

HYDROLOGICAL SULFUR CYCLING IN THE VOLCANIC COMPLEX OF VALLES CALDERA, NEW MEXICO – GEOCHEMICAL IMPLICATIONS FOR MARS. A. Szyrkiewicz¹, D. M. Borrok², D. T. Vaniman³, and F. Goff⁴, ¹Geological Sciences, University of Texas at El Paso, 500 W. University Ave., El Paso, TX 79968 (aaszynkiewicz@utep.edu), ²University of Louisiana at Lafayette, 611 McKinley Street, Lafayette, LA 70504 (dborrok@louisiana.edu), ³Planetary Science Institute, 1700 East Fort Lowell, Tucson, AZ 85719 (dvaniman@psi.edu), ⁴University of New Mexico, Albuquerque, NM 87131 (candf@swcp.com).

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 giant 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. 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) and then converting the units of mg/s to kg/day or kg/month. 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.

Initial Results and Conclusions: In the first step of our study, we have: i) quantified the present SO₄ loads attributable to reduced volcanic S emission (H₂S gas) and chemical weathering (e.g. pyrite oxidation, evaporite dissolution); and ii) assessed the historical annual SO₄ removal from Valles Caldera that occurs through surface water flow, using historical USGS data of stream discharges and SO₄ concentrations.

Aqueous SO₄ fluxes of the Valles Caldera streams vary widely during base-flow conditions (dry period) in Nov 2012 (Fig. 1):

1) Significantly higher SO₄ fluxes (up to 5,262 kg/month) were observed for the San Antonio drainage system (SO₄ concentrations of 2-11 mg/L) compared to lower fluxes in the East Fork Jemez drainage (up to 1,003 kg/month and SO₄ concentrations of 2-8 mg/L). This drainage has more abundant hydrothermal S-rich alteration of bedrock and active volcanic H₂S emission than the East Fork Jemez drainage with less S mineralization/emission;

2) Despite the high SO₄ concentrations (1,360 mg/L) in Sulphur Creek, a major stream draining the Sulphur Springs area with elevated H₂S volcanic emission (Fig. 1), the SO₄ fluxes were significantly lower (up to 776 kg/month; 12.7% of the total SO₄ flux in Valles Caldera) compared to the San Antonio and East Fork Jemez streams. This is mainly due to low stream discharges (less water available for hydrological SO₄ transport) during the Nov base-flow condition in the Sulphur Springs area.

Our initial results imply that during base-flow (dry) conditions, chemical weathering is likely a bigger SO₄ contributor to the hydrological system (87.3 %) compared to smaller and localized oxidation of H₂S from volcanic emission (12.7 %). This contrasts with the suggested S-rich volcanic emission as a major source to explain the sulfate enrichment of Martian surface. Conversely, our results are more in accord

