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Disentangling the overlapping zonation of dissimilatory iron and sulfate reduction in a carbonate-buffered sulfate-rich and ferruginous lake water column

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In the oligotrophic bottom waters of a post-mining lake (Lake Medard, Czechia), ferruginous conditions occur without quantitative sulfate depletion. The dissolved organic matter supply to the deep waters is small and, accordingly, sulfate reduction promoting precipitation of stable ferrous sulfides is limited. In line with these observations, an isotopically constrained estimate of the rates of planktonic sulfate reduction (SRR) suggests that despite a high genetic potential—as determined by genome analyses, SRR are limited by substrate competition exerted by nitrogen and iron respiring prokaryotes. The microbial succession across the nitrogenous and ferruginous zones of the bottom water column also indicates a sustained genetic potential for chemolithotrophic sulfur oxidation, probably accompanied by disproportionation of S intermediates[1].

The bottom waters displayed dissolved Fe concentrations (~0.1 to 33 µM) and δ^{56}Fe values (-1.77 ± 0.03 ‰ to +0.12 ± 0.05 ‰) that increase across the redoxcline and towards the anoxic sediment-water interface (SWI). These parameters pinpoint diffusive transport and partial oxidation of dissolved ferrous iron (Fe(II)) sourced from the lakebed, depletion of the residual Fe(II) in heavy isotopes at the redoxcline and enrichment near the SWI linked to monosulfide precipitation. In the carbonate-buffered lake sediments, however, sulfur re-oxidation appears to prevent substantial stabilization of iron monosulfides as pyrite, but it enables the interstitial precipitation of small proportions of equant microcrystalline gypsum. This gypsum isotopically fingerprints sulfur oxidation proceeding at near equilibrium with the ambient anoxic waters, whilst authigenic pyrite-sulfur displays a 38 to 27 ‰ isotopic offset from ambient sulfate, suggestive of incomplete sulfate reduction and indicative of the openness of the system[1].

Overall, our results demonstrate that under transitional redox states producing the meromictic stability described here, the simple biogeochemical zonation models based on energetic

considerations of pure phases at standard conditions may not accurately describe the overlapping zonation of dissimilatory iron and sulfur reduction. Vigorous sulfur and iron co-recycling in the water column can be fuelled by ferric and manganic particulate matter and notably by the redeposited siderite stocks of the upper anoxic sediments. In the absence of ferruginous coastal zones today, the current water column redox stratification in the post-mining Lake Medard has scientific value for (i) testing emerging hypotheses on how a few interlinked biogeochemical cycles operated in low productivity nearshore paleoenvironments during transitional states between ferruginous and euxinic conditions; and (ii) to acquire insight on potential avenues for early diagenetic overprinting of redox proxy signals in ferruginous-type sediments.

[1] Petrash, D. A., Steenbergen, I. M., Valero, A., Meador, T. B., Pačes, T., and Thomazo, C.: Aqueous system-level processes and prokaryote assemblages in the ferruginous and sulfate-rich bottom waters of a post-mining lake, Biogeosciences Discuss. [preprint], https://doi.org/10.5194/bg-2021-253, in review, 2021.