Unsteady sulfur diagenesis in freshwater sediments under changing oxygenation conditions

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We measured the vertical distribution of sulfur (S) and other geochemical variables in the pore-water (sulphate and sulfides, elemental sulfur) and in the solid-phase (iron monosulfide, pyrite, ester-sulfate and thiols) of sediment cores taken from a perennially oxygenated and a seasonally anoxic basin of an oligotrophic lake in Québec, Canada. The cores were dated and analyzed for ancilliary parameters using a combination of techniques, including sequential extractions of the solid-phase and X-ray absorption near edge structure (XANES). A non-steady state early diagenetic model was developed and calibrated against this extensive dataset to help unravel the pathways and quantify the rates of S transformations coupled to those of O, C and Fe.

Results showhat the main source of S to the sediments is the settling of organic ester-sulfate (R-O-SO_3-H) originating from the catchment. Hydrolysis of deposited R-O-SO_3-H and supply of aqueous sulfate from the water column fuel microbial sulfate reduction, releasing elemental sulfur and sulfide to the pore-water. Reduced solid-bound S species accumulate as thiols (R-SH) and iron sulfides (i.e., FeS and FeS_2) in the perennially oxygenated and seasonally anoxic basin, respectively. The solid sediment S profiles, however, carry the imprint of the time-dependent sulfate input to the catchment. Iron sulfide enrichments formed during past decades of elevated atmospheric SO_4 deposition are presently dissolving. In the sediments of the perennially oxygenated basin this will likely cause the continued build-up of Fe(III) (oxy)hydroxide near the sediment-water interface and promote further S sequestration through organic matter sulfidization. The model-estimated rate constant for R-SH formation similar to that proposed for marine shelf sediments