

HYDROLOGICAL SULFUR CYCLING IN THE VOLCANIC COMPLEX OF VALLES CALDERA, NEW MEXICO – GEOCHEMICAL IMPLICATIONS FOR MARS. A. Szykiewicz¹, D. T. Vaniman², F. Goff³, T. Subia⁴, D. Sanchez⁴, A. M. Faiia¹, J. Coleman¹: ¹Earth & Planetary Sciences, University of Tennessee, 1412 Circle Drive, Knoxville, TN 37996 (aszynkie@utk.edu), ²Planetary Science Institute, 1700 East Fort Lowell, Tucson, AZ 85719, ³University of New Mexico, Albuquerque, NM 87131, ⁴Geological Sciences, University of Texas at El Paso, 500 W. University Ave., El Paso, TX 79968.

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 and past 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% [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 SO₄ flux. This flux corresponds to the mass of dissolved SO₄ ions that flows through a unit area per unit time (e.g., kg SO₄ per day). The stream SO₄ flux is determined by multiplying the stream-water SO₄ concentrations (in mg/L) by the volumetric flow rates (in L/s). A standard current meter (FP101-FP201 Global Flow Probe) is used to determine the average water velocity across

cross-sections of major streams in the Valles Caldera. The measured flow rates (discharge in L/s) are computed by multiplying the surface area of water in a channel cross section by the average velocity of the water in that cross section. A Dionex IC is used to determine SO₄ concentrations.

Results: Aqueous SO₄ fluxes of the Valles Caldera streams showed similar patterns both in November 2012 and May 2013 (Fig. 1). Significantly higher SO₄ fluxes (~5,000-8,000 kg/month) were always observed for the San Antonio drainage system (SO₄ concentrations of 2-11 mg/L) compared to lower fluxes in the East Fork Jemez drainage (~1,000-2,000 kg/month and SO₄ concentrations of 2-8 mg/L). The San Antonio drainage has more abundant hydrothermal S-rich alteration of bedrock (sulfide/sulfate minerals; up to 3 wt. %) and active volcanic H₂S emission than the East Fork Jemez drainage with less S mineralization and absence of fumarole activity.

Despite the high SO₄ concentrations (up to 1,360 mg/L) in Sulphur Creek, a major stream draining the Sulphur Springs area with elevated H₂S volcanic emission (Fig. 1), in both investigated seasons the SO₄ fluxes were significantly lower (5-13% of the total SO₄ flux in the Valles Caldera watershed) compared to the San Antonio and East Fork Jemez streams (87-95%). This is mainly due to quick dilution of volcanic H₂S gas in the atmosphere and less water available for hydrological SO₄ transport on higher elevations with active volcanic fumaroles. Overall, the SO₄ fluxes appeared to be always correlated with the stream discharges (e.g., amount of water available for hydrological transport) and poorly correlated with SO₄ concentration. Therefore, we infer that the large surface area of snow/rain-rock interaction during chemical weathering enhances leaching of S weathering products from oxidation/dissolution of S-bearing minerals and, thus, increases SO₄ fluxes into the hydrological system.

In order to understand the role of atmospheric SO₄ deposition from volcanic S-rich emissions, in March 2014 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 S emission appeared to be slightly smaller (~0.66 mg/L) compared to other

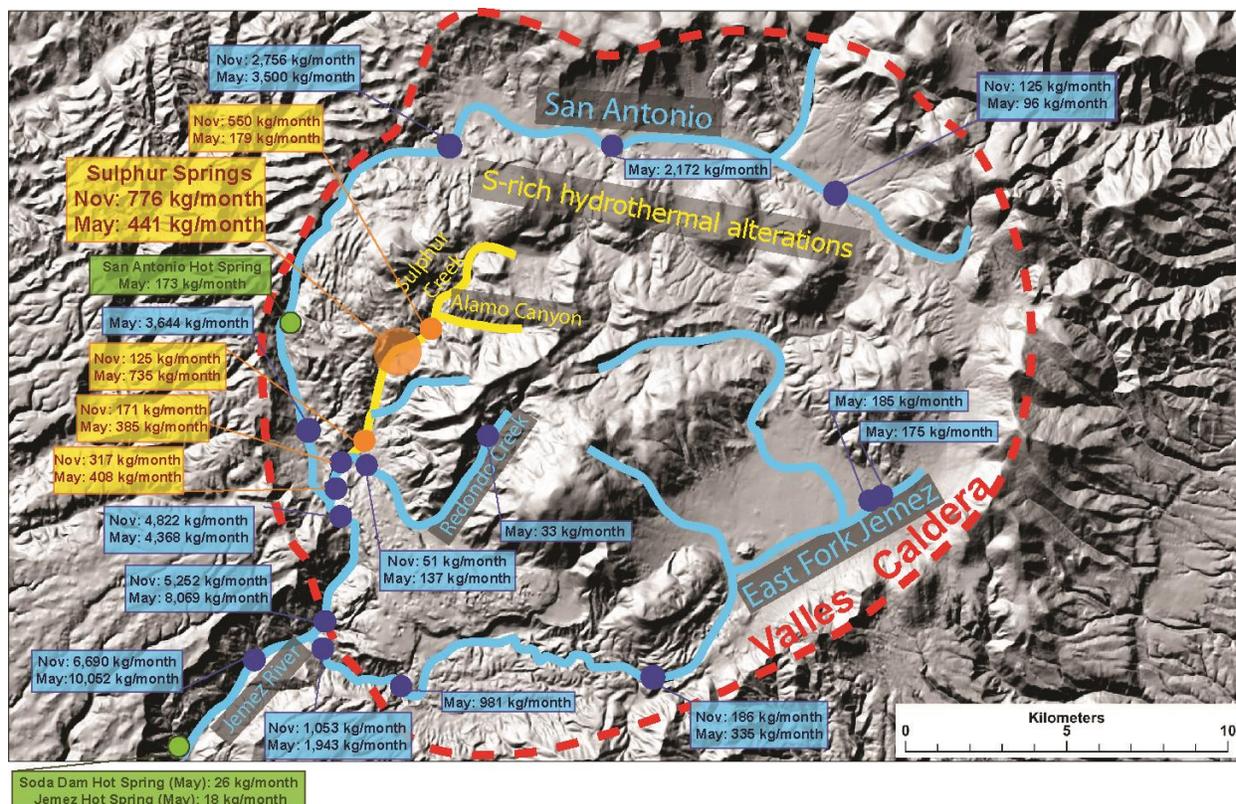


Figure 1. Location of major sampling points and the measured SO_4 fluxes (kg/month) in Nov 2012 and May 2013 on a Digital Elevation Model of Valles Caldera (Courtesy of Los Alamos National Laboratory). Orange and blue dots indicate the stream locations showing low water pH (2 to 5) and high water pH (6 to 8), respectively. Green dots indicate the hot springs with higher discharges to the Valles Caldera streams.

locations showing no surface evidence of fumarole exhalation (~ 0.94 mg/L). Most likely, the observed small deposition of volcanic S in the snow resulted from quick dispersion of volcanic S-rich gases in the atmosphere.

Conclusions: Our initial results imply that chemical weathering (oxidation of pre-existing hydrothermal sulfide minerals, and dissolution of sulfate minerals in various rock formations) is likely a greater SO_4 contributor to the hydrological system (87-95%) compared to smaller and localized oxidation of H_2S from volcanic emissions (5-13%). Additionally, direct atmospheric deposition of SO_4 from volcanic 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 a significant role for chemical weathering in the S cycle on Mars [4, 9, 11].

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