 116 Pelagial</td>
<td>100-1000</td>
<td>3.8</td>
<td>this study</td>
</tr>
<tr>
<td>Lake 116 Littoral</td>
<td>300-1500</td>
<td>6.9</td>
<td>this study</td>
</tr>
<tr>
<td>Skagerrak S 4</td>
<td>20-60</td>
<td>20.4</td>
<td>Canfield et al. 1993a</td>
</tr>
<tr>
<td>Skagerrak S 6</td>
<td>20-60</td>
<td>20.8</td>
<td>Canfield et al. 1993b</td>
</tr>
<tr>
<td>Skagerrak S 9</td>
<td>100-1500</td>
<td>0.0</td>
<td>Canfield et al. 1993a</td>
</tr>
</tbody>
</table>

* to calculate the rates in electron equivalents, multiply sulfate reduction rates by 8.

To our knowledge, this is the first time that sulfate reduction rates of this magnitude could be documented for sediments that were located under a water column with a pH-value below three. The observations demonstrate that pH values below 3 in the lake wa...
principally do not prevent an alkalinity generation in the sediments comparable to those in sediments of moderate eutrophic natural waters. The effect of the acetate amendment to subcores suggests that the microbial turnover of sulfate is limited by the availability of suitable organic substrates (Figure 8). Below -13 cm no increase of the rate was observed. The mixing increase should be caused by the absence of acetate utilizing sulfate reducing bacteria, while other strains of sulfate reducing bacteria might have been present (Sass et al., 1997).

The results of rate measurements suggest that, based on the consumption of electron equivalents, sulfate reduction predominated over iron reduction (Table 4). Sulfate reduction may even have been the dominant pathway of carbon mineralization since other electron accepting reactions seemed to be of minor importance. Oxygen was unlikely to have penetrated deeply into the sediments as indicated by pe-values below 0 (Frevert 1984, Figure 2). Methanogenic bacteria should have been outcompeted by sulfate and iron reducers (Lovley 1987). This was in accordance to low methane concentrations of 10-60 µmol L\(^{-1}\). Manganese oxides were not detectable (Hoffmann, unpublished data). Unfortunately no data about denitrification were available.

This conclusion, based on rate ratios and plausibility, has to be evaluated with care. The rate measurements could be erroneous since pore-water modeling and \(^{35}\)S-radiotracer measurements are affected by several methodological problems. The employed methods principally do not provide gross rates and underestimate them to an unknown extent (Bernier 1980, Elsgaard and Jørgensen, 1992; Jørgensen, 1978; Moeslund et al., 1994). Nevertheless, it seems probable that in the sediments of RL 116, dominated by iron(III)oxides and dissolved iron, sulfate reducers at least accounted for a substantial part of carbon oxidation and were not outcompeted by iron reducing bacteria.

4.2 THERMODYNAMICS:

High Fe\(^{2+}\) concentrations, as determined in this study, decrease the energy yield from iron reduction and increase the energy yield from sulfate reduction, as \(\text{H}_2\text{S}\) concentrations are controlled by the solubility product of FeS. As a consequence, in lake 116 the energy yield advantage of iron reduction to sulfate reduction was reduced from 11 KJ(eq)\(^{-1}\) at conditions usually assumed for natural waters (Fe\(^{2+}\) = 10\(^{-7}\)mol L\(^{-1}\), pH = 7; Bernier, 1980; Canfield, 1993; Stumm and Morgan, 1996) to values about 8 KJ(eq)\(^{-1}\) at maximum and -6 KJ(eq)\(^{-1}\) at minimum, depending on the type of iron oxide. Below a depth of 1-2 cm iron reduction was favored, compared to sulfate reduction, and even to methanogenesis, only in case poorly crystallized forms of iron(III)oxides like ferricydrhite and schwertmannite were present (Figure 10). The resulting energy advantage has to be considered small compared to the differences between other pathways of carbon oxidation (e.g. Stumm and Morgan, 1996) and may be below the energy quantum necessary to influence the predominance of a certain carbon oxidation pathway. Hoehler et al. (1994) estimated this amount of energy to be between 9 and 15 KJ(mol)\(^{-1}\) of substrate. In accordance to the considerations of Postma and Jacobsen (1996), our findings indicate that the interpretation of carbon oxidation pathways in sediments based on energy yields for fixed reactant concentrations and one type of mineral can be misleading and should be avoided. Furthermore, the reduced or missing energy advantage of iron reduction compared to sulfate reduction is in accordance with our general finding that sulfate reducers were not outcompeted by iron reducers, despite total iron oxide contents of up to 80 % of dryweight (Table 3). Experimental observations by Lovley (1987) and Lovley and Phillips (1988) stating that the occurrence of amorphous iron oxides is of importance regarding the
effectiveness of iron reduction and the competitiveness of iron reducers are confirmed by the results of the energy yield difference calculations. Though, the results of this approach are not in accordance to the different ratios between sulfate and iron reduction rates at the pelagial and littoral (Table 4) and at different depths (Figures 7 and 9). Since this finding could also be a result of the chosen measurement design, we discuss data obtained by different methods and from different sediment cores - further research on this point is needed.

