

# Early Diagenesis Modelling of Sediments from a Water Reservoir Affected by Acid Drainage

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## INTRODUCTION

The sediments from Acid mine drainage (AMD) contaminated water reservoirs are rich in crystalline iron oxides eroded from the river bed and in low crystallinity iron oxyhydroxides formed in the reservoir water column settling to the bottom. Sulfate and trace metals are also present in the water column in high concentrations. Once into the sediments, iron, sulfur and trace metal cycling can be promoted by physico-chemical changes in the water column (e.g. O<sub>2</sub>, pH, Eh).

Similarly to lakes, reservoir stability can be classified according to the ratio between surface and depth of the water column. High stability means an

insufficient vertical circulation to mix the entire water column, whereas low stability (holomictic behaviour) exists when the water column is mixed (turnover) at least once per year. During the mixing period oxygen reaches the sediments, while during the stratified period the bottom of the reservoir has hypoxic conditions due to organic matter oxidation. This results in a periodic oscillation of oxygen concentration at the bottom from completely anoxic to oxic conditions.

Recently, Scholz et al. (2011) studied the effect of El Niño Southern Oscillation (ENSO) on V, Mo and U cycling related to oxygen oscillations in bottom waters from a Peruvian upwelling area. They found that during shelf oxygenation

periods V and Mo adsorbed to Fe and Mn (oxyhydr)oxides and after the recurrence of anoxic conditions, metal (oxyhydr)oxides were reductively dissolved and V and Mo were liberated.

To better understand the effects of oxygen fluctuation on iron, sulfur and metal cycling in the sediments, a laboratory experiment was carried out. Sediments and water from an AMD affected water reservoir were used. The data obtained were used in a diffusion reaction model.

## STUDY SITE AND SAMPLING

The Sancho water reservoir is located in the Odiel Basin, Huelva (SW Spain) in the Iberian Pyrite Belt. The reservoir has

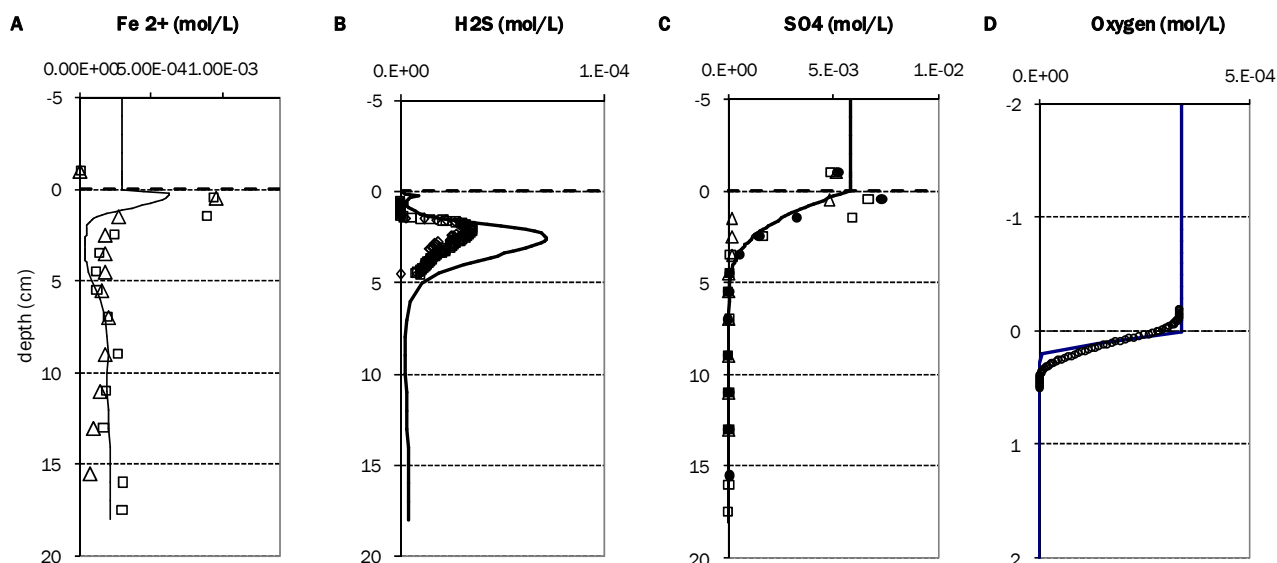


fig 1 A) Fe<sup>2+</sup>, B) H<sub>2</sub>S, C) SO<sub>4</sub> and D) Oxygen profiles in the pore water of the sediments after step 2 (OXIC): Dots, triangles and squares are the measured values and the line is the modeled concentrations. The dashed line represents the water-sediment interface.

**key words:** Drenaje ácido de mina, Embalse, Sedimentos, Diagénesis, Metales, Transporte reactivo, Modelo.

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a pH of ~3.5, with high SO<sub>4</sub> (200 ppm) and heavy metal concentrations in the water column. The water column is mixed in winter, allowing oxygen to reach the bottom.

Field sampling was carried out in the stratified period (November 2010). Twelve sediment cores were collected using a cylindrical box corer (6 cm i.d.). Each core contained approximately 30 cm of sediment and 30 cm of overlying water, which was analyzed as bottom water. 50 liters of anoxic water from the bottom of the reservoir were taken to provide natural water for the experiment. The cores were protected from light to avoid any photo-oxidizing process and stored on ice (around 4°C) until return to the laboratory in the same day.

