

## Electron flow in an iron-rich acidic sediment—evidence for an acidity-driven iron cycle

Ariane Peine and Andrea Tritschler

Limnological Research Station, University of Bayreuth, 95440 Bayreuth, Germany

Kirsten Küsel

Department of Ecological Microbiology, BITÖK, University of Bayreuth, 95440 Bayreuth, Germany

Stefan Peiffer<sup>1</sup>

Limnological Research Station, University of Bayreuth, 95440 Bayreuth, Germany

### Abstract

The anoxic sediment of an acidic (pH ~3) iron- and sulfate-rich lake and its pore water was studied with respect to the turnover rates of solid and dissolved iron and sulfur species. High sedimentation rates of iron ( $570 \text{ g m}^{-2} \text{ a}^{-1}$ ) lead to an enrichment of the upper (0–5 cm) acidic sediment zone (pH < 4) with schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_4(\text{SO}_4)_4$ , ( $\approx 350 \text{ g kg}^{-1}$ ). Microbial iron-reduction rates measured by closed vessel incubation technique were highest close to the sediment-water interface ( $250 \text{ nmol cm}^{-3} \text{ d}^{-1}$ ), sulfate reduction measured by the  $^{35}\text{S}$ -tracer technique was not detectable in this zone. The absence of sulfide allowed complete reoxidation of dissolved Fe(II) diffusing into oxic parts of the lake water. Thus, an iron cycle is established where acidity generation through this process ( $1.0\text{--}4.7 \text{ mol m}^{-2} \text{ a}^{-1}$ ) balanced the alkalinity gain through microbial iron reduction in this zone ( $0.65\text{--}4.0 \text{ mol m}^{-2} \text{ a}^{-1}$ ). Predominance of iron over sulfate reduction under acidic conditions is further stabilized by the transformation of schwertmannite to goethite at a depth of 3–5 cm, which releases acidity at a rate of  $3.5 \text{ mol m}^{-2} \text{ a}^{-1}$ . Below, pore-water pH increased to values between 5 and 6, sulfate reduction occurred with a maximum rate of  $14 \text{ nmol cm}^{-3} \text{ d}^{-1}$  at 9 cm depth. Release of Fe(II) and a short turnover time of reduced sulfur relative to the sediment age implies that most of the sulfide formed seemed to be recycled to sulfate at this depth, presumably coupled to the reduction of iron. Consequently, net alkalinity is generated at low rates only ( $0.12 \text{ mol m}^{-2} \text{ a}^{-1}$ ).

Acidification of lakes can occur through a variety of processes such as incomplete mineralization of plant material and the formation of organic acids or mineral weathering under conditions of low acid neutralization capacity in the soils of a lake's catchment (Schnoor and Stumm 1985). Of particular relevance is the oxidation of pyrite, which can decrease the lake water pH to values as low as pH 2 (Geller et al. 1998). Acidification through pyrite oxidation can be induced by the inflow of anoxic ground water rich in Fe(II) and its subsequent oxidation and precipitation as ferric (hydr)oxides (McArthur et al. 1991). It can be observed both, as a natural process (Childs et al. 1998), or as the result of mining activities (Geller et al. 1998). Such environments are characterised by high amounts of ferric iron and sulfate (Childs et al. 1998; Peine and Peiffer, 1998), and, due to the low pH, by low primary production rates (Gyure et al. 1987; Nixdorf and Kapfer 1998).

Knowledge about the anaerobic electron flow in the sediments of lakes exposed to anoxic Fe(II)-rich groundwater is required for the understanding of such different processes as the formation of ore deposits (Hines et al. 1992) or the

production of alkalinity (Peine and Peiffer 1998). Contrary to acidified soft-water lakes, where the enhanced sulfate input into the lakes stimulated anaerobic sulfate reduction and alkalinity generation (e.g., Giblin et al. 1990), sulfate reduction is not necessarily the dominating terminal electron accepting process in the iron-rich sediments typically observed in such lakes. Competition between iron-reducing and sulfate-reducing bacteria for common electron donors exists, if microbially reducible Fe(III) oxides are abundant (Munch and Otto 1980; Lovley 1991). From a thermodynamic point of view, the low pH may even favour the predominance of iron reduction (Postma and Jakobsen 1996; Blodau et al. 1998). Moreover, coupling between sulfate reduction and reductive dissolution of ferric (hydr)oxides by  $\text{H}_2\text{S}$  can be expected based on observations in other iron-rich aquatic systems (Thamdrup et al. 1993; Jakobsen and Postma 1999), a process that will affect the recent formation of pyrite (Peiffer 1994).

In this study, we therefore have focused our attention on the processes regulating the electron flow in the sediment of an acidic, sulfate-rich lake being exposed to high deposition rates of solid ferric iron. We will further discuss the effects of the metabolic activity on the alkalinity budget of the sediment.

*Site description*—The study site is located in the Lausitz mining area, Germany, about 100 km south of Berlin near Lauchhammer (Fig. 1). Geology consists of tertiary sediments. Mine tailings are mainly sands with a pyrite content of  $1.4 \text{ g FeS}_2$  per kg (Landesumweltamt Brandenburg 1995).

<sup>1</sup> Author for correspondence.

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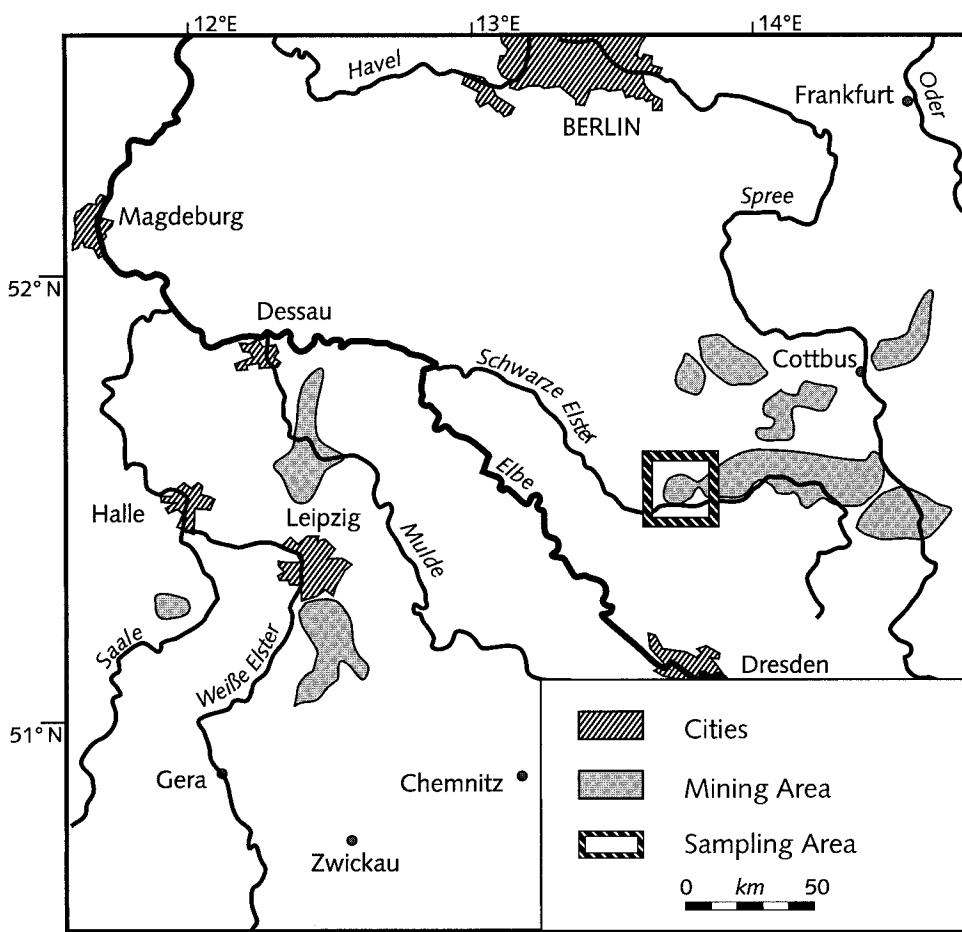


Fig. 1. East German coal fields and sampling site.