4.3 REACTIVE IRON SURFACES

The DRIFT-IR spectra (Figure 4) indicate carboxylic and phenolic functional groups and aromatic structures which favor adsorptive and ligand exchange reactions of the DOM on oxide surfaces (McKnight et al., 1992; Gu et al., 1994; Stumm and Morgan, 1996). Since the IR spectra of the DOM used by Gu et al. (1994) and of the pore-water DOM from this study were similar and DOC concentrations were substantial (up to 40 mg L⁻¹ at the pelagial and 80 mg L⁻¹ at the littoral), we assume that the surface of reactive iron to a great part was covered with DOM. In order to confirm this hypothesis we estimated the surface coverage of iron oxides in the sediments applying a Langmuir adsorption model and data (Table 7) provided by Gu et al. (1994).

\[ q = \frac{K_q \cdot q_{\text{max}} \cdot C_{\text{DOC}}}{K_q \cdot C_{\text{DOC}} + 1} \]  

(28)

With \( q \): sorption density of iron oxides at constant pH [mg m⁻²]; \( q_{\text{max}} \): maximum sorption density of iron oxides at constant pH [mg m⁻²]; \( K_q \): surface affinity parameter [m⁵ g⁻¹]; \( C_{\text{DOC}} \): Concentration of DOM [mg L⁻¹]; a pH of 6.5 or 4.1, respectively; crystalline iron oxides and DOM being identical to the DOM used by Gu et al. (1994) were assumed.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH 4.1</th>
<th>pH 6.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_q ) [m⁵ g⁻¹]</td>
<td>1.41 [0.36]</td>
<td>1.50 [0.926]</td>
</tr>
<tr>
<td>( q_{\text{max}} ) [mg m⁻²]</td>
<td>0.33 [0.017]</td>
<td>0.176 [0.004]</td>
</tr>
</tbody>
</table>

Using this rough approximation between 93% and 98% of the maximal sorption density \((q/q_{\text{max}})\) of iron oxides was attained by sorption of DOM in the pelagial and between 9 and 99% in the littoral. This is a upper boundary estimate because with increasing surface coverage the affinity of the remaining sites for DOM is likely to decrease and competitive between DOM and the high amounts of sulfate for sorption sites exists (Chuggenberger and Zech, 1993; Moore et al., 1992). To our knowledge it has not been investigated whether adsorption of DOM on iron oxide surfaces could inhibit iron reduction. However investigations suggested that both direct contact of oxidized and reduced species at the surface and direct contact of cells and iron oxides is necessary for microbial iron reduction (Munch and Ottow, 1981; Fischer 1983; Grantham et al., 1997). Like stated in the thermodynamic considerations, also the results of this approach are in accordance to the high competitiveness of sulfate reducing bacteria, but do not explain the different ratios between sulfate and iron reduction rates at the pelagial and littoral (Table 4) and at different depths (Figures 7 and 9).
4.4 DIAGENETIC ASPECTS

More clarity on the last point can be obtained by considering the specific conditions of early diagenesis in the sediments. In marine sediments, renewal of reactive iron is typically driven by bioturbation. Reactive iron oxides and stronger oxidants, e.g. manganese(IV)oxides and O$_2$ are mixed into greater depths, where iron sulfides are oxidized and Fe$^{3+}$ reprecipitates as reactive iron oxide (Aller and Rude, 1988; Canfield, 1989; Canfield et al., 1993b). It is likely that this bioturbation driven iron recycling ultimately sustains high rates of iron reduction (Canfield et al., 1993b). Our data suggest that at the pelagial neither bioturbation nor iron sulfide recycling occurred and that at the littoral iron sulfide recycling did occur, but was probably driven by a differing mechanism.

