

Sulfur-carbon-oxygen cycling and the role of polysulfide as a cryptic molecule

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The bioavailability of sulfur compounds in any aqueous setting is potentially affected by (a)biotic reactions between sulfur and other dissolved inorganic species, (nano)particles, and organic materials. The coupling of element cycles can have a significant effect on the sulfur intermediates present at any point in time, and pools of potential electron donor and acceptors is often controlled by fluxes of material that can display chaotic periodicity. Yellowstone National Park thermal areas serve as a field analog where in situ voltammetry and other field data serve as starting point to describe the speciation and coupling of sulfur, carbon, and oxygen molecules. We then utilize a kinetic approach to characterize key reactions in the system to define the role of elemental sulfur nanoparticles and a flux of sulfide to generate polysulfides, key intermediates that can link to the carbon cycle through organic matter sulfurization and to oxygen in the formation of thiosulfate. Kinetic models utilizing the rate laws we have determined for nanoparticulate elemental sulfur reaction with sulfide demonstrate the key role of polysulfides even at conditions where polysulfide would be present at nanomolar levels. This same reaction may also be a key component controlling the overall bioavailability of elemental sulfur, opening up roles for elemental sulfur and polysulfide oxidoreductases in metabolic pathways.