During mining activities the groundwater level was lowered beneath the mining surface. After reclamation in 1965, flooding of the pits started. Within a few years, several lakes were formed near Lauchhammer. Sediments were taken from lake 77, which is located downgradient of sulfide-containing mine tailings and receives high loads of ferrous iron and sulfate-containing ground water. Lake 77 has a pH of 3 throughout the whole water body, is thermally stratified during summer and under ice. Lake chemistry was described by Peine (1998). It is controlled by high concentrations of sulfate ( $c \approx 8 \text{ mmol L}^{-1}$ ) and dissolved iron. The concentration of ferrous iron ranges between  $20 \mu\text{mol L}^{-1}$  in the epilimnion and  $6 \text{ mmol L}^{-1}$  in the seasonally anoxic hypolimnion. The concentration of ferric iron is fairly constant between 1 and  $2 \text{ mmol L}^{-1}$ . The water residence time is approximately 2 yrs (Weber pers. comm.). Maximum depth is 7 m, lake area is 24.4 ha.

#### Sampling and analytical methods

*Sampling site*—All samples were collected at the deepest point of lake 77 approximately at the middle of the lake.

*Pore-water and lake-water analysis*—Pore water and water overlying the sediment were sampled in May 1996, Au-

gust 1996, November 1996, and February 1997 with a dialysis chamber (Höpner 1981). The chamber consisted of forty 1-cm cells covered with a cellulose acetate membrane of  $0.2 \mu\text{m}$  pore diameter. The chamber was filled with de-aerated ultrapure water before they were installed by divers. They were allowed to stay for 3 weeks in the sediment for equilibration. At the sampling date, the chamber was closed air-tight and brought to the laboratory. The pH was measured after taking a sample from one dialysis cell and injecting it into an air-tight vessel into which a pH electrode cell was inserted. Ferrous iron was measured using the phenanthroline method after adding an aliquot of the sample to a pH 4 acetate buffer solution ( $c = 0.2 \text{ mol L}^{-1}$ ) (Tamura et al. 1974).

Lake-water depth profiles were sampled every month from January 1996 to May 1997 every 2 to 4 weeks (and partly in August 1997) and analyzed for pH, ferrous and ferric iron, and sulfate. Ferrous iron was determined as described above. Total iron was measured in acidified samples by flame atomic absorption spectroscopy. Ferric iron was calculated by the difference between ferrous to total iron. Sulfate was analyzed using ion chromatography. Oxygen and pH were measured in situ with a multiprobe. The deepest point of the measurement was just above the sediment-water interface.

*Measurement of sedimentation rates*—Sediment traps were installed 1 m above the bottom in May 1996 and sampled every two weeks except for those periods during winter, when the ice cover could not be entered. Sampling ended in May 1997. The traps consisted of cylindrical tubes (inner diameter: 5 cm, length: 30 cm) constructed after Bloesch and Burns (1980). Sedimented material was freeze dried and analyzed for total iron by flame atomic absorption spectrometry after digestion with concentrated nitric and hydrochloric acid in a microwave digester. Total sulfur content was measured with a CNS analyzer.

*Characterization of the solid phase*—Sediment cores were collected in May 96, August 96, November 96, and February 97 from a boat with a gravity corer in plexiglas tubes (inner diameter: 5.9 cm). Only cores with a visually undisturbed sediment-water interface were used. At each sampling date, three cores were obtained, transported to the laboratory, and sectioned into 1-cm intervals under a constant nitrogen flux in the laboratory within 24 h. Total sulfur and carbon were analyzed with a CNS analyzer after drying.

Fresh sediment was analyzed for total reduced inorganic sulfur (TRIS). Additionally, in two cores, acid volatile sulfur (AVS) and elemental sulfur ( $S^0$ ) were determined. TRIS is generally considered to comprise pyrite ( $FeS_2$ ), amorphous  $FeS$ , and  $S^0$ . TRIS was determined after hot acid digestion ( $c = 0.5 \text{ mol L}^{-1} \text{ HCl}$ ) of an aliquot of the wet sediment and reduction with  $Cr(II)Cl_2$  to  $H_2S$ ; AVS after digestion with  $HCl$  and heating (Canfield 1989). The sulfide released was trapped in  $0.2 \text{ mol L}^{-1} \text{ NaOH}$  solution and then measured photometrically by the methylene blue method (Budd and Bewick 1952).  $S^0$  was extracted from fresh sediment by methanol and measured by high pressure liquid chromatography and UV-detector (Ferdelmann et al. 1991).

Reactive iron was extracted from fresh sediment by treatment with acid ammonium oxalate solution (Canfield 1989). Reactive iron denotes the fraction of iron that easily undergoes chemical or microbial dissolution and therefore can be regarded as potentially available for microbial reduction (Canfield 1989). For the determination of total iron, dried sediment was treated as described for sediment-trap samples. Iron was measured by flame atomic absorption spectrometry,  $Fe(II)$  by the phenanthroline method as described above. Mineralogical composition was analyzed by Fourier transformed infrared spectroscopy (FTIR) without treatment of the samples prior to the measurement.

*Microbial metabolism measurements*—Ferric iron reduction was determined by the closed-vessel incubation technique (Roden and Wetzel 1996). Two undisturbed sediment cores (inner diameter: 9 cm) were sampled in June 1996. The sediment from both cores was sectioned in 1-cm intervals, and approximately 50–60 g sediment (fresh wt) were immediately transferred to replicate sterile  $N_2$ -flushed 140-ml infusion bottles. Bottles were closed with rubber stoppers and screw-cap seals and incubated in the dark at the in situ temperature of  $12^\circ\text{C}$ . Ferric iron reduction rates were estimated from production of dissolved  $Fe(II)$  over an 11-d incubation period under the assumption that the formation of iron sulfides was negligible. There was no visible formation

of black iron sulfides. Aliquots of 1 ml were taken by sterile syringes. For long-term incubation experiments, sediment of the first upper zone (0–4 cm) from three replicate cores was pooled under anaerobic conditions, and 50g (fresh wt) sediment was transferred to 140-ml infusion bottles. Bottles were flushed with sterile argon for 15 min and incubated at  $12^\circ\text{C}$ . Aqueous samples were clarified by centrifugation and microfiltration and analyzed for ferrous iron and sulfate, as described above.

Sulfate reduction rates were measured according to Jørgensen (1978). After collecting 4 sediment cores in November 1997 with the gravity corer, 3–4 subcores were taken from each core with plexiglas tubes (length: 12 cm, inner diameter: 2.5 cm). In each subcore the  $^{35}\text{S}$ -tracer was injected every 2 cm. The subcores were incubated for 10–14 hours at the in situ temperature of  $7^\circ\text{C}$ . The sediment was sectioned between injection levels and analyzed for its TRIS content, as described above. Activity of the sulfide released was measured by a scintillation counter. The sulfate concentration was measured in parallel subcores taken from the same core as the subcore for  $^{35}\text{S}$ -injection. The subcores were sectioned into 2 cm intervals. After centrifugation, the pore water was filtered and sulfate was determined photometrically as barium sulfate (Tabatabai 1974).

