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Chemical controls on iron reduction in schwertmannite-rich sediments

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Abstract

In sediments of acidic mining lakes, iron is generally reduced in mixtures of schwertmannite and goethite and under strongly varying pH values of <3 to 7. We examined the effects of iron sources (schwertmannite, goethite, dissolved Fe^{3+}), peat humic acid, and pH (3–6) on iron reduction rates in schwertmannite dominated sediment slurries. At pH 3, addition of schwertmannite and goethite and dissolved ferric iron strongly increased, and addition of the humic acid decreased iron reduction rates. Goethite promoted iron reduction more strongly than schwertmannite. Raising pH from 3 to 4.5–6 strongly decreased iron reduction rates. When the pH was not fixed, addition of schwertmannite increased (6.3 ± 0.9 mmol g^{-1} day^{-1}) and addition of goethite decreased (1.9 ± 0.7 mmol g^{-1} day^{-1}) iron reduction compared to a control (3.9 ± 1.0 mmol g^{-1} day^{-1}). This effect can be attributed to pH values being higher and dissolved ferric iron concentrations being lower in the goethite amended samples, compared to control and schwertmannite treatment, which was acidified by transformation of the mineral. The study suggests that the acidifying effect of schwertmannite is more critical for maintaining high rates of iron reduction than bulk mineral properties.

Keywords: Iron reduction; Goethite; Schwertmannite; Acid mine drainage; Pit lake

1. Introduction

Microbial iron reduction is of importance for the anaerobic carbon flow and the mobility of iron and trace metals and various organic contaminants in soils, sediments and aquifers (Lovley, 1991; Roden and Wetzel, 1996; Roden and Urrutia, 1999; Benner et al., 2002). In lakes and rivers polluted by acid mine drainage (AMD), iron reduction moreover controls the internal generation of alkalinity and acidity by consumption of protons in the sediments (Eq. (1)). Protons are furthermore released in the surface waters when ferrous iron is exported from the sediments, oxidized and precipitates as ferric iron minerals (Knorr and Blodau, 2006; Blodau, 2006).

$$FeOOH + 1/4\langle CH_2O\rangle + 2H^+ \Rightarrow Fe^{2+} + 1/4(CO_2) + 7/4(H_2O) \quad (1)$$

The ferric iron minerals schwertmannite and goethite are primarily available for iron reduction in these environments. Schwertmannite was found to precipitate at pH 2.6 to 4 and millimolar concentrations of sulfate in

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surface waters (Eq. (2); Regenspurg et al., 2004). The mineral is characterized by a variable composition ($Fe_8O_8(OH)_{8-2x}SO_x$, $1.0<x<1.75$) and a low crystallinity (Bigham et al., 1990, 1996). Deposited schwertmannite subsequently transforms into the thermodynamically stable goethite, which is generally better crystallized and often also has a smaller surface area than schwertmannite (Bigham et al., 1996; Peine et al., 2000; Eq. (3)).

$$Fe_8O_8(OH)_{8-2x}(SO_4)_x + (24-2x)H^+ \Leftrightarrow 8Fe^{3+} + xSO_4^{2-} + (16-2x)H_2O \qquad (2)$$

$$Fe_8O_8(OH)_{8-2x}(SO_4)_x + 2xH_2O \Rightarrow 8FeOOH + xSO_4^{2-} + 2xH^+ \qquad (3)$$

Owing to this suite of geochemical processes, several chemical properties, i.e. mineral surface area, pH, and dissolved ferric iron and DOC concentration, may vary within AMD polluted sediments and influence iron reduction. A decreasing iron reduction rate can be expected when schwertmannite transforms to goethite because the surface area of iron hydroxides correlated positively to bacterial iron reduction in batch experiments with various iron hydroxides (Roden, 2003). Such an effect was also reported from experiments with cultured organisms (*Acidiphilium cryptum* JF5) and synthetic schwertmannite, ferrihydrite and goethite (Kuesel, 2003).

The sediment pore water pH has been reported to vary in a wide range from <3 to >7 (Blodau, 2006). Low pH values seem to favour iron reduction vs. bacterial sulfate reduction, which typically occurs only at higher pH and low ferric iron contents in acidic mine lake sediments (Kuesel, 2003; Blodau and Peiffer, 2003). As schwertmannite transformation generates protons, pH values of about 3 are often attained in schwertmannite dominated and buffered sediments. In contrast, pH frequently increases to neutral values in the presence of goethite due to proton consumption by iron and sulfate reduction (Table 1; Peine et al., 2000).

Dissolved ferric iron concentrations may vary because schwertmannite transformation requires dissolution of the mineral and because schwertmannite is more soluble than goethite (Bigham et al., 1990, 1996; Cornell and Schwertmann, 1996). Solubility and ferric iron release may affect iron reduction, because dissolved ferric iron is more readily used than iron hydroxides (Arnold et al., 1986; Lovley and Woodward, 1996). Humic substances, a byproduct of organic matter decomposition in the sediments (Chabbi et al., 2006), may stabilize ferric iron in sediment pore waters by complexation (Luther et al., 1996) and also affect the surface properties of iron hydroxides.