The strong gradients of Fe$^{2+}$ concentration, pH and pe-values at the sediment-water interface of the pelagial and littoral of lake 116 (Figure 2) are indicators that no significant bioturbation or re-suspension of sediments occurred during the sampling period (Berner, 1980). Burrowing macrofauna was not observed by visual examination, either. We further believe that at the pelagial no significant bioturbation occurred during the entire sedimentation period, since the $^{137}$Cs profile of the pelagial (Figure 5) displayed two distinct concentration peaks which we assigned to the fall out of the 1960's bombing period on the former mine ground and the Chernobyl accident (1986) (Rowan et al., 1993; Wieland et al., 1993). The assignment of the lower peak is confirmed by the rapidly decreasing compactness of the sediment above this peak which should coincide with the beginning of flooding of the pit hole in 1968 (Figure 5).

To assess the rapidity of iron recycling we estimated the period that is necessary to reduce the determined stock of amorphous iron oxides in a layer at the determined rates of iron reduction.

$$ T_{Fe^{2+}} = C_{Fe^{2+}} \cdot (P_{Fe^{2+}})^{-1} $$  \hspace{1cm} (29)

$ T_{Fe^{2+}}$ : Period necessary to reduce the pool of iron oxides [yrs]; $ C_{Fe^{2+}}$ : Concentration of iron oxides [nmol (cm$^2$)]$^{-1}$; $ P_{Fe^{2+}}$ : Iron reduction rate [nmol (cm$^2$) yr$^{-1}$]

We further tried to obtain information about a reoxidation of iron sulfides by estimating the period necessary to accumulate the stock of iron sulfides in a layer at the determined rates of sulfate reduction.

$$ T_{TRIS} = C_{TRIS} \cdot (R)^{-1} $$  \hspace{1cm} (30)

$ T_{TRIS}$ : Period necessary to accumulate the pool of TRIS [yrs]; $ C_{TRIS}$ : Concentration of TRIS [nmol (cm$^2$)]; $ R$ : Sulfur reduction rate (nmol (cm$^2$) yr$^{-1}$)

In order to assess how fast recycling was, both periods are compared to the approximate age of the respective layer, obtained by linear interpolation between peaks of the $^{137}$Cs profile (pelagial), and the former mine ground (littoral), respectively (Table 6).

As a prerequisite for obtaining realistic accumulation periods it is necessary to show that the iron sulfides are of biogenic origin and accumulated during the formation of the sediment. The $^{34}$S-profiles of the sulfur fractions provide insight into this point (Figure 6). Oxidation of sulfides in the mining deposits causes only little fractionation of sulfur isotopes (Taylor et al., 1984). For this reason iron sulfides in mining deposits should reflect the $^{34}$S values of the dissolved sulfate (~4 %) in the lake and groundwater. Following this argument, iron sulfides from mining deposits should not account for a large portion of the TRIS fraction in the sediment which displays much lower $^{34}$S-values. In contrast, isotope fractionation by microbial sulfate reduction results in $^{34}$S values of the
sulfide formed which are 4-46 % lower than of the sulfate utilized for the formation, (Hochella, 1997). This effect probably caused the low $\delta^{34}S$ values of the TRIS fraction. Microbial disproportionation of $S^0$, that occurred at significant concentrations (Table 3) to $H_2S$ and $SO_4^{2-}$ (Canfield and Thamdrup, 1994) may have further decreased $\delta^{34}S$ value to about -45 %, as observed below -12 cm. According to this reasoning a biogeochemical formation of the sediment must be assumed.

Returning to the issue of iron recycling, we estimate that at the pelagial site the period necessary to accumulate the TRIS fraction was in the range of years and therefore in the range of the approximate mean age of the respective sediment layers (Table 6).

**Table 6**

Mean residence time of HCl diissolvable iron oxides, accumulation period of reduced inorganic sulfur, based on the estimated rates and concentrations of solids, and approximate age of the corresponding layers obtained from $^{137}Cs$ dating.