## Results

*Sedimentation*—The total sedimentation rate ranged between  $1.2$  and  $11.7 \text{ g m}^{-2} \text{ d}^{-1}$  and integrated to  $1,660 \text{ g m}^{-2}$  within one year. Based on this number the deposition rate of the sediment was calculated using Eq. 1:

$$\omega = \frac{F}{\rho(1 - \phi)} \quad (1)$$

where  $F$  is the sedimentation rate,  $\rho$  is the density of the sediment material ( $2.4 \text{ g cm}^{-3}$ ), and  $\phi$  is the porosity [-].

A sediment age of 10.4 yrs was calculated with this method for the top 10 cm of the core taken in 1997. This age agrees with the age derived from the  $^{137}\text{Cs}$  peak of the Chernobyl event in 1986, which was observed at a depth of 10 cm (Peine 1998) and implies that at least during the last 10 years the sediment is at steady state.

The mean molar ratio between Fe and S in the sediment traps was 4.7. Iron was permanently sedimented during the whole sampling period at a mean rate of  $10.3 \text{ mol m}^{-2} \text{ a}^{-1}$ .

*Solid phase*—Visually, the sediment could be sectioned into four different zones. The first upper zone contained brownish orange fluffy sediment and had a dry weight of 7%. The second zone ranged in most cores from 3–5 cm to 8–10 cm depth; the sediment had a yellowish brown color (12% dry wt). The third sediment zone had the same color as the second one except some additional black stripes (19% dry wt). The fourth sediment zone beginning in a depth of 16–19 cm was brownish black (33% dry wt). In general, cores from different sampling dates were similar with respect to all measured parameters.

The iron content of the solid phase was constant in the upper 10 cm of the sediment with about  $350 \text{ g kg}^{-1}$  (Fig.

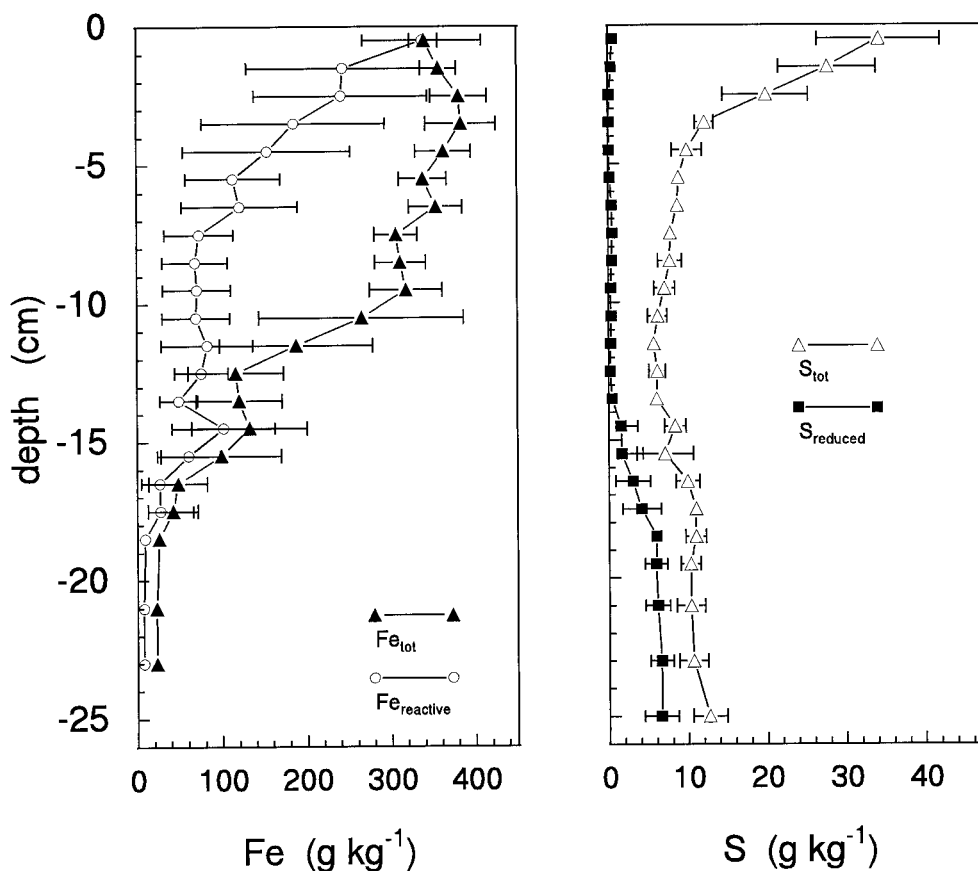


Fig. 2. Depth profiles of mean values ( $n = 4$  cores) of solid phase data: Left: total and reactive iron ( $\text{g kg}^{-1}$  dry wt sediment), Right: total sulfur and total reduced inorganic sulfur (TRIS) ( $\text{g kg}^{-1}$  dry wt sediment). Error bars denote standard deviations.

2). Below, the iron content decreased and reached a constant value of about  $20 \text{ g kg}^{-1}$  below 18 cm. In the first centimeter, the reactive iron content was about the same as the total iron content (Fig. 2) and decreased to about 60% in the upper zone. It further decreased in the second zone to  $\approx 100 \text{ g kg}^{-1}$ . In parallel, the sulfur content decreased in the upper zone from 40 to  $10 \text{ g kg}^{-1}$  (Fig. 2). The amount of reduced sulfur measured as TRIS was very small in this core down to a depth of 18 cm ( $<0.2 \text{ g kg}^{-1}$ ) and increased in the deeper sediment (Fig. 2). AVS and  $\text{S}^0$  typically made up 10–20% of the TRIS-fraction. Batch desorption experiments demonstrated that high amounts of sulfate were released from the sediment of the first zone compared to sediment of the third zone (Peine 1998). The predominant sulfur species in the upper part of the sediment should thus be sulfate.

Total organic carbon content approximated 10% of the solid phase throughout the sediment profile with the exception of the deepest zone that visually contained some pieces of lignite.

IR-spectra clearly demonstrated the occurrence of schwertmannite (SM) in the upper centimeter of the sediment (Fig. 3) and in the sediment traps (data not shown). The stretch vibrations at  $702 \text{ cm}^{-1}$  and  $1,132 \text{ cm}^{-1}$  corresponded to structural sulfate (Cornell and Schwertmann 1996) and are characteristic of SM, as indicated by the spectrum of a pure SM (Fig. 3 top, courtesy Schwertmann),

which perfectly matched that of the natural sample. In the deeper zones (5 cm) infrared-spectroscopy (IR) revealed the occurrence of goethite (Fig. 3) with the characteristic bands of the deformation vibrations measured at  $891 \text{ cm}^{-1}$  and  $794 \text{ cm}^{-1}$ . At a depth of 10 cm, the solid iron seemed to consist mainly of goethite (Fig. 3).

*Pore and lake water*—The pH-values at the sediment-water interface ranged from 3.0 to 3.5 (November 96 and August 96, respectively). At three sampling dates, the pH increased in the sediment at a depth of 9–10 cm from 3.5 to  $\approx 6$  within 2 cm (Fig. 4). In the profile from February 1997, the increase in pH was at 5 cm depth. Below the depth of 20 cm, the pH decreased down to pH-values between 4 and 5. The lake remained stratified from summer 1995 until the end of October 1996 due to a five-months ice cover in the winter 1995/1996. The oxygen saturation was 0% above the sediment-water interface from January 96 until October 96. From November 96 until May 97 the saturation was between 85 and 107% indicating circulation of the lake water.

