

ICELANDIC HOT SPRINGS AND MUDPOTS AS AN ANALOG FOR SULFATE FORMATION ON MARS: J. J. Ende¹ (jende@vols.utk.edu), A. Szynkiewicz¹ and A. Faiia¹, ¹Earth & Planetary Sciences, University of Tennessee, 1412 Circle Drive, Knoxville, TN 37996.

Introduction: Mars likely never had an oxygen-rich atmosphere, thus, the abundance of sulfate (SO_4^{2-}) on the Martian surface poses a major question: what mechanisms facilitated reduced sulfur oxidation in the anoxic Martian environment? The surface of Mars has been mainly shaped by volcanism and impact cratering. Volcanic gas emission on Mars has been proposed to be rich in reduced sulfur (e.g., H_2S , SO_2). Conversely, sedimentary and fluvial processes appear to have a smaller imprint on the Martian surface. Therefore, it is likely that sulfate is linked to hydrothermal activity associated with volcanism or the formation of impact craters [2, 3, 4] rather than fluvial processes.

Earth analogs provide a unique opportunity to better characterize and quantify the mechanism of reduced sulfur (S) oxidation to SO_4^{2-} in hydrothermal systems as a way to better understand oxidation on oxygen-depleted planets such as Mars. One previous study in Valles Caldera, New Mexico [5] indicates that the majority of hydrogen sulfide (H_2S) from modern hydrothermal emissions is oxidized to SO_4^{2-} by water oxygen (O) rather than atmospheric oxygen (O_2).

This report addresses the initial results from a field campaign in Iceland. The goal of this study is to elucidate the mechanisms that facilitate oxidation of reduced sulfur in hydrothermal system using sulfate concentrations [SO_4^{2-}] and $\delta^{18}\text{O-SO}_4$.

Oxygen Isotopes as Tracers: O isotope composition ($\delta^{18}\text{O}$) of sulfate can be used to determine oxidation mechanisms and major sources of oxygen during the formation of aqueous SO_4^{2-} in hydrothermal systems. This is due to the significant difference of the isotopic ratio between water and atmospheric O_2 . Water oxygen has a $\delta^{18}\text{O}$ range of approximately -50 to 0 ‰ and atmospheric O_2 has a $\delta^{18}\text{O}$ of around + 23.5 ‰ [6]. While there is some O isotopic fractionation during oxidation of H_2S , we can assume that the O isotopic ratio of SO_4^{2-} will be similar to the isotopic ratio in the source of O, particularly when formed at high temperatures. Generally, SO_4^{2-} formed from O_2 should have more positive $\delta^{18}\text{O}$ than SO_4^{2-} utilizing O from water.

Field Sampling and Laboratory Methods: Initial fieldwork was conducted in Iceland and included sampling of 13 acidic hot springs and 11 acidic mud pots during the summer of 2016. A Thermo Scientific™ Dionex™ ion chromatography (IC) system was brought to the field to conduct in-situ anion measurements because reduced S species can oxidize quickly in the presence of O_2 . A YSI 556 Multi Probe System

(MPS) was used to take in-situ measurements of temperature, pH, and dissolved oxygen (DO). Total dissolved iron concentrations [Fe] were measured using a Hach colorimeter. O isotope analyses were measured using a Thermo Scientific™ Delta Plus Isotope Ratio Mass Spectrometer and a Thermo Finnigan™ TC/EA

Statistical Methods: Linear regression analyses were conducted using the *Data Analysis* package in Excel. Only those correlation coefficients with ‘Significance F’ values less than 0.05 (confidence interval of 95 %) are considered statistically significant.

Initial Results: Both mud pots and hot springs showed statistically significant relationships for pH and [Fe] versus $[\text{SO}_4^{2-}]$. pH had a negative correlation with $[\text{SO}_4^{2-}]$ (Fig. 1), while [Fe] had a positive correlation with $[\text{SO}_4^{2-}]$ (Fig. 2). Although temperature did not have a statistically significant relationship to $[\text{SO}_4^{2-}]$ for either mud pots or hot springs, there was a statistically significant positive correlation between temperature and $\delta^{18}\text{O-SO}_4$ values in hot springs (Fig. 3). This same trend was seen for [Fe] for hot springs, but with a negative correlation (Fig. 4).