Table 1
Terminal electron accepting process (TEAP), related equations, and thermodynamic values of Gibbs free energies, standardized to 1 mol H_2 consumption

e^- acceptor	TEAP	Equation	ΔG^0 (kJ mol^{-1}, H_2)
Goethite	$H_2+2FeOOH+4H^+ \Leftrightarrow 2Fe^{2+}+4H_2O$	$\Delta G_r = \Delta G_r^0 + RT\ln\frac{a(Fe^{2+})^2}{p(H_2)\cdot a(H^+)^4}$	−129.26
Schwertmannite[a]	$H_2+2FeO(OH)_{0.75}(SO4)_{0.125}+3.5H^+ \Leftrightarrow 2Fe^{2+}+0.25SO_4^{2-}+3.5H_2O$	$\Delta G_r = \Delta G_r^0 + RT\ln\frac{a(Fe^{2+})^2\cdot a(SO_4^{2-})^{0.25}}{p(H_2)\cdot a(H^+)^{3.5}}$	−137.83
Dissolved Fe^{3+}	$H_2+2Fe^{3+} \Leftrightarrow 2Fe^{2+}+2H^+$	$\Delta G_r = \Delta G_r^0 + RT\ln\frac{a(Fe^{2+})^2\cdot a(H^+)^2}{p(H_2)\cdot a(Fe^{3+})^2}$	−148.54
Sulfate	$4H_2+SO_4^{2-}+2H^+ \Rightarrow H_2S+4H_2O$	$\Delta G_r = \Delta G_r^0 + RT\ln\frac{p(H_2S)}{p(H_2)^4\cdot a(H^+)^2\cdot a(SO_4^{2-})}$	−59.42
Carbonate	$4H_2+CO_2 \Rightarrow 2H_2O+CH_4$	$\Delta G_r = \Delta G_r^0 + RT\ln\frac{p(CH_4)}{p(H_2)^4\cdot p(CO_2)}$	−32.70

Gibbs free energies of formation for schwertmannite and ferrihydrite were taken from Majzlan et al. (2004); other thermodynamic data from Stumm and Morgan (1996), and using data for gases in their gaseous state.

[a] Schwertmannite of ideal composition.

Iron is hence reduced across gradients of mineral type, pH, and dissolved ferric iron and DOC concentration in AMD polluted sediments. We know surprisingly little yet about the effects of these gradients on iron reduction. In this contribution we sought to identify such effects. At constant pH 3, we added schwertmannite and goethite to sediment samples dominated by schwertmannite, increased ferric iron and DOC concentrations, measured iron in dissolved and solid phase, and interpret the data using Gibbs free energies of iron reduction and alternative electron accepting processes. The effect of pH was identified by titrating sediment slurries to differing pH values. To obtain information about the combined effect of iron addition and pH change, the minerals were finally added allowing the pH to vary freely.

2. Materials and methods

Samples were obtained by gravity coring from sediments (0–5 cm) of Lake 77 in Lusatia, Germany, homogenized in PE-bags, keeping exposure to air to a minimum, and kept frozen until used. The uppermost layers of the sediment consisted mainly of schwertmannite (>60%), and minor quantities of goethite (<5%), organic carbon (5–7%), kaolinite (<5%) and other silicates (Peine et al., 2000; Blodau, 2004). Total iron contents, determined by AAS after digestion with concentrated nitric and hydrochloric acid (1:1) in a microwave digester, were 398 ± 20 g kg^{-1}. The pH of the homogenized sediment used for incubation experiments was 2.91. Schwertmannite was synthesized in the laboratory according to the method of Bigham et al. (1990). An average stoichiometry of $Fe_8O_8(OH)_{5.4}(SO_4)_{1.3}$ was determined (Regenspurg et al., 2004). Goethite was synthesized according to Cornell and Schwertmann (1996). The minerals were dried at 60 °C and their identity was examined with XRD and FTIR prior to the experiments. The BET surface areas of the minerals were 51 m^2 g^{-1} (goethite) and 177.5 m^2 g^{-1} (schwertmannite; Gade, personal communication). Three different experiments were carried out with the sediment samples.

2.1. Experimental series A, pH-stat.

We investigated the effect of adding goethite, schwertmannite, dissolved ferric iron, and DOC (Pahokee Peat, standard humic substance, IHSS) on iron reduction under iron limited conditions (called experimental 'treatments'). To this end, we incubated sediment slurries at room temperature in the dark under an argon atmosphere for 88 days. Ten grams of wet sediment (75.2% water), 5 g of peat as a carbon source (90.9% water) from the Schlöppnerbrunnen II peatland (Horn et al., 2003), and 10 g of quartz sand as additional, inert matrix were mixed in incubation flasks. Deaerated solution (5 mM sulfate, 7.5 mM NaCl) was added to reach a liquid volume of 100 mL under continuous flushing with nitrogen.

The flasks were equipped with sulfide barred and gas-tight pH electrodes. Values of pH were adjusted by adding 0.1 M HCl or NaOH with a microliter syringe, beginning with day 24. Treatments began at day 31 by adding 2 g (20.1 mmol L^{-1} Fe) of synthetic schwertmannite or either 2 g (22.5 mmol L^{-1} Fe) or 4 g of goethite, and adjusting ferric iron concentrations with $FeCl_3$ (0.05 M) to ~0.5 and ~2.5 mmol L^{-1}, and DOC concentrations to 25 and 100 mg L^{-1}. Native schwertmannite content in the solution/suspension was estimated from reactive iron content (see below) and was approximately 9.9 mmol L^{-1} (Fe). Solute (1.5–2.5 mL) was sampled through permanently installed and stoppered syringes and replaced by the oxygen free sulfate solution. In the ferric iron treatments, standard solution was repeatedly added to maintain ferric iron concentrations. The headspace was sampled for CO_2, CH_4 and H_2 after day 42 through permanently installed syringes by extracting 12 mL of sample. The sampled volume was replaced with argon. Occasionally, headspace and septa were replaced to avoid contamination with oxygen and leakage. The assays were shaken after each sampling, which was carried out in time steps of 1–2 days at the beginning and up to 2 weeks towards the end. On the last sampling date, material from the assays was used for wet chemical extractions.

