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Sulfur, manganese and iron transformations in low-sulfate iron-rich Lake Sihailongwan

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We studied he cycling of the redox-sensitive elements in the water column and sediments of the seasonally stratified Lake Sihailongwan, China, which has epilimnetic sulfate concentrations <100 μmol L^{-1} [1]. The hypolimnion of the lake becomes seasonally anoxic and contains iron, manganese and low concentrations of hydrogen sulfide. These conditions are similar to those suggested to exist in the Archean ocean, and therefore the biogeochemical cycles in Lake Sihailongwan may be analogous to those in the Archean ocean. The concentration profiles of the redox species in the water column and in the sediments show that dissolved Fe(II) and Mn(II) diffuse from the sediments into the water column, while hydrogen sulfide and sulfate diffuse into the sediment. In the hypolimnion, the sulfur isotope fractionation values are consistent with microbial sulfate reduction, possibly combined, to a minor extent, with disproportionation of zero-valent sulfur. Sulfur isotope fractionation factor increases between spring and autumn. Highly reactive iron in the sediments mainly consists of Fe(II) carbonates and reactive Fe(III) (hydr)oxides. Iron-based redox proxies are consistent with sediment deposition under ferruginous water column conditions. In the sediment, concentrations of sulfate and hydrogen sulfide are low, and sulfur isotope composition of sedimentary pyrite is equal to that of the epilimnetic sulfate. Our results demonstrate that despite a low sulfate concentration in the water column, sulfur isotope fractionation is high. However, due to the complete reduction of the sulfate reservoir in sedimentary pore-waters, the large isotope fractionation is not preserved in the sedimentary record. Our results are consistent with the absence of difference between isotopic composition of sulfur in epilimnetic sulfate and sedimentary pyrite predicted by the compilation of Gomes and Hurtgen [2].

[1] Boyko, Avetisyan, Findlay, Guo, Yang, Pellerin & Kamyshny (2021) *Geochimica et Cosmochimica Acta* 296, 56-74.

[2] Gomes & Hurtgen (2015) *Geochimica et Cosmochimica Acta* 157, 39-55.