Above the sediment, ferrous iron concentrations ranged from  $2 \text{ mmol L}^{-1}$  (November 96 and February 97) to  $8 \text{ mmol L}^{-1}$  (August 96) (Fig. 4). Establishing a Fe(II) budget for the lake water indicated a loss of  $-12.8 \text{ mol Fe(II) m}^{-2} \text{ a}^{-1}$ . The Fe(II)-flux was determined by integrating the change of

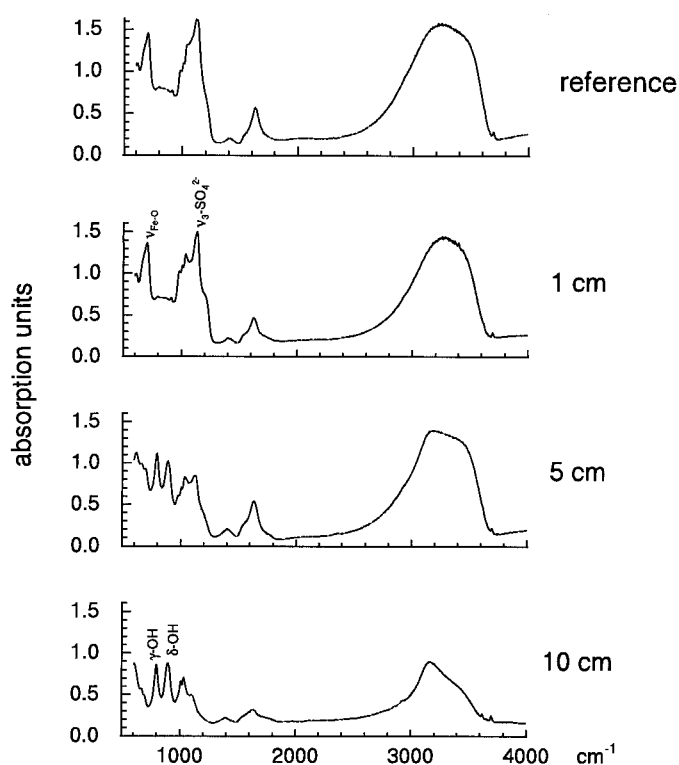


Fig. 3. IR-spectra of cm 1, 5, and 10 of the sediment and a reference sample of schwertmannite (courtesy Schwertmann).  $\delta$ -OH and  $\gamma$ -OH denote deformation vibrations of goethite at  $892\text{ cm}^{-1}$  and  $795\text{ cm}^{-1}$ , respectively.  $\nu_1$ - $\text{SO}_4^{2-}$  and  $\nu_3$ - $\text{SO}_4^{2-}$  are stretch vibrations of structural sulfate in schwertmannite at  $702\text{ cm}^{-1}$  and  $1132\text{ cm}^{-1}$  (Cornell and Schwertmann 1996).

the Fe(II) mass in the lake water between two sampling dates from May 1996 to May 1997 according to Eq. 2:

$$\Delta\text{Fe(II)} = \frac{\sum_{i=1}^n c(\text{Fe(II)})_n V_n}{A\Delta t} \quad (2)$$

where  $\Delta\text{Fe(II)}$  is the change of mass of Fe(II) between two sampling dates [ $\text{mol m}^{-2} \text{d}^{-1}$ ],  $c(\text{Fe(II)})_n$  is the concentration of Fe(II) in depth sediment  $n$  [ $\text{mol L}^{-1}$ ],  $V_n$  is the volume of depth segment  $n$  [L],  $A$  is the sediment area [ $\text{m}^2$ ], and  $\Delta t$  is the time interval between two sampling dates [d].

The lake water was acidic ( $\text{pH} \approx 3$ ) throughout the year. Pore-water concentrations of ferrous iron increased in the sediment at all sampling dates (Fig. 4). Its maximum ( $12\text{ mmol L}^{-1}$ ) peaked at the same sediment depth as did the pH maximum. In the deeper sediment, ferrous iron concentrations decreased. Ferric iron concentrations were at the detection limit in all pore-water samples. The sharp concentration gradients observed under oxic lake-water conditions (November 96, February 97) indicated reoxidation of ferrous iron at the redox cline of the lake. Oxidation rates were calculated to be  $180\text{ nmol cm}^{-2} \text{d}^{-1}$  (November 96) and  $820\text{ nmol cm}^{-2} \text{d}^{-1}$  (February 97) from the diffusive fluxes of Fe(II) using Eq. 3,

$$R_{\text{Fe(II)}} = \sum_n \Delta \left( -D_{(\text{s,Fe}^{2+})_n} \frac{\Delta c_n}{\Delta z_n} \right), \quad (3)$$

where  $R_{\text{Fe(II)}}$  is the Oxidation rate of Fe(II) in  $\text{nmol cm}^{-2} \text{d}^{-1}$ , and  $D_{(\text{s,Fe}^{2+})_n}$  is the whole sediment diffusion coefficient of  $\text{Fe}^{2+}$ , which was calculated as

$$D_{(\text{s,Fe}^{2+})_n} = \frac{D_{\text{Fe}^{2+}}}{\theta_{z_n}^2},$$

where  $D_{\text{Fe}^{2+}}$  is the molecular diffusion coefficient of  $\text{Fe}^{2+}$  ( $4.09 \cdot 10^{-6}\text{ cm}^2 \text{s}^{-1}$ ; Li and Gregory 1974) and  $\theta$  is the tortuosity which was approximated using the relation  $\theta = \phi^{-1}$  (Ullman and Aller 1982).

Sulfate concentrations were high throughout the whole sediment profile; the concentrations ranged from  $10$ – $30\text{ mmol L}^{-1}$ . In pore-water profiles from August 1996, November 1996, and February 1997, maximum sulfate concentrations were detected at a depth of  $5$ – $15\text{ cm}$ , which is about the same depth where the ferrous iron concentration and the pH-value peaked.

**Anaerobic metabolism experiments**—The rate of Fe(II) release determined with the closed-vessel incubation technique was linear over the 11-d incubation period (data not shown). The highest Fe(II) release rate ( $250\text{ nmol cm}^{-3} \text{d}^{-1}$ ) was observed at the top of the sediment and decreased to about  $75\text{ nmol cm}^{-3} \text{d}^{-1}$  at a depth of  $5\text{ cm}$  and to values between  $20$  and  $40\text{ nmol cm}^{-3} \text{d}^{-1}$  in deeper zones of the sediment below the depth of  $12\text{ cm}$  (Fig. 5). The gross iron reduction rate calculated for the upper  $6\text{ cm}$  of the sediment from this experiment ( $690\text{ nmol cm}^{-2} \text{d}^{-1}$ ) was similar (February 97) or higher (November 96) than the net rates derived from pore-water concentration gradients ( $790\text{ nmol cm}^{-2} \text{d}^{-1}$  and  $130\text{ nmol cm}^{-2} \text{d}^{-1}$ , respectively). Long-term incubation experiments performed with sediment of the upper zone demonstrated that the formation of Fe(II) was approximately linear over a 140-d incubation period (Fig. 6). At the end of the incubation,  $25.5\text{ mmol L}^{-1}$  soluble Fe(II) were released, which corresponds to a Fe(III)-reduction rate of about  $170\text{ nmol cm}^{-3} \text{d}^{-1}$ . The pH-value remained below pH 4 during incubation. The concentration of sulfate also increased from  $25$  to  $45\text{ mmol L}^{-1}$  (Fig. 6).