2.2. Experimental series B, pH varied

To test the influence of pH on iron reduction rates and formation of iron sulfides, we adjusted the pH to 3, 4.5, and 6, as described above, in flasks containing the sediment, sand and peat. Constant pH was initially kept for 7 days to test comparability between the individual flasks. In this experiment the headspace was not sampled but regularly replaced after day 20 to avoid precipitation of iron carbonates. This was necessary in the flasks that came close to or reached saturation with respect to iron carbonates (pH 4.5 and 6 treatments).

2.3. Experimental series C, net effects of mineral addition

To test the net effect of schwertmannite and goethite addition on iron reduction without keeping pH constant, a control, containing the sediment slurries only, a schwertmannite (0.2 g; 20.1 mmol L^{-1}), and a goethite assay (0.2 g; 22.2 mmol L^{-1}) were carried out at room temperature in three replicates per treatment and time step for 58 days. Airtight vials with butyl rubber stoppers and crimped aluminium caps were used in this experiment. Compared to the other experimental series, all volumes and weights were lower by a factor 10. Samples were shaken regularly and vials were sacrificed for the determination of solute chemistry at each sampling date. H_2S and pH were determined potentiometrically (AgS/glass-electrode, Watertest) immediately after opening the incubation vials. Material from the assays was used for wet chemical extractions on the first and last sampling dates.

2.4. Analytical techniques and calculations

Sulfate was analyzed by ion chromatography (Metrohm IC-system, METROSEP Anion Dual 1 column and chemical suppression). Iron(II) was measured spectrophotometrically by the phenanthroline method (Tamura et al., 1974) and addition of ascorbic acid, which reduces ferric to ferrous iron. The concentration of dissolved ferric iron was calculated by difference from total and ferrous iron. Hydrogen was measured on an H_2/CO analyzer (TraceAnalytical ta3000R), using a 1 mL sample loop, and converted to dissolved concentrations using Henry′s law ($K_H = 7.8 \times 10^{-4}$ mol L^{-1} atm^{-1}). CO_2 and CH_4 were measured on an SRI 8610 GC of SRI INSTRUMENTS, INC. (carrier gas N_2; 500 μL sample loop, equipped with FID and methanizer). To determine adsorbed and exchangeable iron contents, an aliquot of the wet sample was extracted for 1 h using 10–20 mL of 0.5-M NH_4Cl. Adsorbed and mineral-bound reactive iron was extracted for 1 h using 10–20 mL of 0.5-M HCl (Lovley and Phillips, 1986). Goethite is not extractable using this HCl extraction procedure (Wallmann et al., 1993). The content of total reduced inorganic sulfur components (TRIS: FeS_2, FeS, S°) was determined by the method of Fossing and Jørgensen (1989) as described by Blodau et al. (1998). The Gibbs free energy ΔG_r of terminal electron accepting processes with hydrogen as electron donor was calculated for the utilization of dissolved ferric iron, goethite, schwertmannite, sulfate and CO_2 (Table 1). Gibbs free energies of formation were taken from Stumm and Morgan (1996) and from Majzlan et al. (2004) with respect to schwertmannite. The dissolved ferric and ferrous iron activity was calculated using the PHREEQC algorithm version 2.8.02 and thermodynamic database (Parkhurst, 1995). Ferrous iron was the predominating species in solution, whereas ferric iron was predominantly present as $FeSO_4^+$, and secondarily as $FeOH^+$ and free Fe^{3+}.

3. Results and discussion

3.1. Experimental series A, pH-stat.

Carbon dioxide was released in a similar manner in the first week of the experiment, ensuring that metabolic activity in the flasks was nearly identical (supporting information, Fig. 1). Owing to the regular replacement of headspace gases and flushing with argon, production of CO_2 could not be accurately quantified later on. Iron was also similarly released (Fig. 1, insert), ensuring that differences in ferrous iron release could be attributed to the treatment effects.

Lowering the pH from 3.5±0.13 to 3.0±0.16 after day 20 accelerated the ferrous iron release in all flasks (Fig. 1, insert). Addition of goethite, schwertmannite, and dissolved ferric iron raised ferrous and ferric iron concentrations compared to the control and addition of DOC diminished it (Fig. 1). The effect was roughly proportional to the added quantity only for goethite. In contrast to expectation, schwertmannite promoted iron reduction less than goethite did. Most of the ferrous iron was released into the water, but substantial quantities were also recovered from the exchangeable and reactive fraction of the solid phase in the goethite and dissolved ferric iron treatments (Table 2). A pH of 3 thus did not inhibit the adsorption of ferrous and ferric iron on surfaces, although iron hydroxides were well below the documented pH of zero charge (Stumm and Morgan, 1996). In the control, DOC, and schwertmannite treatments, ferrous iron concentrations began to decrease after 30–50 days (Fig. 1).

The treatments altered the proton balance compared to the control (Fig. 2). Protons were net consumed at decreasing rates with time in the control (Fig. 2). Addition of goethite and small quantities of dissolved ferric iron increased the consumption of protons. Addition of schwertmannite, large quantities of dissolved ferric iron, and DOC at least temporarily increased proton release. The shift to net proton production can be attributed to lower iron reduction rates (see DOC addition, Fig. 1), increasing schwertmannite transformation rates (schwertmannite addition, Fig. 1), and precipitation of iron hydroxide from the water (addition of dissolved ferric iron, Fig. 1).

Common to all treatments was the predominance of iron reduction vs. sulfate reduction and methanogenesis. Iron sulfide contents remained very low, which suggests that little or no sulfate was reduced (Table 2). Methane concentrations remained <0.1 Pa, and the gas was not produced (data not shown). The predominance of iron reduction is not surprising in light of the ΔG_r available for microorganisms mediating these processes (Fig. 3).