### EXPERIMENTAL DESIGN

The experiment was divided into three stages. At the end of each stage 3 cores were removed to be analyzed in triplicate.

- 1 day: kept under hypoxic (~10 μmol O<sub>2</sub> L<sup>-1</sup>) conditions in the laboratory in an aquarium with natural water bubbled with nitrogen gas.
- 50 days: oxic conditions were induced by bubbling with air.
- 10 days: hypoxia was reestablished.

### Sample Analysis

At the end of each stage, dissolved oxygen (DO), H<sub>2</sub>S and pH profiles were measured using microsensors. Afterwards the cores were transferred from the tank to a nitrogen purged glove box and sectioned in 1cm slices. Pore water was extracted by centrifugation and pH, DO and Eh measures were done with calibrated electrodes. Sub-samples for As, Co, Cu, Cd, Cr, Ni, Pb and Zn and for SO<sub>4</sub> and Fe were filtered through 0.2 μm pore size filters, acidified with HNO<sub>3</sub> 20% and stored at 4°C until analysis by ICP-MS and by ICP-OES, respectively. Aliquots for DOC analyses were filtered through 0.45 μm pore size nylon filters, acidified with HCl 2N and stored in pre combusted glass bottles at 4°C.

Iron monosulfides and pyrite were extracted from the freeze-dried sediment with ammonium acetate (pH 4.5) and HNO<sub>3</sub> 8M, respectively. Fe (III)-amorphous and Fe(III)-oxides were also extracted with 0.2M oxalic acid (pH 3) at different temperatures (Dold, 2003). Organic matter fraction was extracted by

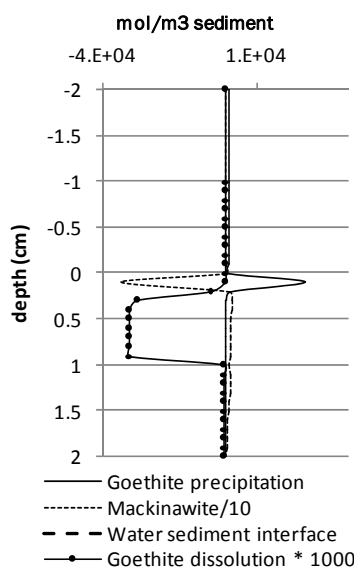


fig 2. The dissolution and precipitation profiles of goethite and mackinawite. The dotted line represents the water-sediment interface.

0.5M NaOH (Sposito, 1989).

### MODEL FORMULATION

A diffusion-reaction model was used to obtain the rates of biogeochemical reactions by fitting to the experimental data. The reaction network includes three primary reactions describing the degradation of organic matter via oxic respiration, Fe(III) and SO<sub>4</sub><sup>2-</sup> reduction. The secondary reactions considered were the oxidation of pore water Fe(II) by O<sub>2</sub>, and of H<sub>2</sub>S by Fe(OH)<sub>3</sub>(s). Precipitation and dissolution of iron monosulfide, Fe(III)-oxides and amorphous Al(OH)<sub>3</sub>, and pyrite precipitation were also considered.

### RESULTS AND DISCUSSION

During hypoxic conditions (step 1 and 3 in the experiment) sulfate and Fe-(oxy)hydroxides were reduced, due to the anaerobic oxidation of organic matter, at the first few cm, releasing sulfide and Fe(II) which precipitated as iron monosulfide (mackinawite). Pyrite precipitated deeper than iron monosulfide.

When oxygen diffuses into the sediment (step 2), sulfate-reduction and the sulfide peaks were displaced deeper into the sediment. Oxygen penetration depth and its consumption rates in the sediment increase quickly, resulting in the re-oxidation of the iron sulfides that had precipitated during hypoxic conditions. Sulfide and Fe(II) were released and reoxidized again to Fe(III) and sulfate, by

oxygen and Fe(III).

Goethite precipitates during oxidizing conditions and was reductively dissolved under hypoxic conditions. The precipitation of the goethite led to a pH decrease during the oxygenated period. In this areas where the pH is lower than 5.5 the Al(OH)<sub>3</sub> is dissolved releasing Al to the pore water.

Copper, Cd and Zn co-precipitated with the iron monosulfide and pyrite. During the dissolution of sulfides Cu, Cd and Zn are released and diffuse to the water column. Arsenic, Cr and Pb are mainly found in Fe(III)-oxides, and are released during their reductive dissolution of them.

Preliminary runs of the model fit reasonably well the observed trends of Fe, H<sub>2</sub>S and SO<sub>4</sub> (Fig. 1), and confirm the major reactions described above. Moreover, as shown in Fig. 2, the model allows discriminating distinct mineral zones with a detail beyond the analytical one (usually cm-thick). Thus, FeS dissolve and goethite precipitate in the upper 2 mm of sediment affected by O<sub>2</sub> diffusion. The reverse process take place in the following 7 mm below the oxygen front (Fig. 2): FeS precipitate from H<sub>2</sub>S and Fe(II), and goethite experience a reductive dissolution. It has to be noted that oxic processes are three fold more intense than reductive ones.

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