

Triple sulfur isotopes fractionations associated with abiotic sulfur transformations in Yellowstone National Park hydrothermal springs

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We present a quantification of main (hydrogen sulfide and sulfate) and intermediate (zero-valent sulfur, thiosulfate, sulfite, thiocyanate) sulfur species in hydrothermal springs and pools of the Yellowstone National Park. We combined these measurements with the measurements of triple sulfur isotope composition of sulfate, hydrogen sulfide and zero-valent sulfur. The main goal of this research was to reveal multiple sulfur isotope fractionation in the system, which is dominated by complex, mostly abiotic, sulfur cycling. Water samples from six springs and pools were sampled and characterized by pH, chloride to sulfate ratios, sulfide and intermediate sulfur species concentrations. Sulfur isotope fractionation between zero-valent sulfur and hydrogen sulfide was close to zero at pH<4. At higher pH, zero-valent sulfur is slightly heavier than hydrogen sulfide due to equilibration in the rhombic sulfur – polysulfide – hydrogen sulfide system. The $\delta^{34}\text{S}$ values of hydrogen sulfide and sulfate in four of six systems were found to be close to those calculated using a mixing line of the model based on dilution and boiling of a deep hot parent water body. The isotopic composition of sulfur species of only one system fits the predicted range of values for microbial sulfate reduction. None of the isotopic compositions fit experimental data for microbial sulfur disproportionation. We suggest that a combination of (a) difference in $\delta^{34}\text{S}$ values of sulfide and sulfate that is too low to be interpreted as microbial sulfur disproportionation ($\leq 10\text{‰}$), and (b) difference in $\Delta^{33}\text{S}$ values of sulfide and sulfate that is too low to be interpreted as microbial sulfate reduction ($\leq 0.00\text{‰}$), may serve as an indicator for complex abiotic transformations of sulfur species. Implications of mass-dependent multiple sulfur isotope fractionation by abiotic sulfur cycling for the understanding of biogeochemical processes in the sulfide-rich Proterozoic ocean will be discussed.