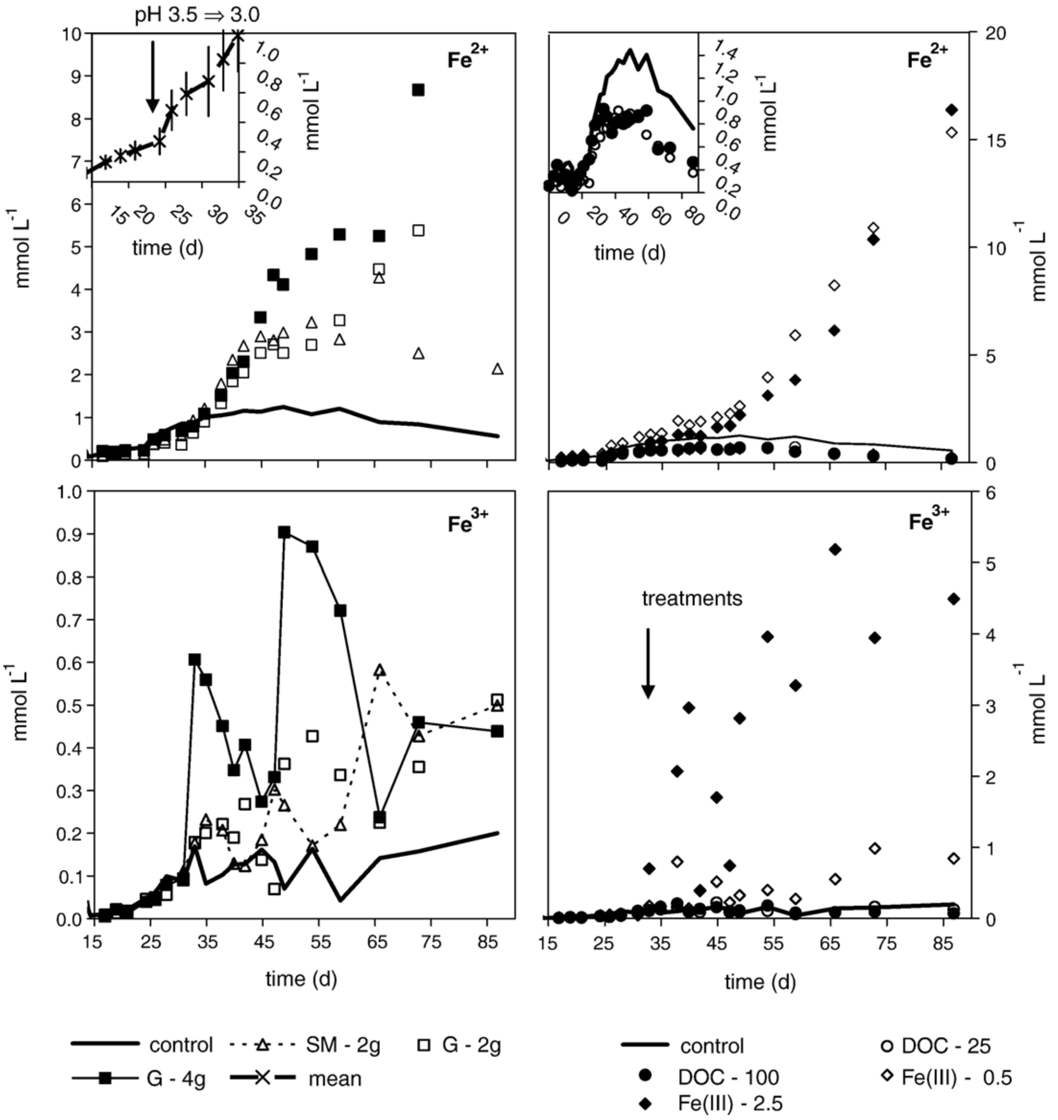

Fig. 1. Concentrations of ferrous and ferric iron in pH-stat. experiments. The pH was adjusted beginning with day 24, iron and DOC were added on day 31. The insert in the upper left panel illustrates the effect of pH decrease from 3.5 to 3.0 on the mean of ferrous iron release in the flasks before treatments were established. ('G' = goethite; 'SM' = schwertmannite; 'Fe(III)' = dissolved ferric iron; 'DOC' = dissolved organic carbon, Pahokee peat humic acid).

Previous work showed that the iron reducer *A. cryptum* JF5 utilizes H_2 in the sediments used (Kuesel and Dorsch, 2000). Hydrogen is moreover a common substrate for bacterial sulfate reduction and methanogenesis (Conrad, 1999). It has further been documented that the utilization of H_2 by anaerobic bacteria generally stops with ΔG_r values that are more positive than ~ -20 kJ mol^{-1} (H_2), which is probably a consequence of physiological constraints on ATP generation in bacteria (Conrad, 1999).

Values of ΔG_r were <-20 kJ mol^{-1} only for hydrogenotrophic iron reduction (Fig. 3). The exact magnitude of ΔG_r for sulfate reduction could not be ascertained because concentrations of H_2S were not quantified. However, ΔG_r of sulfate reduction is fairly insensitive to H_2S concentration owing to the reaction stoichiometry (Table 1). A change in H_2S concentration by a factor 10, for example, only changes ΔG_r by 1.35 kJ mol^{-1}. Regardless of this uncertainty, ΔG_r was thus small for bacterial sulfate reduction and it was positive for methanogenesis at partial pressures of H_2 equalling or being higher than 0.1 Pa.