Discussion: The initial results of this study suggest that in the acidic hydrothermal systems of Iceland, with elevated emission of H_2S , pH and [Fe] are two major influencing parameters in affecting $[\text{SO}_4^{2-}]$ in both mud pots and hot springs. Negative correlations between pH and $[\text{SO}_4^{2-}]$ are expected as the oxidation of reduced sulfur species produces sulfuric acid, thus, the increases in $[\text{SO}_4^{2-}]$ are often associated with low pH values.

As temperature increases, evaporation causes preferential loss of lighter oxygen isotopes, leaving the remain water depleted in ^{16}O isotopes and thus causing more positive $\delta^{18}\text{O}$ values. Therefore, it is not surprising to see such a positive correlation between temperature and $\delta^{18}\text{O-SO}_4$ for hot springs. However, other factors may influence $\delta^{18}\text{O-SO}_4$ such as O isotope fractionation during SO_4 formation and/or O isotope exchange between SO_4 and water. This causes $\delta^{18}\text{O-SO}_4$ values to reflect additional isotope fractionations rather than the initial $\delta^{18}\text{O}$ of oxygen source.

As Fe^{3+} is known to facilitate oxidation of sulfide in aquatic systems by its reduction to Fe^{2+} [6], negative correlations between $\delta^{18}\text{O-SO}_4$ and [Fe] support the concept that metals may serve as a catalyst in the oxidation of reduced sulfur species in hydrothermal settings. This notion is supported by the data as increases in $[\text{SO}_4^{2-}]$ and negative $\delta^{18}\text{O-SO}_4$ values (as low as -8 ‰ and -4 ‰) were associated with the highest concen-

trations of [Fe] (Figs. 2 and 3). This, in turn, is in agreement with oxidation of H_2S to SO_4^{2-} by Fe^{3+} reduction, which involves incorporation of water oxygen into SO_4^{2-} molecule. The latter has been commonly observed for pyrite oxidation in terrestrial systems [7]. These results indicate that oxidation of reduced S species (e.g., H_2S) may be facilitated by the presence of [Fe] which leads to low $\delta^{18}\text{O-SO}_4$ values. For more robust quantitative analyzes, additional sampling would be required.

Conclusion: The results of this study support the conception that oxidation of H_2S in hydrothermal systems may be facilitated by the presence of dissolved Fe and involves incorporation of water O with low $\delta^{18}\text{O}$ into the SO_4^{2-} molecule. Without O to serve as an electron acceptor, it is possible that Fe^{3+} may facilitate oxidation. Given the basaltic mineralogy and the abundance of Fe^{3+} on Mars [8], it is possible that sulfate formation on Mars took place in hydrothermal systems with low pH and rich in dissolved ferric iron.

References: [1] Sigurdsson, H. et al. (2000) *Encyc. of Volcanoes*. [2] Chojnacki M. and Hynek B. M. (2008) *J. Geophys. Res.* 113, E12005. [3] Bishop J. L. et al. (2009) *J. Geophys. Res.* 114, E00D09. [4] Abramov O. and Kring D. A. (2005) *J. Geophys. Res.* 110, E12S09. [5] Szynkiewicz A. et al. (2015) 46 LPSC, Abstract #1303. [6] Kroopnick P. and Craig H. (1972) *Science*, 175, 54-55. [7] Taylor B. E. et al. (1984) *Nature*, 308 (5959), 538-41. [8] Poulet F. et al. (2007) *J. Geophys. Res.* 112, E08S02.

