

Low sulfate systems: Does organic sulfur affect isotopic fractionations?

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Sulfur isotopes are critical in reconstructions of S cycling in both modern and ancient environments. Strong isotopic fractionation is imparted by sulfate reduction (>~30‰), and minor contributions come from sulfide oxidation and S⁰ disproportionation (~5‰). The sulfate is typically drawn into sediments from overlying waters. In low-sulfate (<500 μM) environments, however, a significant (up to 50-100%) fraction of sulfate reduction can be supported by the sulfate generated within the sediment by mineralization of organic sulfur (OS) [1]. This may affect the S-isotopic signatures recorded in solid sulfides by altering the diagenetic cycling of S, or via a direct fractionation during OS hydrolysis. Thermodynamic considerations allow isotopic fractionations during hydrolysis of up to 18‰, but experimental verifications are lacking. We investigate the potential effect of OS through a combination of indirect measurements and modeling. Sulfur concentrations, speciations, and isotopic compositions are analysed in sediments from environments ranging from well-oxygenated Lake Superior to anoxic Lake Malawi. A diagenetic reaction-transport model, calibrated to the conditions in ferruginous Lake Matano, reproduces the contrasting S isotopic profiles in oxygenated vs. anoxic sediments and suggests fractionations during hydrolysis of up to 15‰. In environments with sulfate levels <50 μM, the effects of OS may make sedimentary sulfides isotopically lighter by about 7‰. If confirmed, the results will affect the interpretations of isotopic sulfur records in modern freshwater environments and ancient low-sulfate marine systems, such as during the Archean and Proterozoic eons.

[1] Fakhraee, Li & Katsev (2017) *Geochem. Cosmochim. Acta* 213: 502-516.