The absence of sulfate reduction can thus be attributed to the low partial pressures of H_2 that were attained in the flasks by iron reducers and that lowered the available ΔG_r

Table 2
Summary of dissolved Fe^{2+}, Fe^{3+}, and sulfate concentrations, exchangeable (CEC) and reactive solid phase iron, and total reduced inorganic sulfur (TRIS) contents in the experiments

Assay	(*d*)	Fe^{2+}	Fe^{3+}	SO_4^{2-}	Fe II CEC	Fe tot CEC	Fe II reactive	Fe tot reactive	TRIS
(A)									
Control	88	0.27	0.16	6.45	0.097	0.208	0.28	7.54	0.025
SM—2 g	88	1.5	0.43	12.94	0.308	0.475	0.96	22.95	0.37
G—2 g	88	4.8	0.45	5.90	1.481	1.535	1.65	6.51	0.47
G—4 g	88	7.8	0.32	5.30	3.276	4.54	4.76	9.01	0.55
Fe(III) 0.5	88	14.1	0.73	7.53	3.02	3.23	4.32	7.48	0.43
Fe(III) 2.5	88	15.3	3.90	8.80	9.81	10.76	11.72	18.54	0.37
DOC 25	88	0.022	0.094	6.13	0.016	0.087	0.31	3.78	0.18
DOC 100		0.089	0.039	6.23	0.038	0.094	0.18	3.62	0.22
(B)									
pH 3	56	13.1	0.85	9.23	1.088	1.43	2.31	11.84	14±2.8
pH 4.5	56	6.6	0.25	11.66	1.039	1.19	1.28	22.99	100±19
pH 6	56	2.6	0.065	9.66	0.575	0.791	0.85	5.41	248±11
(C)									
Control	0	0.47±0.04	0.035±0.017	3.84±0.34	n.d.	n.d.	0.098	7.27	4.7±0.9
	58	3.94±0.59	1.06±0.38	8.85±0.52	n.d.	n.d.	1.16±0.28	1.64±0.25	52±5.0
SM	0	0.57±0.14	0.050±0.025	4.95±0.06	n.d.	n.d.	0.23	30.3	4.7±7.8
	58	7.46±0.88	0.44±0.10	15.98±1.38	n.d.	n.d.	0.46±0.056	9.45±3.75	7.2±5.0
Goethite	0	0.19±0.06	0.0009±0.006	4.47±0.10	n.d.	n.d.	0.12	7.83	8.1±0.6
	58	2.29±0.68	0.066±0.074	7.47±0.91	n.d.	n.d.	1.19±0.62	2.35±0.37	59±1.0

All concentrations are in mmol L^{-1} except for TRIS (µmol L^{-1}). Schwertmannite background in the sediment slurries was 9.9 mmol L^{-1}. Addition of schwertmannite was 20.1 mmol L^{-1}, and of goethite 22.2 and 44.4 mmol L^{-1}, respectively.

for all hydrogenotrophic processes. Hydrogen partial pressures were extraordinarily low in all treatments (supporting information, Fig. 2), ranging on average from 0.0034 Pa (0.027 nmol L^{-1}) to 0.0084 Pa (0.066 nmol L^{-1}). In pH circum-neutral sediments, partial pressures in this range have only been found when nitrate, whose utilization provides a much larger Gibbs free energy under standard conditions, was used as electron acceptor (Lovley and Goodwin, 1988; Cord-Ruwisch et al., 1988; Chapelle et al., 1996). The acidic conditions increased the Gibbs free energies available for iron hydroxide reduction relative to sulfate reduction and methanogenesis, as can be seen from a comparison of the equations used for calculation of Gibbs free energies in Table 1. Moreover, the low pH increased the activity of dissolved ferric iron, which is utilized more easily, and provided the highest Gibbs free energy (Fig. 3).

3.2. Experimental series B, pH varied

Increasing pH from 3 to 4.5 and 6 strongly lowered dissolved ferrous iron release and ferric iron concentrations (Fig. 4, Table 2B). Ferrous iron contents in the exchangeable and reactive solid phase also decreased compared to the pH 3 treatment (Table 2B). A similar pH-effect was reported earlier by Wieder (1994), who observed inhibition of iron reduction when pH approached 6 in wetland peats. Sulfate reduction occurred only in the pH 4.5 and pH 6 treatments, as indicated by increases in TRIS contents (Table 2B, note different units for solid phase contents).

Hydrochloric acid had to be added to the pH 3 and NaOH to the other treatments to keep the pH at the chosen levels (Fig. 5). In terms of proton release and consumption, schwertmannite transformation was fast compared to iron reduction at pH 4.5 and 6, and slow at pH 3 (Fig. 5). After days 20 to 30 the hydroxyl ion demand in the pH 4.5 and 6 treatment decreased and schwertmannite transformation apparently slowed down. Raising the pH in this acidic sediment had thus two effects: First, it accelerated schwertmannite transformation and proton release, which is in agreement with previous studies (Bigham et al., 1996; Regenspurg et al., 2004). Second, it slowed iron reduction and proton consumption. In schwertmannite bearing sediments both effects may contribute to buffering the pH in the acidic range.