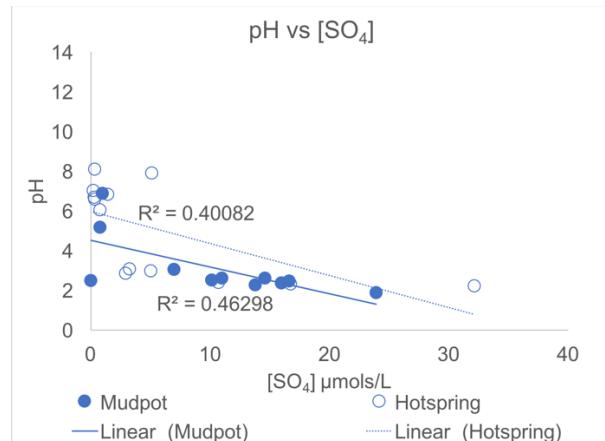


Figure 1: Graph of pH vs $[\text{SO}_4]$. Mud pots in closed circles, hot springs in open circles. Dashed line linear regression for hot springs, solid line for mud pots.

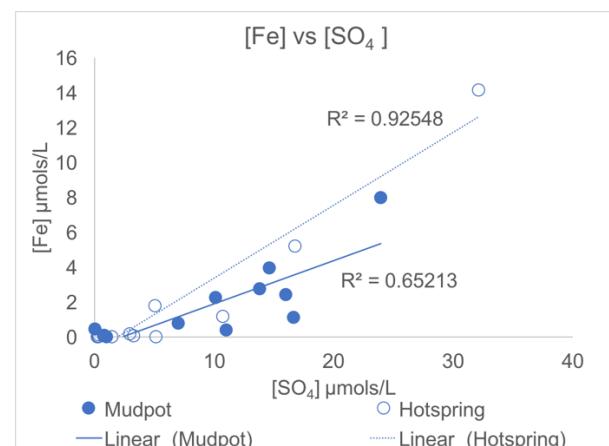


Figure 2: Graph of $[\text{Fe}]$ vs $[\text{SO}_4]$. Mud pots in closed circles, hot springs in open circles. Dashed line linear regression for hot springs, solid line for mud pots.

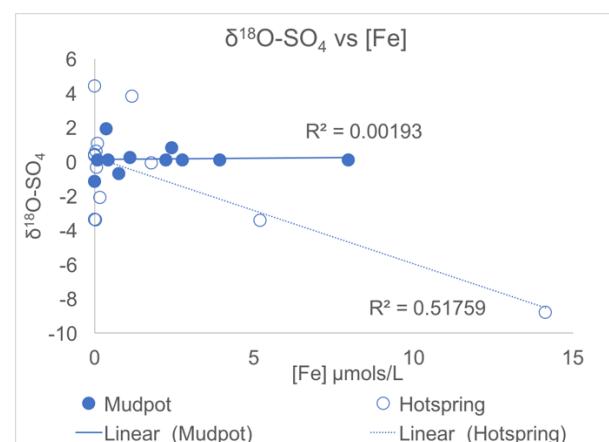


Figure 3: Graph $\delta^{18}\text{O-SO}_4$ vs Temperature. Mud pots in closed circles, hot springs in open circles. Dashed line linear regression for hot springs, solid line for mud pots.

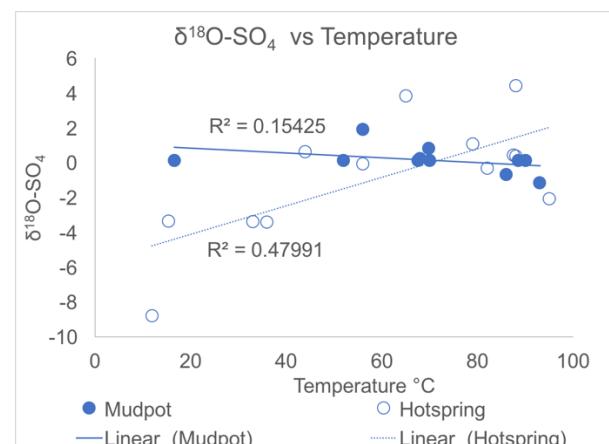


Figure 4: Graph $\delta^{18}\text{O-SO}_4$ vs Temperature. Mud pots in closed circles, hot springs in open circles. Dashed line linear regression for hot springs, solid line for mud pots.