In general, sulfate reduction rates measured by  $^{35}\text{S}$ -tracer experiments in subcores were lower than iron reduction rates. Negligible activity was observed in the upper  $5\text{ cm}$  of the sediment, followed by a sharp increase in activity with maximum rates of  $14\text{ nmol cm}^{-3} \text{d}^{-1}$  at a depth of  $9\text{ cm}$  (Fig. 5). At  $18\text{ cm}$  depth, the rate of sulfate reduction approximated  $5\text{ nmol cm}^{-3} \text{d}^{-1}$  and was negligible at a depth of  $25\text{ cm}$  (not shown in Fig. 5).

**Turnover time of reduced sulfur**—The turnover time  $\tau_s$  of reduced sulfur in the sediment, i.e., the time necessary to accumulate reduced sulfur at a certain sulfate reduction rate, was estimated by comparing the measured amount of TRIS with the depth-integrated sulfate reduction rate. Only the sediment layers above a depth of  $16\text{ cm}$  were considered for the calculation, because the high amounts of TRIS observed below  $16\text{ cm}$  depth reflect pre-reclamation conditions and can

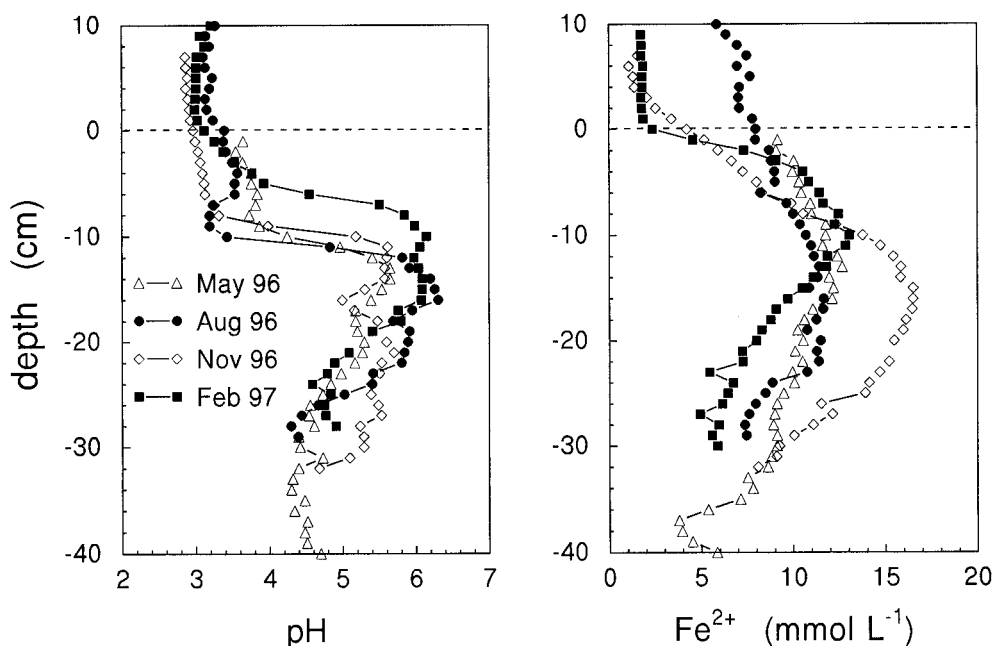


Fig. 4. Depth profiles of pore-water data from May 1996, August 1996, November 1996, and February 1997: Left: pH-value, Right: ferrous iron.

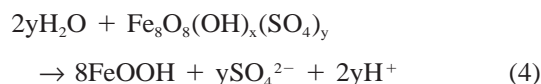
not be attributed to a recent formation of reduced sulfur. The amount of TRIS, measured in nine cores from lake 77, ranged between 80 and 927 mmol m<sup>-2</sup> with an average of 319 mmol m<sup>-2</sup>. The depth-integrated sulfate reduction rate was 0.8 ± 0.2 mmol m<sup>-2</sup> d<sup>-1</sup> and was assumed to be constant since flooding of the lakes. The turnover time for TRIS thus calculates to range between 3 and 37 months with an average of 13 months.

## Discussion

**Transformation reactions of solid ferric iron**—The sediment is characterized by a high input (10.3 mol m<sup>-2</sup> a<sup>-1</sup> on average) and a high content of ferric iron (approx. 35 wt %). The good agreement between the iron sedimentation rate and the Fe(II)-flux (12.8 mol m<sup>-2</sup> a<sup>-1</sup>, Eq. 2) indicates that the loss of Fe(II) observed in the lake water is mainly due to oxidation. Most of the iron in the upper 3 cm was reactive iron (Fig. 2). The molar Fe:S ratio ranged between 5.0 and 7.8, indicating the occurrence of SM (Bigham et al. 1990). SM is a poorly crystallized iron-oxyhydroxysulfate, which has been found both, in mine drainage influenced environments (Bigham et al. 1990), and in natural systems (Bigham et al. 1996; Childs et al. 1998). SM is formed in iron and sulfate-rich waters within a pH-range from 2.8 to 4.5 (Bigham et al. 1996). The pH-optimum for formation lies between 2.8 and 3.2 (Bigham et al. 1996), conditions which are similar to the chemical situation of lake 77 with pH values between 2.7 and 3.1 in the water column and 3.0 and 3.5 at the sediment water interface. The coincidence between an IR-spectrum from reference material and that from the first centimeter of the sediment (Fig. 3 top) suggests that SM is the predominant solid iron phase in the sediment of Lake 77, being precipitated in the water column and subsequently

deposited on the lake bottom. Below 4 cm sediment depth, the Fe:S ratio was shifted to higher values (5.7–14.6). SM may still be present at this depth but at a lower quantity. In addition, the amount of reactive iron decreased while the total iron content remained constant. Because ferrous iron does not significantly account for total iron at this depth, it must be concluded that ferric iron becomes more crystalline with depth. This assumption was confirmed by IR spectroscopy, which showed distinct bands corresponding to goethite (Fig. 3). Obviously, SM had transformed into goethite, a process experimentally demonstrated by Bigham et al. (1996).

This process generates protons according to Eq. 4



with  $x = 4.6$  and  $y = 1.7$ , as derived from sediment trap data. Equation 4 implies that at a depth below 3 cm an acidity source existed in the anaerobic sediment. We estimated the acidity production rate to be 3.5 mol m<sup>-2</sup> a<sup>-1</sup> by relating the amount of reactive iron transformed per centimeter to the corresponding age of this depth according to Eq. 5:

$$R_{\text{H}} = \sum_{n=1}^{10} (\text{Fe}_{\text{tot}_n} - \text{Fe}_{\text{reac}_n}) \cdot \text{BD}_n \cdot \omega_n \cdot F \cdot 10^4 \quad (5)$$

where  $R_{\text{H}}$  is the proton formation rate according to Eq. 4 [mol m<sup>-2</sup> a<sup>-1</sup>],  $\text{Fe}_{\text{tot}}$  is the mass of total iron [mol (g dry substance)<sup>-1</sup>],  $\text{Fe}_{\text{reac}}$  is the mass of reactive iron [mol (g dry substance)<sup>-1</sup>],  $\text{BD}$  is the bulk density [(g dry substance) cm<sup>-3</sup>],  $\omega$  is the deposition rate of the sediment [cm a<sup>-1</sup>],  $F$  is the stoichiometric factor for the proton formation through conversion from SM to goethite where  $F$  was determined