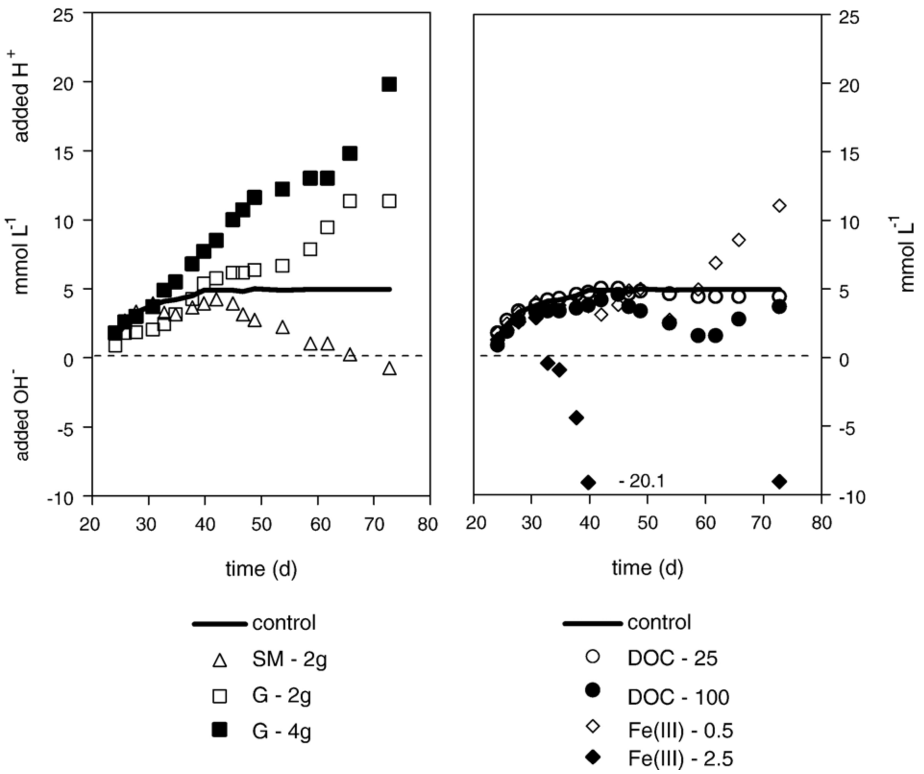

Fig. 2. Cumulative titrated H^+ (positive values) and OH^- in experimental series A (pH-stat.).

3.3. Experimental series C, net effects of mineral addition

In contrast to the pH-stat. experiments, ferrous iron was most rapidly released in the schwertmannite (6.3± 0.9 mmol $g^{-1}day^{-1}$), and more slowly in the control (3.9± 1.0 mmol g^{-1} day^{-1}) and goethite treatment (1.9± 0.7mmol g^{-1} day^{-1}; Fig. 6). Differences in the reactive ferrous iron fraction of the treatments remained small (Table 2C). Dissolved ferric iron was strongly released before reaching a concentration peak after 30 to 50 days (Fig. 6). Sulfate was continuously released in all treatments indicating schwertmannite transformation to goethite. Total reactive iron contents decreased and reactive ferrous iron contents increased over the incubation period indicating conversion of ferric to ferrous iron (Table 2C). H_2S could not be detected in any of the 90 samples but some sulfate was reduced in the goethite and control treatment, because small quantities of TRIS accumulated (Table 2C, note different units for solid phase contents). Sulfate reduction was, therefore, again restricted to treatments attaining a higher pH. Our expectation that the poorly crystalline schwertmannite would be more readily used than goethite was thus met only in this experimental series. Furthermore, goethite addition decreased iron reduction rates in the iron limited sediment slurry compared to the control.

To identify the reasons for the differences in iron reduction rates, the changes in pH and ferric iron concentrations between the treatments have to be considered: in the goethite treatment, the pH never fell below 4.3 and later increased to about 6, whereas it remained lower in the schwertmannite treatment (Fig. 6). Dissolved ferric iron concentrations were moreover very small in comparison to the schwertmannite and control treatments (Fig. 6) and also to the goethite treatment that was titrated to pH 3 in experimental series A (Fig. 1). According to the results from experimental series A and B, a high pH and low dissolved ferric iron concentrations decreased iron reduction rates in the sediment slurries. The difference in iron reduction rates between the goethite and schwertmannite treatments in experimental series C were, therefore, most likely caused by the acidifying and dissolved ferric iron releasing effect of the added schwertmannite.

3.4. Factors controlling iron reduction in acidic and iron rich sediments

The experiments suggest that iron reduction rates in the sediment slurries were directly controlled by iron availability and indirectly controlled by geochemical

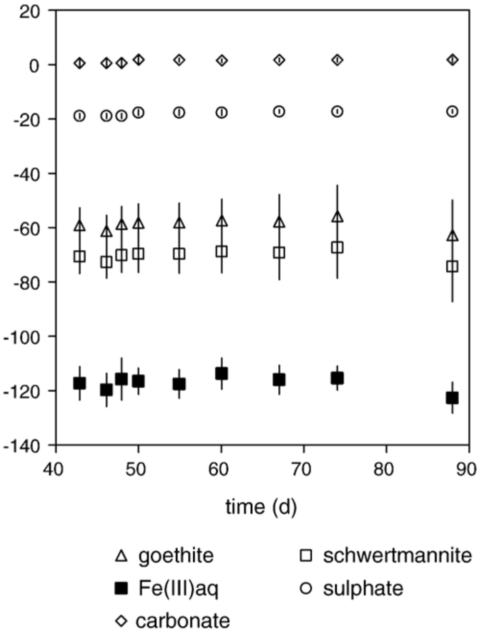

Fig. 3. Approximate Gibbs free energy (ΔG_r) of terminal electron accepting processes in experimental series A (pH-stat.), standardized on formula unit of H_2. In the calculation (Table 1), H_2 served as electron donor and schwertmannite, goethite, dissolved ferric iron (labelled Fe(III)aq), sulfate, and carbonate as electron acceptors. A partial pressure of 0.1 Pa was used for H_2S (=0.08 μmol L^{-1}) and CH_4 (=0.0013 μmol L^{-1}). Mean and standard deviation of energies of treatments are displayed.

