

AQUEOUS SULFUR BUDGET AND OXIDATION OF FUMAROLIC H₂S IN THE VOLCANIC COMPLEX OF VALLES CALDERA, NEW MEXICO – GEOCHEMICAL IMPLICATIONS FOR MARS.

A. Szyrkiewicz¹, F. Goff², A. M. Faiia¹, D. T. Vaniman³, T. Subia⁴, D. Sanchez⁴, J. Coleman¹, M. J. Pribil⁵: ¹Earth & Planetary Sciences, University of Tennessee, 1412 Circle Drive, Knoxville, TN 37996 (aszynkie@utk.edu), ²University of New Mexico, Albuquerque, NM 87131, ³Planetary Science Institute, 1700 East Fort Lowell, Tucson, AZ 85719, ⁴Geological Sciences, University of Texas at El Paso, 500 W. University Ave., El Paso, TX 79968, ⁵United States Geological Survey, P.O. Box 25046, Mail Stop 973, Denver, CO 80225.

Introduction: The sulfur (S) cycle is important in many geological processes on Mars [1]. Volcanic degassing, hydrothermal circulation, groundwater recharge, ephemeral surface flows, evaporation and polar weathering are all believed to play significant and unique roles in depositing the sulfate-rich minerals present on the surface of Mars [2,3,4,5]. Despite the fact that the sulfate-rich minerals on Mars provide key evidence of past fluid movement, chemistry, and potential habitability, many of the key processes controlling the hydrological S cycle on Mars remain unclear. For example, we are uncertain about the relative influence of volcanic S emissions, aqueous chemical weathering, and climate conditions on the S cycle, and we poorly understand the hydrological environment that transported S on or to the Martian surface. To address the research problems discussed above, we have been studying the modern hydrological S cycle related to volcanic S emission and aqueous chemical weathering of the large terrestrial volcanic system of Valles Caldera, New Mexico.

Analogue Setting: The 22 km-wide Valles Caldera of northern New Mexico (USA) has hosted volcanic and geothermal activity since the last caldera-forming eruption at 1.25 Ma (Fig. 1). The presence of active H₂S-rich fumaroles [6], volcanic sulfide-rich mineralization up to 3.4% in some locations [7], the high elevation (2,600 to 3,400 m asl), snow cover during the winter, low annual temperatures (average ~8°C), and numerous streams and ancient intracaldera lakes, make the Valles Caldera an excellent geochemical analogue for Mars. Furthermore, the availability of well-preserved and age-constrained core sediments of a mid-Pleistocene intracaldera caldera lake [8] make this site ideal for quantifying the relative contributions of S/SO₄²⁻ from volcanogenic and bedrock sources and for evaluation of S preservation in the sedimentary record.

Field/Lab Methods: The amount of SO₄ transported in the surface hydrological system can be determined by calculating the SO₄ flux. The stream SO₄ flux is determined by multiplying the stream-water SO₄ concentrations by the volumetric flow rates. This flux corresponds to the mass of dissolved SO₄

ions that flow out of the caldera per unit time (e.g., kg SO₄ per day).

The S isotope composition ($\delta^{34}\text{S}$) of SO₄ can be used to distinguish S sources in aqueous environments. Additionally, the O isotope composition ($\delta^{18}\text{O}$) of SO₄ can be used to understand oxidation pathways of volcanic H₂S to SO₄ and contributions of atmospheric O₂.

Aqueous Sulfur Budget in Valles Caldera:

According to the measured SO₄ fluxes, our initial results imply three major SO₄ sources in the studied aqueous volcanic system of Valles Caldera:

- 1) chemical weathering (e.g. oxidation/dissolution of hydrothermal S-rich minerals) contributing 71-86 % of SO₄;
- 2) snowmelt contributing 9-16 % of SO₄;
- 3) hydrothermal gas emission (oxidation of fumarolic H₂S in surface environments) contributing 5-13 % of SO₄.

Accumulation of Hydrothermal S-rich Gases in Snow:

In order to understand the role of atmospheric SO₄ deposition from hydrothermal S-rich emissions, we collected several snow samples from fumarole-active and non-active sites in Valles Caldera. Generally, the concentrations of SO₄ in snow samples collected in close proximity (a few meters) to the active fumaroles with H₂S emission appeared to be slightly lower (~0.66 mg/L) when compared to other locations showing no surface evidence of fumarole exhalation (~0.94 mg/L). Considerably higher $\delta^{34}\text{S}$ of SO₄ were observed in the snow samples (+5.6 to +7.8‰) when compared to the hydrothermal H₂S emission of Valles Caldera (+0.8 to +3.4‰). This suggests that most of the SO₄ in the snow was sourced by non-hydrothermal sources such as dissolution of dust particles and anthropogenic pollution (+6 to +7‰). This lack of significant deposition of hydrothermal S in snow most likely resulted from quick dispersion of S-rich gases in the atmosphere.