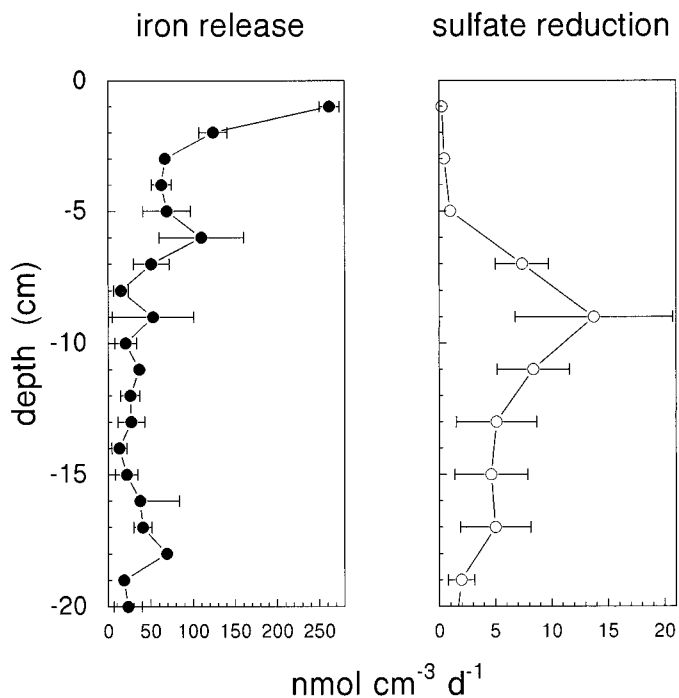


Fig. 5. Reduction of iron and sulfate in the sediment: Left: depth profile of iron reduction rates incubated with the closed vessel technique by Roden and Wetzel (1996) at 12°C, Right: depth profile of sulfate reduction rates measured by  $^{35}\text{S}$ -tracer technique at 7°C.

from the mean iron and sulfur content of the sediment traps to be 0.425, and  $n$  is the depth of a sediment layer.

At a depth below 16 cm, the total iron content decreased to a constant low value indicating a shift in the sediment composition from material that had been sedimented since the flooding of the lake, to former pit ground material.

**Reduction of ferric iron**—The ability to use ferric iron as an electron acceptor is widespread among neutrophilic fermentative, nonfermentative, and sulfate-reducing bacteria (Lovley 1991). However, acidic environments are dominated by a distinct group of acidophilic or acid-tolerant microorganisms; both autotrophic and heterotrophic acidophiles have the capacity to reduce ferric iron (Brock and Gustafson 1976; Johnson 1995). Recently, it was demonstrated by Küsel et al (1999) that the reduction of Fe(III)-(hydr)oxides in the sediment of Lake 77 can be mediated by heterotrophic *Acidiphilium* species that are capable of coupling the reduction of Fe(III) to the complete oxidation of a large variety of substrates including glucose and  $\text{H}_2$ .

The reactivity of Fe(III)-(hydr)oxides as electron acceptors for microbial processes is linked to the degree of crystallinity (Munch and Ottow 1980; Lovley and Phillips 1986; Pronk and Johnson 1992), which implies that SM may be easily reducible by Fe(III)-reducing microorganisms. This assumption is confirmed by the release of sulfate during the long-time incubation experiment, which paralleled the release of ferrous iron (Fig. 6). Typically, if coupled to the reduction of ferric oxides under acidic conditions, the release of sulfate would be indicative for the oxidation of reduced sulfur, e.g., mediated by autotrophic acidophilic bacteria like

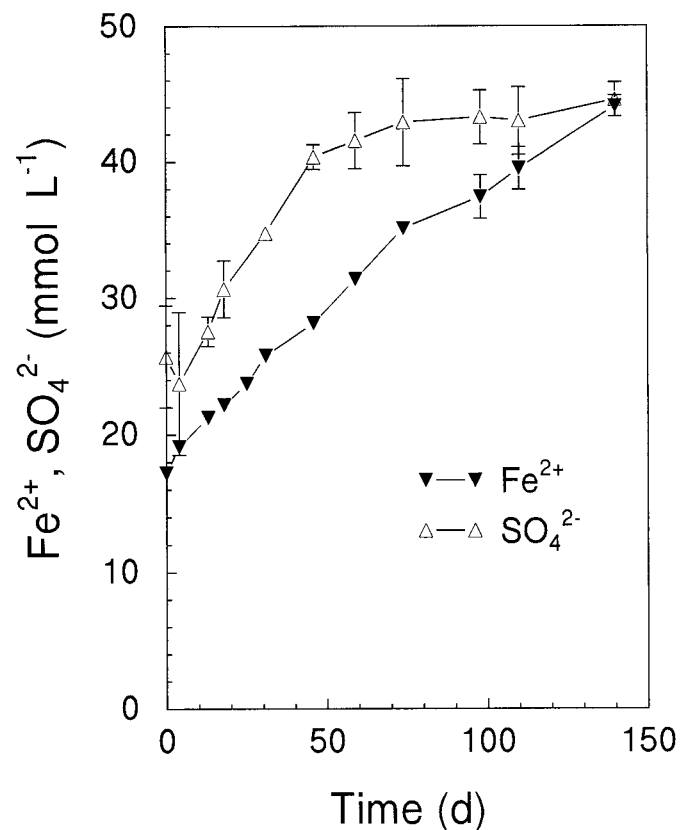


Fig. 6. Long-term anaerobic incubation of the acidic upper sediment zone: production of soluble ferrous iron and release of sulfate (incubated at 12°C).

*Thiobacillus ferrooxidans* and *T. thiooxidans* (Pronk and Johnson 1992). However, the amount of reduced sulfur in the upper sediment is very low (Fig. 2) and cannot explain the amount of sulfate released within the 140 days of the experiment. We therefore conclude that the release of sulfate during long-term incubation conditions was mainly caused by the reductive microbial dissolution of schwertmannite. This process can also explain the high iron reduction rates observed in the upper sediment zone relative to the lower rates detected in deeper zones of the sediment (Fig. 4), where the amount of reactive iron decreases and goethite seems to predominate.

**Sulfate reduction and sulfide accumulation**—Dissolved sulfate was available throughout the sediment at high concentrations. However, negligible sulfate-reducing activity was observed in the upper part of the sediment (Fig. 5) suggesting that Fe(III) reduction was the dominating reductive process under acidic conditions (up to  $250 \text{ nmol cm}^{-3} \text{ d}^{-1}$ ). Although sulfate reducers can be isolated from acidic ponds, sulfate reduction has not been observed in the laboratory below a pH of 5.5 (Fortin et al. 1996). Within the sediment profile, sulfate reduction was enhanced with increasing pH. The maximum rates with values up to  $14 \text{ nmol cm}^{-3} \text{ d}^{-1}$  were observed at a depth where also the pH showed a maximum. The average rate observed in the zone of sulfate reduction activity was  $6 \text{ nmol cm}^{-3} \text{ d}^{-1}$ , which is low com-