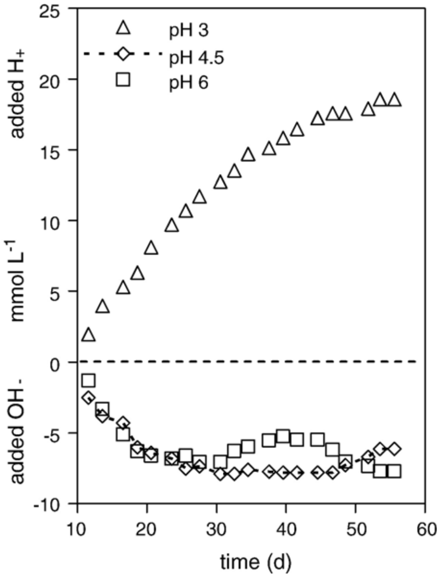

Fig. 5. Cumulative titrated H^+ (positive values) and OH^- in experimental series B (pH varied).

changes following iron addition. When the pH was kept acidic, any addition of ferric iron raised iron reduction rates, suggesting a simple limitation of the process by iron availability. The large effect of dissolved ferric iron addition was expected, because dissolved ferric iron species are preferentially utilized in pH neutral environments (Arnold et al., 1986; Straub et al., 2001). In batch experiments with suspensions of poorly crystalline ferric iron hydroxides and *Geobacter metallireducens*, and the chelator nitrilotriacetic acid (NTA), Lovley and Woodward (1996) observed an increase in dissolved ferric iron concentrations from barely detectable up to 0.3 mM. Iron

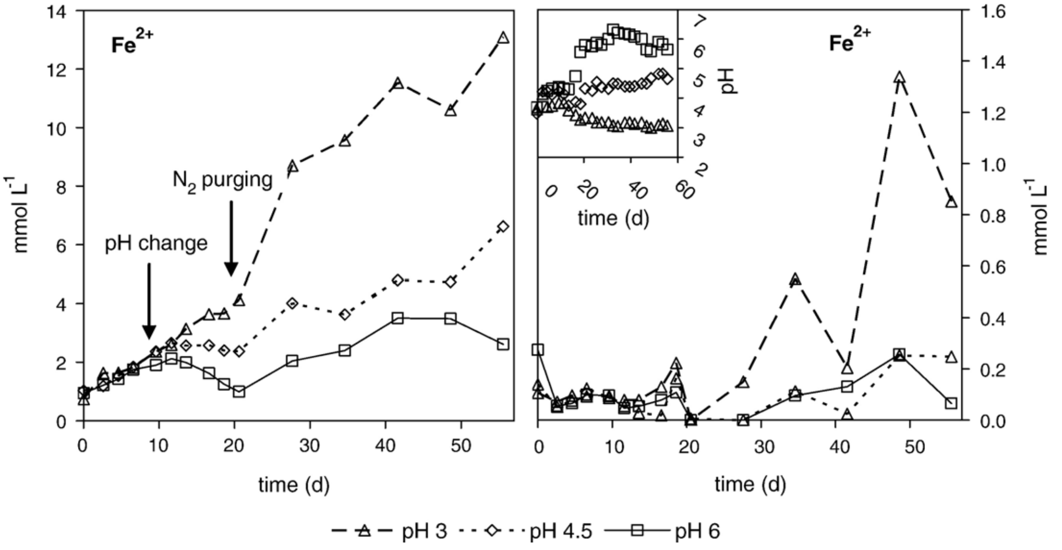

Fig. 4. Concentrations of ferrous and ferric iron in experimental series B (pH varied). The insert in the right panel shows the pH in the flasks. Flasks were purged with nitrogen after day 20 to avoid precipitation of iron carbonate in the high-pH treatments.