Oxidation of hydrothermal H₂S to SO₄: The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of stream SO₄ showed greater variation in the Sulphur Creek catchment, which has active fumaroles and elevated emission of hydrothermal H₂S into stream

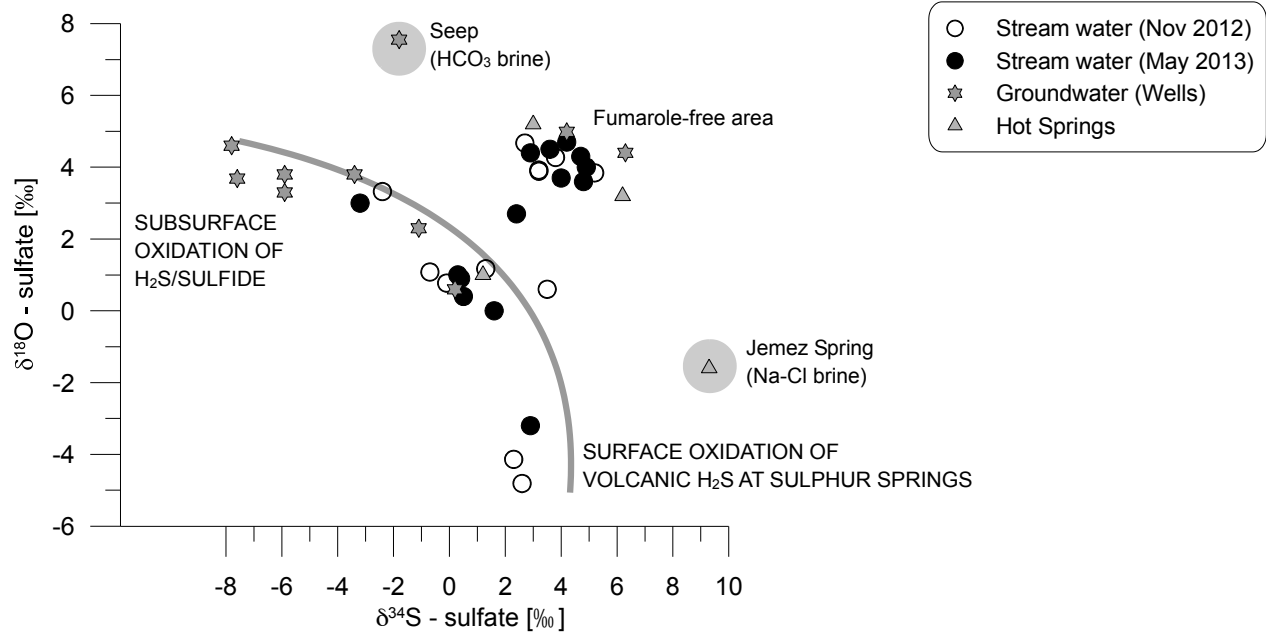


Figure 1. Variations of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of stream SO_4 in the Valles Caldera watershed.

water (-8 to +3 ‰ and -5 to +5 ‰, respectively). Other catchments with no H_2S emission had less variation in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ (+4 to +6 ‰ and +3 to +5 ‰, respectively) (Fig. 1). The low $\delta^{18}\text{O}$ of SO_4 at Sulphur Springs (-5 to -3 ‰) is indicative of prevailing oxidation of H_2S to SO_4 with water oxygen (-9 ‰) rather than atmospheric O_2 (+23 ‰). In terrestrial systems, this type of oxidation is usually microbially mediated.

Implications for Mars: Our initial results imply that chemical weathering (oxidation of pre-existing hydrothermal sulfide minerals, and dissolution of sulfate minerals in various rock formations) is a much greater contributor to the sulfur flux (71-86%) than the smaller and localized oxidation of H_2S from fumarolic emissions (5-13%). Additionally, atmospheric deposition of SO_4 from fumarolic emissions in the snow cover appears to be negligible compared to the SO_4 dissolved in the stream network draining Valles Caldera. This contrasts with the suggestion of S-rich volcanic emissions as a major source explaining sulfate enrichment of the Martian surface [5, 10]. Conversely, our results are more in accord with studies suggesting subsequent aqueous processes and a significant role of chemical weathering of bedrock minerals in the S cycle on Mars [4, 9, 11].

In hydrothermal sites of Valles Caldera (e.g., Sulphur Springs catchment), the oxygen in SO_4 originating from oxidation of hydrothermal H_2S gas appears to be sourced by water oxygen. Although

atmospheric O_2 is present, it does not appear to significantly contribute to H_2S oxidation. Given that Mars probably never had an O_2 -rich atmosphere, this finding may provide important insight regarding plausible oxidation pathways of S gases in Martian surface environments.

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