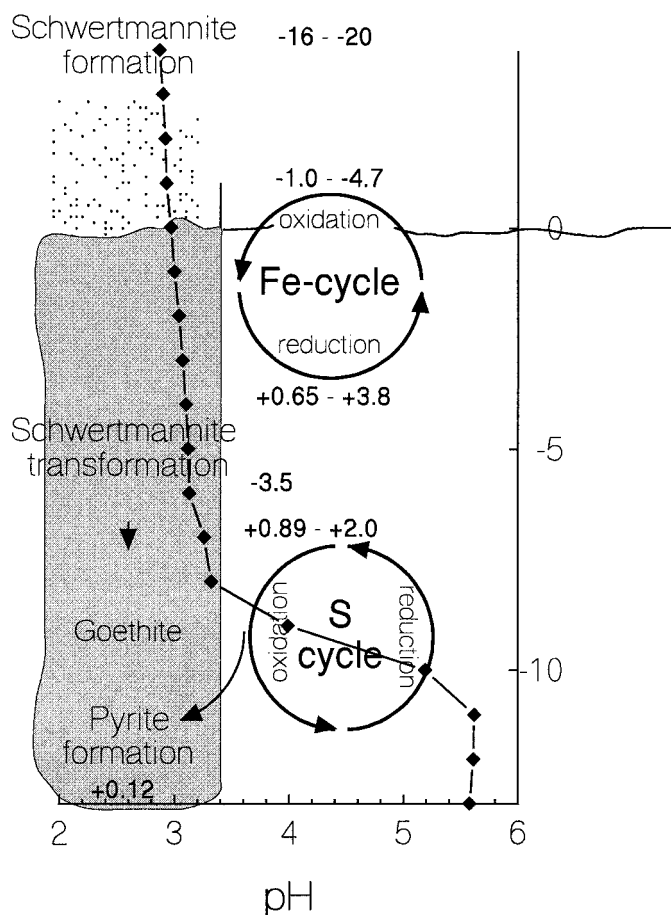


Fig. 7. Scheme for the processes involved in the alkalinity budget of the sediment-pore water system in Lake 77. Numbers denote alkalinity fluxes in  $\text{mol m}^{-2} \text{a}^{-1}$ . See text for a detailed discussion.

pared to the iron reduction rate of this zone ( $50 \text{ nmol cm}^{-3} \text{d}^{-1}$ ). However, sulfate reduction may be slightly underestimated compared to iron reduction due to the lower in situ incubation temperatures ( $7^\circ\text{C}$ ) compared to those for the iron reducing activity ( $12^\circ\text{C}$ ).

The increase of pH in the sediment can be attributed to the combined fermentative and sulfate reducing activity, which lead to a consumption of acidity (e.g., Giblin et al. 1990). Depth integrated rates of sulfate reduction down to a sediment depth of 40 cm averaged  $1.1 \pm 0.2 \text{ mmol m}^{-2} \text{d}^{-1}$ ; the rate of sulfate reduction in the reactive zone between 6 and 24 cm sediment depth (Fig. 4) accounted for 90% of this rate. Sulfate reducing activity in sediments of acidic lake 77 is at the lower end compared to rates measured under freshwater and marine conditions (0.1 to 35 and 0.2 to several hundred  $\text{mmol m}^{-2} \text{d}^{-1}$ , respectively; Urban 1994).

The amount of reduced sulfur retained in the zone of sulfate reduction appears to be low (Fig. 2) relative to the sulfate reduction rate. The turnover time  $\tau_s$  of reduced sulfur in the sediment with an average of 13 months is distinctly shorter than the lake age of approximately 30 yrs. We therefore conclude that reduced sulfur is permanently reoxidized in the zone of sulfate reduction, the oxidant being solid ferric iron. The ferrous iron release rate observed in this zone

would then stoichiometrically correspond to the sulfide formation rate measured as sulfate reduction. No net consumption of sulfate could be observed in the pore water, which further suggests that sulfide is recycled to sulfate in a combined abiotic/microbial multi-step process.

The oxidation of hydrogen sulfide in contact with Fe(III)-(hydr)oxides is generally assumed to be chemical, the products being polysulfides or elemental sulfur (Peiffer 1994). To our knowledge, complete inorganic oxidation of sulfide directly to sulfate with ferric iron has not been documented in the literature to date. There are, however, several pathways reported in the literature about further oxidation of elemental sulfur to sulfate, e.g., microbial disproportionation of sulfur to sulfide and sulfate coupled to the chemical reduction of ferric iron (Thamdrup et al. 1993) or microbial reduction of ferric iron coupled to the oxidation of sulfur to sulfate by acidophilic autotrophic bacteria (Brock and Gustafson 1976; Pronk and Johnson 1992).

*Availability of organic carbon*—Primary production in acidic lakes is generally regarded to be low (Gyure et al. 1987), an observation also made in the Lausitz mining area (Nixdorf and Kapfer 1998). Mineralization processes in this sediment therefore must be regarded to be limited by the availability of organic carbon. This assumption is confirmed by the low depth-integrated Fe(III) reduction rate for the upper 6 cm, which was about  $120 \text{ nmol cm}^{-3} \text{d}^{-1}$ , in spite of the high amount of reactive iron (Fig. 2). In organic-rich freshwater wetland sediments containing lower amounts of iron, the Fe(III) reduction rate of the sediment approximated  $2.2 \mu\text{mol cm}^{-3} \text{d}^{-1}$ , the sediments, however, being Fe(III)-(hydr)oxide depleted within two weeks of anaerobic incubation (Roden and Wetzel 1996). In our study, the formation of Fe(II) was approximately linear over the 140-d incubation period (Fig. 6) indicating that the amount of reducible iron is not limiting the overall process. Rather, low availability of electron donors will explain the relatively low rates of both, dissimilatory iron and sulfate reduction.

*Alkalinity budget*.—The previous discussion shows that the sediment can be geochemically divided into three zones: (1) the upper zone (0–5 cm) with low pore-water pH values ( $<4$ ), maximum microbial iron-reduction rates, the absence of sulfate reduction, the predominance of reactive iron, mainly as SM which transforms into goethite; (2) an intermediate zone (5–9 cm) with increasing pore-water pH and an increasing activity of sulfate reducing bacteria; and (3) the lower zone (9–16 cm) with pH values between 5 and 6, a maximum of the sulfate-reduction rate at 9 cm, decreasing iron-reduction rates compared to the values measured in the upper zone, a release of ferrous iron, the predominance of goethite, and the potential recycling of sulfide to sulfate.

The most striking result is the observation that the pH significantly increases only at a depth below 8 cm (in one profile already below 5 cm), despite the microbial reduction of ferric (hydr)oxides in the upper centimeter, a process that one would expect to consume pore-water acidity. It appears that there is some geochemical control exerted on the system that stabilizes the pH on the low level and that we will try

Table 1. Calculation of an alkalinity budget for lake water, sediment and pore water of Lake 77 based on the various processes identified in this study (column 1). Column 2 contains the information which was used to calculate the fluxes, column 3 and 4 the underlying stoichiometries and mathematical relations, and column 5 the calculated fluxes. Negative values denote loss of alkalinity.