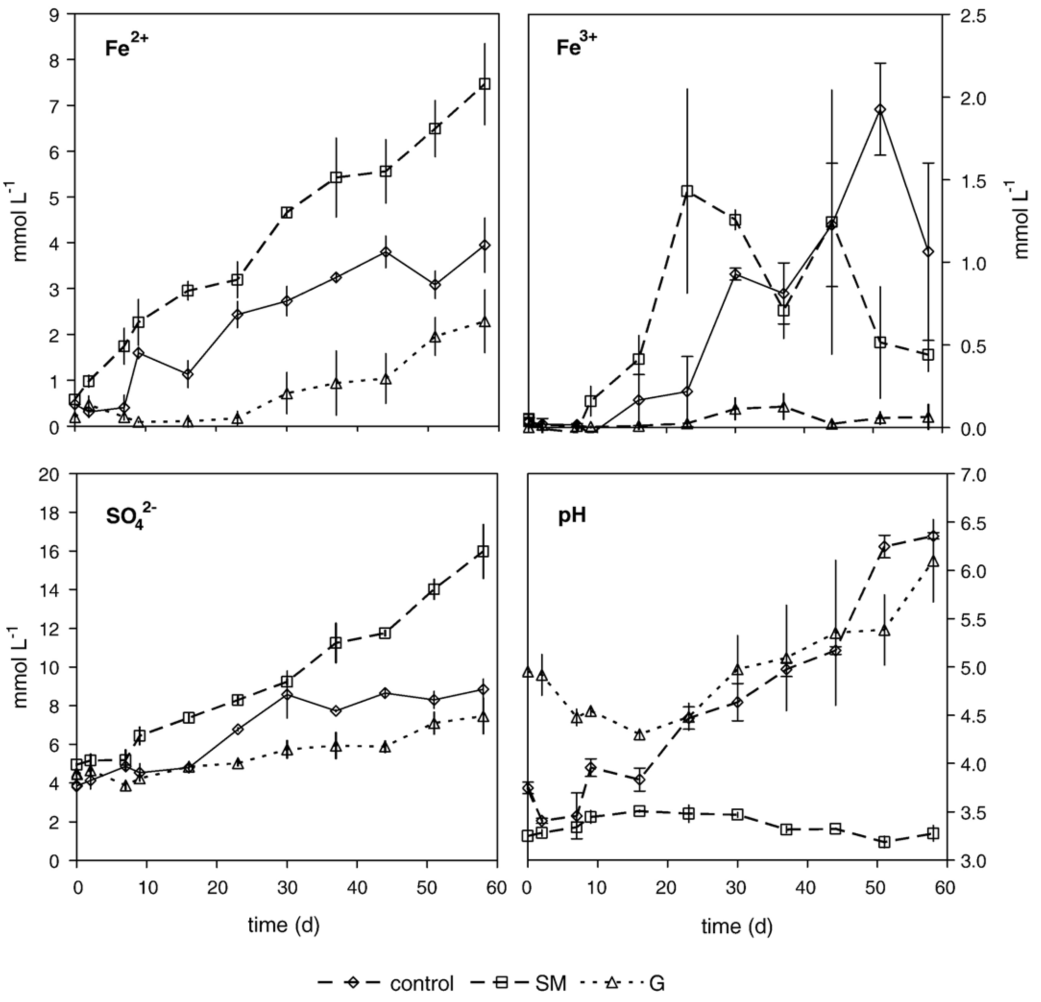

Fig. 6. Concentrations of dissolved ferrous and ferric iron, sulfate, and pH in mineral addition experiments. All analyses were carried out in threefold experimental and two- to threefold analytical replication. Error bars represent the standard deviation of experimental replicates (SM: schwertmannite; G: goethite).

reduction rates increased as a consequence. Part of the effect may have been also due to complexation of ferrous iron, which can reduce the affinity of iron hydroxide surfaces to iron reducers (Urrutia et al., 1999). Utilization of dissolved ferric iron for dissimilatory iron reduction was most beneficial also from a thermodynamic point of view. It provided the largest ΔG_{Fe} among the potential sources of ferric iron (Fig. 3) and hence the largest possible biomass yield per unit of substrate used.

A number of results came to our surprise, though. It is well known that not only synthetic chelators but also humic substances may stabilize ferric iron in solution and thus prevent it from precipitation (Luther et al., 1996). We did not observe a concentration increase of dissolved ferric iron after addition of humic acid. The addition, however, inhibited ferrous iron production in both liquid and solid phases. This effect may have been caused by formation of stable dissolved complexes between ferric iron and humic acid, or, if the analogy to experimental studies with soils is drawn, by adsorption of humic substances on hydroxides (Gu et al., 1994). The availability of hydroxides for iron reducers was lowered with adsorption of linear alkylbenzene sulfonate in soils (Kristiansen et al., 2003). In our experiments, adsorption was likely enhanced by the positive net charge of the iron hydroxide surfaces at low pH.

It was also surprising that iron was more rapidly reduced when goethite was added compared to schwertmannite in experimental series A, at constant pH 3. This finding contradicts previous experiments with cultures of *A. cryptum* JF5, goethite and schwertmannite (Kuesel, 2003). It is also in conflict with the notion that increasing iron hydroxide crystallinity decreases microbial availability (Lovley and Phillips, 1986) and recent work by Roden (2003). At near-neutral conditions (pH 6.8), using a variety of minerals differing in thermodynamic properties and surface area, and *Shewenella putrefaciens* as iron reducer, the author demonstrated that bacterial iron reduction was primarily controlled by differences in surface area rather than by the thermodynamic stability of the bulk mineral.

In our experiments, the BET surface area of added goethite was 51 m^2 g^{-1} and of added schwertmannite 177.5 m^2 g^{-1}, which would suggest a more rapid utilization of schwertmannite. This expectation was not met at pH 3, when dissolved ferric iron concentrations were high in all treatments, but it was met indeed when pH and dissolved ferric iron concentrations diverged between treatments in experimental series C (Fig. 6). The differences in dissolved ferric iron concentrations between treatments, or unidentified effects of pH on bacteria or mineral surface properties obviously compensated for the different surface areas of the minerals. *In situ*, pH may thus be a more important control on iron reduction rates than the mineralogical properties of goethite and schwertmannite. A low tolerance of the acidophilic iron reducers present in acidic sediment of Lake 77 to the rising pH may have also played a role in this phenomenon. Cultures of acidophilic, iron reducing *Acidiphilium* species had a pH optimum of 3.2 in these sediments (Kuesel et al., 1999) and decreasing iron reduction rates with increasing pH may have been the consequence.

In conclusion, iron reduction in sediments of acidic coal mining lakes is controlled by a number of factors. Numerous studies have demonstrated that iron reduction is typically limited by electron donor availability in the sediments (Kuesel, 2003), most likely because the flux of easily decomposable organic matter to the sediments is small in these waters (Blodau et al., 2000; Laskov et al., 2002; Chabbi et al., 2006). If this limitation is eased, as in our experiments by the addition of a carbon source, additional schwertmannite or goethite will promote iron reduction directly by increasing the iron hydroxide content, or indirectly by raising dissolved ferric iron concentrations. If the pore water is not concurrently acidified by schwertmannite transformation, however, iron reduction will raise the pH and thus create geochemical conditions unfavourable for further iron reduction. Acidification by schwertmannite is thus a key factor for supporting high rates of iron reduction in the sediments of such waters. Even under acidic conditions, however, iron reduction may be inhibited in the presence of high concentrations of dissolved humic acids.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2006.08.003.

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