

Geochemical Constraints on the Anaerobic Electron Flow in the Sediment of an Acidic Lake

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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 or the production of alkalinity. Typically, such lakes are characterized by a low pH due to the oxidation of Fe(II). In the sediments, competition between iron-reducing and sulfate-reducing bacteria for common electron donors exists. From a thermodynamic point of view, the low pH may even favour the predominance of iron reduction (Postma and Jakobsen 1996). Moreover, coupling between sulfate reduction and reductive dissolution of ferric (hydr)oxides by H₂S can be expected based on observations in other iron-rich aquatic systems (Jakobsen and Postma 1999), a process that will affect the recent formation of pyrite.

In this study, we therefore have focussed our attention on the processes regulating the electron flow in the sediment of an acidic, sulfate-rich lake being exposed to low organic carbon input and to high deposition rates (570 g/(m² a)) of schwertmannite (Fe₈O₈(OH)_x(SO₄)_y), a mineral formed in iron and sulfate-rich waters within a pH-range from 2.8 to 4.5 (Bigham et al. 1996).

The sediment can be geochemically separated into three zones:

- the upper zone (0-5 cm) with low pore-water pH values (< 4) and being enriched with schwertmannite (" 350 g/kg). Microbial iron-reduction rates measured by the closed vessel incubation technique were highest close to the sediment-water interface (250 nmol/(cm³ d)), sulfate reduction measured by the ³⁵S-tracer technique was not. The absence of sulfide allowed complete re-oxidation of Fe(II) diffusing into oxic parts of the lake water. Thus, an iron cycle is established where acidity generation through this process (1.0-4.7 mol/(m² a)) balanced the alkalinity gain through microbial iron reduction in this zone (0.65-4.0 mol/(m² a)). Additional acidity (3.5 mol/(m² a)) is generated by the transformation of schwertmannite to goethite at a depth of 3-5 cm.
- an intermediate zone (5-8 cm) where the pore-water pH increased to values between 5 and 6
- the lower zone (8-16 cm). Sulfate reduction occurred with a maximum rate of 14 nmol/(cm³ d) at 9 cm depth. Iron-reduction rates decreased compared to the values measured in the upper

zone. Release of Fe(II) and a short turnover time of reduced sulfur relative to the sediment age implies that most of the sulfide formed was recycled to sulfate at this depth, presumably coupled to the reduction of iron.

Overall, 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 schwertmannite, and the low amount of organic matter. Acidic conditions in the lake water are stabilized through re-oxidation of microbially formed Fe(II) at the sediment-water interface and transformation of schwertmannite 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.

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 re-oxidation of sulfide to sulfate with ferric oxide as the terminal electron acceptor. The alkalinity generated through the combined sulfate and iron reduction in zone 3 (0.89-2.0 mol/(m² a)) seems to be consumed by the transformation of schwertmannite to goethite in zones 1 and 2. The transformation process seems to generate 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.

The re-oxidation of sulfide to sulfate seems to be almost complete in this sediment with 90% of the H₂S reacting with goethite back to sulfate. The remaining 10% are transferred into pyrite. Stoichiometrically, this ratio implies a maximum rate of alkalinity generation compared to situations where most of the re-oxidized 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.

Postma D & Jakobsen R, *Geochim. Cosmochim. Acta*, **60**, 3169-3175, (1996).

Jakobsen R & Postma D, *Geochim. Cosmochim. Acta*, **63**, 137-152, (1999).

Bigham JM, Schwertmann U, Traina SJ, Winland RL & Wolf M, *Geochim. Cosmochim. Acta*, **60**, 2111-2121, (1996).