UNDERSTANDING MECHANISMS OF SULFATE FORMATION ON MARS: EXPERIMENTAL STUDY ON THE OXIDATION OF H₂S UNDER LABORATORY CONDITIONS. J. J. Ende\textsuperscript{1} (jende@vols.utk.edu) and A. Szynkiewicz\textsuperscript{1, 2} Earth & Planetary Sciences, University of Tennessee, 1412 Circle Drive, Knoxville, TN 37996

Introduction: The sulfur (S) cycle is important in many geological processes on Mars [1]. Many competing hypotheses have been proposed including formation of sulfate via volcanic S-rich emissions and ice-rock interaction [2,3,4], hydrothermal activity [5,6], deep groundwater discharge [7,8], and/or sulfide weathering [9,10,11,12,13]. Although the sulfate-rich minerals on Mars provide evidence of water activity, many of the key processes involved in oxidation of reduced volcanic S to sulfate (SO₄) remain unclear. For example, we are uncertain about oxidation mechanisms under oxygen-limited conditions on Mars. To address this problem, we have been studying major processes controlling oxidation of H₂S gas under oxygen-limited conditions.

Rationale: Our initial oxygen isotope results from a terrestrial volcano of Valles Caldera, New Mexico show that in surface aqueous environments majority of H₂S from modern hydrothermal emission is oxidized to SO₄ by water oxygen rather than atmospheric oxygen (O₂) [14]. This is inferred from negative δ¹⁸O values of SO₄ (-5 to -3 ‰; Fig. 1) in hot springs which were similar to negative δ¹⁸O of ambient water (-9 to -8 ‰). In case of higher contributions of atmospheric O₂, higher δ¹⁸O of SO₄ (> +5 to +10 ‰) would be apparent. Given that elevated concentrations of O₂ were present in the springs and surface water (9-11 mg/L), it is unclear what environmental factors (pH, temperature, volcanic emission rates, metal catalysts, microbial activity, etc.) are responsible for small contributions of atmospheric O₂ during SO₄ formation in Valles Caldera.

Because it is likely that Mars never had an O₂-rich atmosphere, further quantifying the oxidation of reduced sulfur via water oxygen may provide important insight regarding plausible oxidation pathways of volcanic S-rich gases in Martian surface environments.

Methods: In order to simulate H₂S oxidation under laboratory conditions, pyrite was hand-ground in an agate mortar. A chromium chloride solution was reacted with 148.1 mg of pyrite to form H₂S gas. Afterward, this H₂S gas was bubbled through deionized water with a low oxygen (DO) content of 1.28 mg/L and neutral pH of ~7. The experimental setup simulated an open system where H₂S gas was leaving the reaction flask after bubbling through the deionized water.

Initial Results: The initial results suggest that under low oxygen content in water the H₂S oxidation was limited, with only 0.125 µg of H₂S-sulfur oxidizing to SO₄. Since the reaction time of H₂S with water was relatively short (~4 hours), in the next step we will increase the time and the amount of H₂S reacting with deionized water. This will allow for better characterization of physical conditions necessary for efficient oxidation of H₂S to SO₄ in aqueous systems. Additionally, we will add the Valles Caldera bedrock regolith to the reaction chamber with bubbling H₂S to investigate the plausible roles of metal catalysts (e.g., Fe) and microbes in H₂S oxidation to SO₄.

![Graph showing variations of δ³⁴S and δ¹⁸O of stream SO₄ in the Valles Caldera watershed. Negative δ¹⁸O values of SO₄ have been observed in Sulphur Springs with highest hydrothermal H₂S emission.](image-url)

**Figure 1.** Variations of δ³⁴S and δ¹⁸O of stream SO₄ in the Valles Caldera watershed. Negative δ¹⁸O values of SO₄ have been observed in Sulphur Springs with highest hydrothermal H₂S emission.