Process	Derived from	Stoichiometry	Calculation	Alkalinity gain (mol m <sup>-2</sup> a <sup>-1</sup> )
1) Oxidation of Fe(II) in the lake water	a) Fe(II)-balanced in lake water b) Fe-sedimentation as schwertmannite a) incubation experiments	$8\text{Fe}^{2+} + 2\text{O}_2 + 1.7\text{SO}_4^{2-} + 8.6\text{H}_2\text{O}$ $\rightarrow \text{Fe}_8\text{O}_8(\text{OH})_{4,6}(\text{SO}_4)_{1,7} + 12, 6\text{H}^+$ stoichiometric ratio $\Delta\text{H}^+ : \Delta\text{Fe}^{2+} = 1.575$	$\sum \Delta\text{Fe(II)} \cdot 1.575$ [eq. 2] $R_{\text{sed}} \cdot 1.575$	-20 -16
2) Microbial reduction of ferric iron	a) incubation experiments b) pore-water concentration profiles of Fe(II)	inverse as above —	$\sum_1^6 R_{\text{Fe(II)}} \cdot 1.575$ eq. (3)	+4.0 +3.8 (Feb 97)
3) Reoxidation of Fe(II) at the sediment-water interface	pore-water concentration profiles of Fe(II)	as above	as above	-4.7 (Feb 97) -1.0 (Nov 96)
4) Transformation of schwertmannite to goethite	vertical change of the reactive iron content	eq. (4)	eq. (5)	-3.5
5) Sulfate reduction coupled to reductive dissolution of goethite with H <sub>2</sub> S	incubation experiments	reduction of goethite, 90% reoxidation to sulfate, 10% storage as pyrite $\text{H}_2\text{S} + 7.3\text{FeOOH} + 1.6\text{H}_2\text{O}$ $\rightarrow 0.05\text{FeS}_2 + 7.3\text{Fe}^{2+} + 0.9\text{SO}_4^{2-} + 12.7\text{OH}^-$	$\sum_7^{10} R_{\text{SO}_4} \cdot 12.7$	+2.0
6) Reductive dissolution of goethite with H <sub>2</sub> S	incubation experiments and release of Fe(II)	reduction of goethite, 90% reoxidation to sulfate, 10% storage as pyrite, stoichiometry as above	$\sum_7^{10} R_{\text{Fe(II)}} \cdot 1.73$	+0.89
7) Formation of reduced sulfur	content of TRIS, AVS, S <sup>0</sup>	$\text{SO}_4^{2-} + \text{fH}^+ + (\text{j} + \text{k})\text{FeOOH}$ $+ (1.5\text{i} + 2\text{j} + 1.75\text{k})\text{CH}_2\text{O}$ $\rightarrow \text{iS}^0 + \text{jFeS} + \text{kFeS}_2 + (1.5\text{i} + 2\text{j} + 1.75\text{k})\text{CO}_2$ $+ \frac{1}{2}(\text{f} + \text{j} + \text{k})\text{H}_2\text{O}$ $\text{i} + \text{j} + 2\text{k} = 1; \quad \text{f} = \frac{2}{\text{i} + \text{j} + \text{k}}$ $\text{i} = \frac{\text{c(S}^0\text{)}}{\text{c(TRIS)}}; \quad \text{j} = \frac{\text{c(AVS)}}{\text{c(TRIS)}};$ $\text{k} = \frac{1}{2} \frac{\text{c(TRIS)} - \text{c(S}^0\text{)} - \text{c(AVS)}}{\text{c(TRIS)}}$	$\sum_7^{10} \text{c(TRIS)}_n \cdot \text{f}$	0.12

to elucidate by establishing an alkalinity balance for the sediment. Table 1 summarizes the processes that were considered in this budget, the information that was used to calculate the fluxes, the underlying stoichiometries and mathematical relations, and the calculated fluxes. In Fig. 7 the results are summarized and will be discussed in the following.

The annual acidity flux (negative alkalinity in Table 1) through oxidation of Fe(II) entering the lake water with the ground water ranges between 16 and 20 mol m<sup>-2</sup> a<sup>-1</sup>. In the sediment iron reduction consumes acidity. The rate derived from the incubation data for the upper 6 cm of the sediment was 4.0 mol m<sup>-2</sup> a<sup>-1</sup>. This value lies in the range of net rates derived from pore-water concentration gradients of Fe(II) at two different dates, which were 0.65 and 3.8 mol m<sup>-2</sup> a<sup>-1</sup>, respectively. If one assumes that the zone of iron reduction is not identical to the zone of Fe(II)-oxidation and that beside this process no other sink exists for Fe(II), then the results of both experiments can be compared directly. They can thus be regarded to be reasonable and independent estimates for the alkalinity production rate through microbial iron reduction in the sediment of Lake 77.

The predominance of ferric iron reduction under acidic conditions has severe implications for the alkalinity budget of the sediment: First, ferrous iron will not be retained as iron sulfide in the sediment in the acidic zone because no sulfide will be formed under these conditions. As observed with the pore water data, diffusion of Fe(II) to the sediment-water interface, reoxidation and subsequent formation of SM will regenerate acidity again. The alkalinity consumption rate derived from this process ranges between 1.0 and 4.7 mol m<sup>-2</sup> a<sup>-1</sup>. Given the uncertainty inherent to such calculations, one can conclude that alkalinity production and consumption balance each other in the upper zone so that the net alkalinity gain from the reductive process is zero.

Typically, steep gradients in pH or the redox potential will tend to resolve diffusively with time, i.e., sulfide or alkalinity formed in the deeper zones would diffuse upward and retain ferrous iron in the sediment either as iron sulfide or siderite. In the sediment of lake 77 there are least two processes opposing this mechanism: The oxidation capacity of the sediment in the zone of sulfate reduction appears to be high enough to recycle sulfide back to sulfate. Moreover, and probably even more important, the alkalinity generated through the combined sulfate and iron reduction in zone 3 (between 0.89 and 2.0 mol m<sup>-2</sup> a<sup>-1</sup>, depending on the experimental method underlying the calculation procedure) seems to be consumed by the transformation of SM to goethite in zones 1 and 2 (-3.5 mol m<sup>-2</sup> a<sup>-1</sup>). The alkalinity production rate was calculated based on the observed ratio between sulfate and reduced sulfur at this depth (Fig. 2), i.e., 90% of the H<sub>2</sub>S reacts with goethite back to sulfate and 10% of the H<sub>2</sub>S are transferred into pyrite. The transformation process thus seems to produce enough acidity to maintain iron reduction mediated by acidophilic Fe(III)-reducing bacteria as the predominant metabolic pathway in the upper cm of the sediment of Lake 77.

These calculations show that microbial iron reduction does not affect the alkalinity budget of the sediment. This implies that all ferrous iron oxidized in the lake water finally

transforms to goethite. The stoichiometric ratio  $\Delta\text{H}^+ : \Delta\text{Fe}^{2+}$  in process (1) then changes from 1.575 to 2.0, which increases the total acidity flux to values between 20 and 25 mol m<sup>-2</sup> a<sup>-1</sup>. This flux is opposed by the combined sulfate and iron reduction in zone 3 of which only 0.12 mol m<sup>-2</sup> a<sup>-1</sup> are ultimately neutralized through the formation of reduced sulfur in the sediment.

## Conclusion

Although being untypical for a freshwater system, acidic Lake 77 can be regarded as a model system to understand the biogeochemical processes occurring under conditions, where acidity is generated upon contact of anoxic, ferrous iron containing ground water with the atmosphere. Anaerobic electron flow in the sediment of Lake 77 seems to be driven by the low pH, a high deposition rate of the secondary iron-mineral SM, and the low amount of organic matter. Acidic conditions in the lake water are stabilized through reoxidation of microbially formed Fe(II) at the sediment-water interface and transformation of SM to goethite in the sediment, both of which processes generate acidity. The low pH favors the predominance of microbial iron over sulfate reduction which releases new ferrous iron. Thus, a self-sustaining acidity-driven iron cycle is established at the sediment-water interface, which prevents the build-up of sediment alkalinity in spite the occurrence of an alkalinity generating process.

The iron cycle at the surface appears to be opposed by a sulfur cycle at deeper sediment layers that is based on a low sulfate-reducing activity and a stepwise reoxidation of sulfide to sulfate with ferric oxide as the terminal electron acceptor. Alkalinity production from these processes leads to the consumption of acidity and to the spatial separation of two distinct chemical environments in the sediment accompanied by a sharp pH gradient.

The reoxidation of sulfide to sulfate seems to be almost complete in this sediment, which stoichiometrically implies a maximum rate of alkalinity generation compared to situations where most of the reoxidized sulfide is bound into pyrite. It may be speculated that, from an ecological point of view, this process might be regarded as an optimization of the acidity consumption rate through the microbial community in this zone of the sediment in order to establish proper pH conditions for their metabolic activity.

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