

S isotope fractionations in volcanic aqueous systems on Earth and Mars

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First in situ sulfur (S) isotope measurements of the Martian bedrock by the Curiosity rover resulted in a wide range of $\delta^{34}\text{S}$ values (-47 to +28‰) exceeding those previously measured for Martian meteorites ($\sim 0 \pm 2\%$), suggesting complex hydrothermal-atmosphere interaction on regional scales (Franz et al. 2017). It is unclear whether aqueous S cycling might contribute to these large isotope fractionations and how aqueous systems respond to S heterogeneity of the volcanic reservoir. To better understand S isotope fractionations and SO_4 cycling in volcanic systems, we selected a watershed of Valles Caldera in New Mexico USA as Martian geochemical-hydrological analog. Using isotope compositions of various S forms present in the surface water, groundwater, precipitation, bedrock and hydrothermal gas, we define sources and transport of dissolved SO_4 by the current Valles hydrologic system.

Magmatic sources are major S contributors into the Valles Caldera aqueous systems (streams, shallow groundwater), occurring through steam-dominated H_2S degassing with $\delta^{34}\text{S}$ values of $+0.9 \pm 3\%$. However, subsurface hydrothermal processes have resulted in more negative $\delta^{34}\text{S}$ values in sulfide minerals (-14 to -4 ‰). Two major aqueous SO_4 sources are oxidation of H_2S from modern hydrothermal gas emission, and oxidation and dissolution of sulfide and sulfate minerals in hydrothermally altered bedrock and crater-lake sediments. Minor SO_4 contributions with positive $\delta^{34}\text{S}$ values (+9 to +14‰) come from deeply circulating geothermal fluids and negligible amounts from atmospheric deposition with $\delta^{34}\text{S}$ of +5 to +7‰ (e.g., snow). The aqueous SO_4 inputs are mainly controlled by dissolution/oxidation of the volcanic bedrock and localized surface H_2S gas emission. Because most intracaldera bedrock is S-depleted, so are the younger sedimentary lake deposits and surface aquatic system.

We infer that measured $\delta^{34}\text{S}$ (-47 to +28‰) in Gale crater sediments can be explained by the presence of magmatic-hydrothermal sulfide/sulfate minerals in the igneous protolith of Gale sediments with large range of $\delta^{34}\text{S}$. Later aqueous processes involved oxidation and dissolution of S minerals initially present in this igneous material and led to subsequent formation of diagenetic fluids and alteration products enriched in SO_4 with relatively large $\delta^{34}\text{S}$ variation.