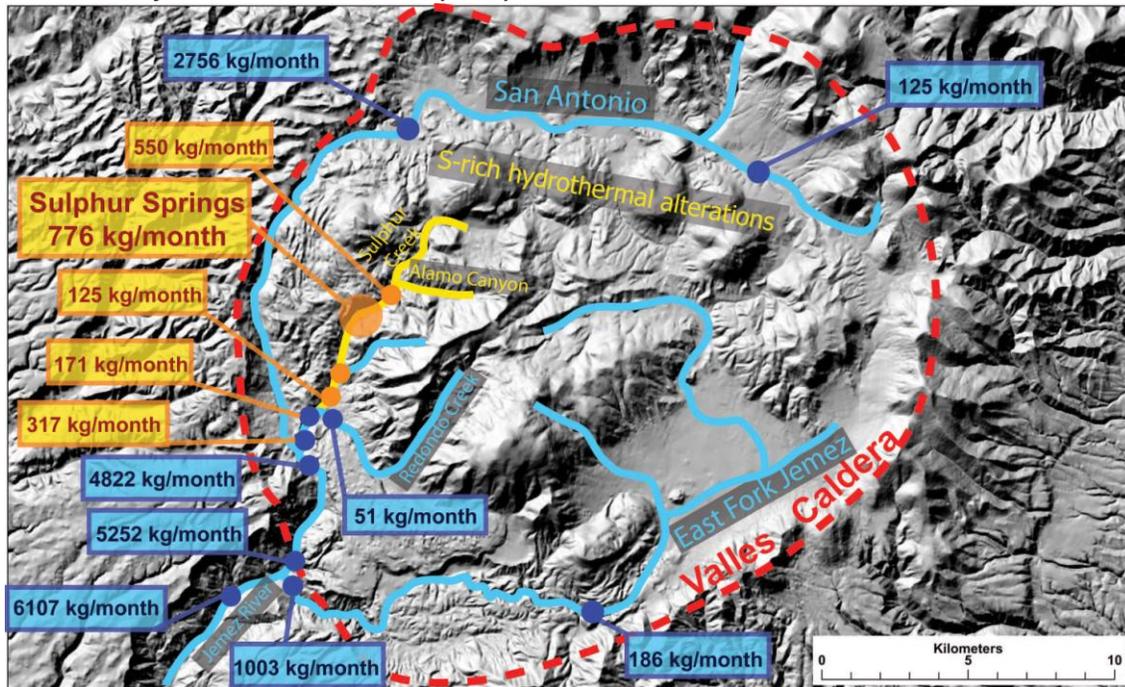


Figure 1. Location of sampling points and measured SO₄ fluxes (kg/month) in Nov 2012 on a Digital Elevation Model of Valles Caldera (Courtesy of Los Alamos National Laboratory). Yellow and blue dots indicate the stream locations showing low water pH (2 to 5) and high water pH (6 to 8), respectively.

with studies suggesting the role of chemical weathering in S cycle on Mars [4,9].

Using historical USGS stream flow measurements and SO₄ concentrations (1958 to 1990), we calculated that on average ~494 tons of dissolved SO₄ is annually removed from the caldera system (Fig. 1) via the hydrological cycle. Comparison of this amount with the SO₄ deposition in White Sands, the largest terrestrial gypsum dune field on Earth, provides a good illustration of the scale of hydrological S transport in Valles Caldera. For example, the annual SO₄ flux in Valles Caldera comprises a very small portion of SO₄ (~1.07×10⁻⁷ %) deposited in the form of gypsum in the White Sands Dune Field. This is likely due to significantly greater inorganic bedrock SO₄ sources in White Sands (Paleozoic gypsum/anhydrite evaporites) compared to smaller bedrock/volcanic sources of S and SO₄ in Valles Caldera (hydrothermal S-bearing minerals, S volcanic emission). However, the larger drainage basin is another important factor increasing SO₄ loads in the surface environment of White Sands.

Using the rates of current SO₄ removal from Valles Caldera via chemical weathering and volcanic emission (494 metric tons/year) and the amount of SO₄ deposited in White Sands (4.6×10⁹ metric tons), it can be roughly estimated that it would take at least 2.7×10⁵ years to contribute a mass of SO₄ similar to White Sands via the hydrological S transport currently active in Valles Caldera, when both basins are normalized to their respective surface areas. Using the same approach

and the estimated mass of SO₄ (3.2×10¹⁰ metric tons) deposited in the Olympia Undae Dune Field on Mars [4], the corresponding hydrological S transport would be at least ~10 times longer in Olympia Undae (7,500 km²) compared to the White Sands drainage area (12,300 km²).

Future Focus: In the next step of our research, we will i) compare SO₄ fluxes between base-flow conditions and high-flow conditions during snowmelt (Apr 2013), ii) measure S isotope compositions of SO₄ to quantify the SO₄ fluxes from surface run-off, groundwater recharge and volcanic S emission, and ii) evaluate how these fluxes change spatially and temporally as a function of changes in climate by looking at the sedimentary record of the ancient lakes that occupied Valles Caldera. These data will be compared to S/sulfate sources and sinks in different environments on Mars.

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