UNDERSTANDING THE MECHANISMS OF SULFATE FORMATION IN ACIDIC VOLCANIC ENVIRONMENTS ON MARS USING TERRESTRIAL ANALOGS. J.J. Ende, A.M. Faiia, P. Burtt, R. Moore, and A. Szynkiewicz, University of Tennessee, Knoxville (1621 Cumberland Ave. 602 Strong Hall, Knoxville, TN, 37916)

Introduction: High accumulations of sulfate (SO$_4^{2-}$) minerals have been identified on the Martian surface in a variety of geologic settings, most of which were formed during the Noachian and Hesperian periods (3.7 to 3.2 Ga) when wet conditions were prevalent [1]. Additionally, sulfide minerals and amorphous sulfur (S) were measured in situ by rovers [2]. Generally, the high SO$_4^{2-}$ enrichment indicates that basaltic weathering alone is not sufficient to accumulate the observed volume of S [3]. While volcanically-derived reduced S (e.g., H$_2$S, SO$_2$) is likely a primary source, the process by which SO$_4^{2-}$ was formed is unclear. As such, it is crucial to better characterize the oxidation mechanism(s) by which SO$_4^{2-}$ could have been formed on Mars.

Metals are known to facilitate oxidation of sulfide minerals in anoxic environments (e.g. acid mine drainage systems). Ferric iron (Fe$^{3+}$) can oxidize pyrite (FeS$_2$) to SO$_4^{2-}$ by its reduction to ferrous iron (Fe$^{2+}$) [4, 5]. Under acidic conditions, metals are soluble in water, thus are available for redox-driven oxidation reactions in aqueous environment. Given the abundance of various metals (e.g., iron, nickel, manganese) and evidence for acidic hydrothermal conditions on the Martian surface [6, 7], it is possible that they may have participated in the oxidation of reduced S from volcanic emission in the past. However, this process has not been considered for Mars due to limited knowledge in terrestrial hydrothermal systems. Therefore, the goal of this project is to determine if Fe-driven oxidation is a viable pathway for H$_2$S oxidation to SO$_4^{2-}$ in acidic volcanic hydrothermal systems on Earth and evaluate whether this process might have occurred on Mars.

Oxygen Isotope Tracers: Field and experimental studies have shown that oxygen isotopes ($\delta^{18}$O) can be used to determine the mechanisms of FeS$_2$ oxidation to SO$_4^{2-}$ because of a large difference in $\delta^{18}$O between atmospheric O$_2$ (+23.5 ‰) and water oxygen [-<0 ‰; e.g., 8]. In this study, we analyzed the $\delta^{18}$O of SO$_4^{2-}$ forming in acidic hot springs and mud pots due to surface oxidation of H$_2$S from modern hydrothermal emission. Four different geographic locations were sampled in Iceland, Lassen, Valles Caldera, and Yellowstone. Additionally, chemical analyses of metals and dissolved O$_2$ concentrations are used to characterize availability of main oxidants (e.g., Fe, atmospheric O$_2$) in the studied hydrothermal sites.

Results and Discussion: Generally, there was no clear relationship between dissolved O$_2$ (DO) and SO$_4^{2-}$ concentrations. Also, the measured DO concentrations were relatively low <2 mg/L, mainly due to higher temperatures of the studied hydrothermal features (50-65°C and 70-95°C, respectively). Given low solubility of O$_2$ in higher temperatures, the investigated hot springs and mud pots show a small potential for H$_2$S to be directly oxidized to SO$_4^{2-}$ via atmospheric O$_2$ in the studied field sites.

The measured $\delta^{18}$O of dissolved SO$_4^{2-}$ and water showed distinctive ranges in the individual sampling sites (Fig. 1). Generally, higher $\delta^{18}$O of SO$_4^{2-}$ corresponded to higher $\delta^{18}$O of water (Fig 1). However, there was larger variability in $\delta^{18}$O of SO$_4^{2-}$ compared to a smaller range of isotope fractionations (0-4‰) previously determined for Fe-driven oxidation [9]. Figure 1 illustrates that only 43% of the studied water samples fall within the range of Fe-driven oxidation. Conversely, of the other water samples 43% were above and 15% below that range suggesting additional processes that may control the $\delta^{18}$O of SO$_4^{2-}$. We infer that evaporation due to elevated temperatures of hydrothermal gases and water-rock interaction likely increase the $\delta^{18}$O of water after formation of SO$_4^{2-}$ (Process 2 on Fig. 1), leading to a shift to the right from the Fe-driven oxidation field. In contrast, inflow of new groundwater and/or meteoric precipitation decrease the $\delta^{18}$O of water, causing the

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{Variation of $\delta^{18}$O of SO$_4^{2-}$ vs. $\delta^{18}$O of water in the studied hot springs, mud pots, and ephemeral streams. Gray shaded area represent 0 to 4 ‰ fractionation between SO$_4^{2-}$ and water for Fe-driven oxidation of H$_2$S. Iceland samples are in black circles (open circles are ephemeral streams), Lassen in red squares, Valles Caldera in green diamonds, and Yellowstone in yellow triangles. Inset in top left shows two processes that affect $\delta^{18}$O of water: Process 1 – inflow of groundwater and/or precipitation, Process 2 – evaporation and/or water-rock interaction.}
\end{figure}
shift to the left from the Fe-driven oxidation field (Process 1 on Fig. 1).

