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Diffusion-reaction modelling of early diagenesis of sediments affected by acid mine drainage.

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The Sancho Reservoir (SW Spain) is a monomictic water reservoir affected by acid mine drainage. It has a pH of ~4, with high sulfate (200 ppm) and heavy metal concentrations in the water column. The reservoir develops reducing conditions at the bottom during the stratification period. A laboratory experiment was carried out to study the effect of this oxygen variation on the early diagenesis processes and the cycling of metals. Sediment cores and bottom water were collected during the stratification period and brought to the laboratory. The cores were maintained in an aquarium bubbled with nitrogen gas to maintain hypoxic conditions (~ 10 μmol O_2 L-1) for 1 day. Then, oxic conditions were induced by bubbling with air and maintained for 50 days. Finally, hypoxia was re-established for 10 days. Triplicate cores were sliced in a anaerobic glove box at each stage. Pore water was extracted by centrifugation and: Eh, pH, DO, DOC, sulfate, Fe and trace metals were analyzed. The sediment was freeze-dried and a sequential extraction protocol was applied to determine the exchangeable, AVS, Fe-(oxy)hydroxides, Fe-oxides, organic matter, pyrite sulfur and residual phase iron fractions. Organic carbon and total C, N, H and S were also analyzed in the sediment. A reactive diffusion model has been used to obtain the rates of biogeochemical reactions by fitting to the experimental data. During hypoxic conditions sulfate and Fe-(oxy)hydroxides are reduced, due to the anaerobic oxidation of organic matter, at the very first few cm, releasing sulfide and Fe(II) which precipitate as iron sulfide. When oxygen diffuses in the sediment, sulfate-reduction and the sulfide peaks are displaced deeper into the sediment. Oxygen penetration depth and its consumption rates in the sediment increase quickly, resulting in the reoxidation of the iron sulfides that had precipitated during hypoxic conditions. Sulfide and Fe(II) are released and are again oxidized to Fe(III) and sulfate respectively. Arsenic can be adsorbed onto the iron sulfides and pyrite. During the dissolution of the iron sulfide As will be released and will diffuse to the water column. Copper and zinc can also precipitate as metal sulfides.