Understanding the mechanism of sulfate formation via metal catalyzers on Mars using Iceland as a terrestrial analog

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High concentrations of sulfate minerals have been identified on the martian surface. However, the oxidation mechanism of volcanic sulfur (H_2S/SO_2) remains unclear given that Mars has likely never had an O_2-rich atmosphere. Metal reduction provides one mechanism by which oxidation of sulfides can occur in terrestrial aqueous environments. During this process, metals such as ferric iron act as electron acceptors. The resulting sulfate (SO_4) has low $\delta^{18}O$, similar to that of the surrounding water ($\delta^{18}O < -5$ ‰;). Conversely, SO_4 formed by atmospheric O_2 oxidation has more positive $\delta^{18}O$ due to the high $\delta^{18}O$ of atmospheric O_2 ($\delta^{18}O$ +23.5 ‰). While sulfide (pyrite) mineral oxidation by iron has been well constrained, little is known whether this process is important during oxidation of hydrothermal H_2S.

In 2016, we sampled four acidic hydrothermal systems in Iceland which had varied dissolved O_2 (0.6 to 1.83 mg/L) and dissolved iron (0 to 1253 mg/L) contents. ~38% of the studied hydrothermal springs showed evidence of oxidation by metals. In these springs, the $\delta^{18}O$ difference between SO_4 and H_2O ($\Delta^{18}O$) was within the range of 0 to 4 ‰ typical for O isotope fractionation during pyrite oxidation by iron reduction. However, ~31 % of the springs showed more positive $\Delta^{18}O$ (5.6 to 9.4 ‰), suggesting varied contributions of SO_4 formed via atmospheric O_2 oxidation and metal reduction. Interestingly, ~31 % of the springs showed more negative $\Delta^{18}O$ (-0.7 to -2.1 ‰), suggesting additional processes controlling O isotope fractionations in the studied system. These include water evaporation, mixing of spring waters during rain events, and/or distinctive O isotope fractionation during H_2S oxidation to SO_4. To better understand the process of SO_4 formation, we will determine O isotope fractionations using laboratory experiments under controlled O_2/metal contents and elevated temperature.

Collectively, the results of this study provide an alternative mechanism by which SO_4 can form in both terrestrial and Martian hydrothermal environments. Metal catalyzers are likely an important oxidation pathway for H_2S gas oxidation to SO_4.