Of the metals analyzed only Fe, Al, Mn, V, and Zn were found in elevated concentrations both in the water column and sediments. Fe and Al had by far the highest concentrations in the water column (1,539 mg/L and 3,330 mg/L, respectively) and sediment (374,217 mg/kg and 271,050 mg/kg, respectively) compared to lower concentrations of Mn (<36 mg/L and <75,474 mg/kg), Zn (<20 mg/L), and V (<4 mg/L). Generally, the increases of total Fe concentrations were accompanied by increases of SO₄ concentrations suggesting that enough Fe is available for oxidation of H₂S to SO₄²⁻.

Acidic conditions created by hydrothermal activity would mainly release Fe³⁺ from the bedrock material because this is most common form of Fe in volcanic rocks. Using field observations, we infer that diurnal and seasonal changes in water availability lead to distinctive dry and wet cycles in the studied field sites. Under dry conditions, hydrothermal gases (e.g., H₂O, CO₂, H₂S) are emitted as fumaroles, thus leaving sediment beds of shallow hot springs, mud pots and ephemeral streams directly exposed to air. While most of emitted H₂S is dispersed in the atmosphere and transported away, Fe³⁺ released from bedrock weathering is likely undergoing oxidation to Fe⁴⁺ in the sediment beds upon exposure to atmospheric O₂. As meteoric precipitation or groundwater inflow increase due to changing hydrological conditions (e.g., rain fall), dry hydrothermal features readily transition to the wet cycle, which might enhance oxidation of H₂S to SO₄²⁻ by newly formed Fe⁴⁺. During our sampling, the concentrations of Fe²⁺ were significantly higher than Fe³⁺. Therefore, it is likely that oxidation of H₂S was already limited due to depletion in Fe⁴⁺.

Generally, without the dry cycle it would be difficult to oxidize Fe²⁺ to Fe⁴⁺ in the absence of other oxidants in water. Note that the DO concentrations were low (<2 mg/L) in the elevated temperatures of the studied hydrothermal systems (50 to 90°C) during our sampling. Therefore, we recognize that the transitioning between dry and wet cycles is crucial for Fe-driven oxidation of H₂S in acidic hydrothermal systems with elevated temperatures.

Implications for Mars: Collectively, the δ¹⁸O of SO₄²⁻ and water in conjunction with the measured low DO concentrations and high concentrations of metals (Fe), suggest that Fe-driven oxidation is likely common pathway for H₂S oxidation to SO₄²⁻ in all of the studied field sites. The episodic nature of hydrothermal water cycle observed in our analog sites shows many similarities to that speculated for Mars, but over much shorter time scales. One unifying feature among different climate models, is the episodic nature of water on the surface of Mars. Some studies argue that early in Martian history, conditions were favorable for oceans and lakes to be formed under long term, warm and wet conditions, even if only intermittently [e.g., 10; 11; 12]. While other models suggest that any liquid water related feature is merely a result of spatial and temporal distribution of thermal energy across the planet, thus hydrological features are localized to regions in which the temperatures allow for melting of ice [e.g., 13, 14]. Nonetheless, throughout its history Mars has experienced both periods of wet and dry conditions.

Our terrestrial results show that alternation between the wet and dry cycle is important process to oxidize hydrothermal H₂S to SO₄²⁻ in volcanic settings depleted in O₂ due to elevated temperatures. This cycling is crucial to reoxidize metals such as Fe during the fumarolic dry cycle which then facilitate H₂S oxidation to SO₄²⁻ during the wet cycle. Oxidation of H₂S to SO₄²⁻ by Fe-driven oxidation has been shown to be significantly faster than by atmospheric O₂ [5], thus explains elevated SO₄²⁻ in the studied field sites. Although Mars likely never had O₂-rich atmosphere as on Earth, H₂O₂ or photochemical processes are both possible alternative oxidants for metals such as Fe [15, 16]. On Mars, Fe is commonly found in association with SO₄²⁻-bearing minerals. While previous studies have linked this relationship to diagenesis [17, 18], we suggest that concomitant Fe and SO₄²⁻ may be to some extent a result of H₂S oxidation to SO₄²⁻ via Fe-driven oxidation in the hydrothermal setting and/or low-temperature oxidation of sulfide mineralization.


Acknowledgements: This study is supported by NASA grant no. 80NSSC17K0727.