<table>
<thead>
<tr>
<th>Accumulation period TRIS$^1$ [yr] and approximate age of the layers [yr]</th>
<th>Residence time, iron oxides [yr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth [cm]</td>
<td>Pelagial</td>
</tr>
<tr>
<td>0-2</td>
<td>11 [3]</td>
</tr>
<tr>
<td>2-6</td>
<td>13 [10]</td>
</tr>
<tr>
<td>6-13.5</td>
<td>45 [93]</td>
</tr>
<tr>
<td>&gt;13.5</td>
<td>42 [&gt;90]</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$ mean of sulfate reduction rates and rates of cores with highest and lowest depth integrated rate were used for the calculation.

This suggests that TRIS accumulated beginning with the sedimentation of a layer that no recent events have occurred at least at the more recent past. The residence time of the HCl diissolvable iron oxides was in the range of years, too. By drawing the analogy to marine sediments we therefore hypothesize that a lack of bioturbation did not allow for reactive iron renewal and has to be considered as a reason for the absence of rapid iron recycling and for iron reduction accounting for a relative small portion of carbon oxidation. The reasoning is in accordance to the solid phase data which indicate that the reactive iron content decreased from 34 % at the uppermost layer to 11 % in the zone of iron reduction (2-6 cm, Table 3).

At the littoral both, accumulation period of iron sulfides and residence time of reactive iron oxides in the zone of maximal iron reduction (4.5-9.5 cm), were in the range of months (Table 6). The renewal rate of reactive iron would then be fast compared to the pelagial and explain the higher relative iron reduction rates at this site (Table 4). A rapid recycling is in accordance to the higher relative concentration of reactive iron at the littoral compared to the pelagial (Table 3) in the zone of iron reduction (2-6 cm and 4.5-9.5 cm, respectively). It is not in accordance to the assumption that bioturbation is essential for the provision of strong oxidants allowing for iron sulfide reoxidation, and reactive iron renewal, since bioturbation was unlikely have occurred, based on the sampling period. However, this dilemma could be solved referring to observations from lake acidification experiments. Reoxidation of reduced inorganic sulfur at the sediment-water interface was also observed in the littoral sediments of lakes artificially acidified to a pH of 4.3 and assigned to a massive spreading out of benthic filamentous green algae (Kelly et al. 1995) which were also observed at the littoral of Lake 116. Oxygen release of the algae at the sediment-water interface in summer, shifting of the maximum of sulfate reduction to the
interface in fall and subsequent reoxidation of iron sulfides during winter was made responsible for the reoxidation process by Kelly et al. (1992) and may have played a role at the littoral of lake 116.

5. Conclusions

In the pore waters of both, the pelagic sediment and the littoral sediment of lake 116, alkalinity was initially produced by sulfate reduction at a similar level as in moderate eutrophic freshwater lakes and continental margin sediments. However only at the pelagial site TRIS was preserved from reoxidation. Sulfate reduction accounted for a significant portion of ultimate carbon mineralization processes in lake 116. At the concentration conditions and gradients in pore waters determined in this study, it cannot be assumed a priori, that iron reduction is thermodynamically favored compared to sulfate reduction: The nature of the iron mineral phase has a crucial influence on this sequence. Only in case amorphous or poorly crystallized iron oxides were available, iron reduction was thermodynamically favored to sulfate reduction. However, even in the presence of amorphous iron oxides the additional energy yield from iron reduction compared to sulfate reduction was small. Hence, even if amorphous iron oxides were present, predominating sulfate reduction could be explained by low concentrations and reduced reactivity of iron oxide surfaces. The absence of bioturbation probably impeded or inhibited renewal of amorphous iron oxides in the zone of maximal iron reduction. DOM was likely to adsorb on iron oxide surfaces and could further reduce the microbial availability of iron oxides. We hypothesize that one or more of these conditions and processes could enable sulfate reducing bacteria to be more competitive than iron reducing bacteria. Pelagial and littoral sediments displayed different dynamics. At the littoral site relative iron reduction rates were probably higher and iron sulfides were not accumulated. We suggest that at the littoral reoxidation of iron sulfides resulted in the renewal of reactive iron oxides, allowing for higher relative iron reduction rates.

Acknowledgements

We gratefully acknowledge four anonymous reviewers for valuable comments, and Prof. Bernhard Mayer from Ruhr University (Bochum, Germany) for the measurement of stable isotopes.

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