

## AQUEOUS SULFUR BUDGET AND OXIDATION OF FUMAROLIC H<sub>2</sub>S IN THE VOLCANIC COMPLEX OF VALLES CALDERA, NEW MEXICO – GEOCHEMICAL IMPLICATIONS FOR MARS.

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**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 H<sub>2</sub>S-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/SO<sub>4</sub><sup>2-</sup> from volcanogenic and bedrock sources and for evaluation of S preservation in the sedimentary record.

**Field/Lab Methods:** The amount of SO<sub>4</sub> transported in the surface hydrological system can be determined by calculating the SO<sub>4</sub> flux. The stream SO<sub>4</sub> flux is determined by multiplying the stream-water SO<sub>4</sub> concentrations by the volumetric flow rates. This flux corresponds to the mass of dissolved SO<sub>4</sub>

ions that flow out of the caldera per unit time (e.g., kg SO<sub>4</sub> per day).

The S isotope composition ( $\delta^{34}\text{S}$ ) of SO<sub>4</sub> can be used to distinguish S sources in aqueous environments. Additionally, the O isotope composition ( $\delta^{18}\text{O}$ ) of SO<sub>4</sub> can be used to understand oxidation pathways of volcanic H<sub>2</sub>S to SO<sub>4</sub> and contributions of atmospheric O<sub>2</sub>.

### Aqueous Sulfur Budget in Valles Caldera:

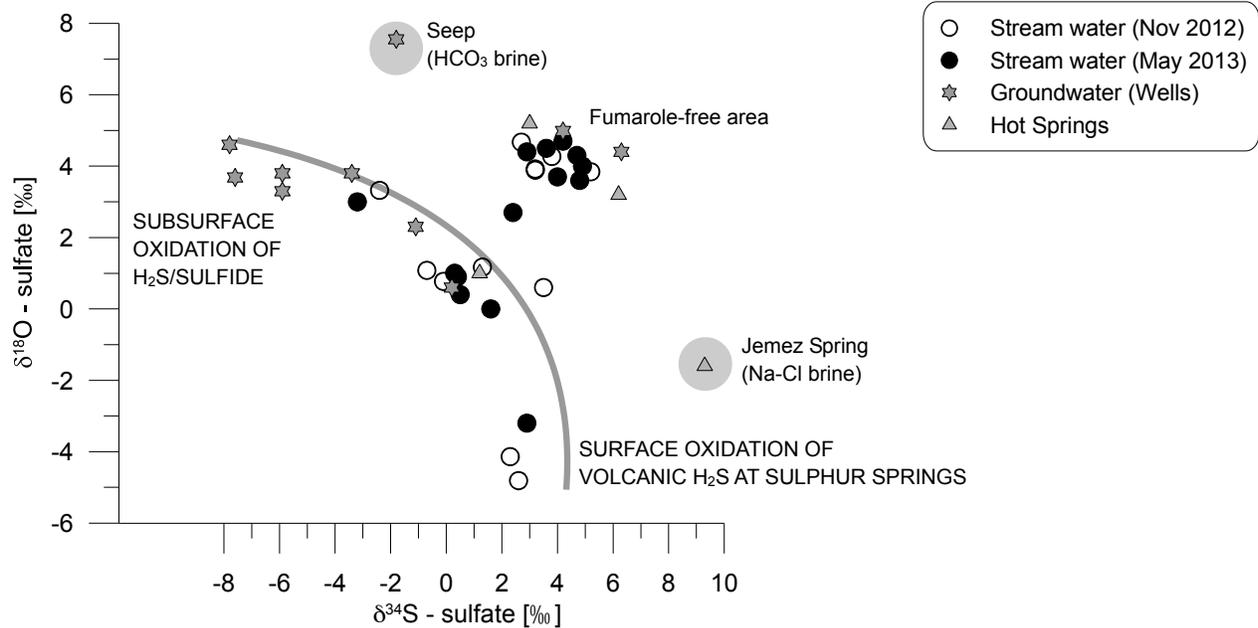
According to the measured SO<sub>4</sub> fluxes, our initial results imply three major SO<sub>4</sub> sources in the studied aqueous volcanic system of Valles Caldera:

- 1) chemical weathering (e.g. oxidation/dissolution of hydrothermal S-rich minerals) contributing 71-86 % of SO<sub>4</sub>;
- 2) snowmelt contributing 9-16 % of SO<sub>4</sub>;
- 3) hydrothermal gas emission (oxidation of fumarolic H<sub>2</sub>S in surface environments) contributing 5-13 % of SO<sub>4</sub>.

### Accumulation of Hydrothermal S-rich Gases in

**Snow:** In order to understand the role of atmospheric SO<sub>4</sub> 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 SO<sub>4</sub> in snow samples collected in close proximity (a few meters) to the active fumaroles with H<sub>2</sub>S 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 SO<sub>4</sub> were observed in the snow samples (+5.6 to +7.8‰) when compared to the hydrothermal H<sub>2</sub>S emission of Valles Caldera (+0.8 to +3.4‰). This suggests that most of the SO<sub>4</sub> 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 H<sub>2</sub>S to SO<sub>4</sub>:** The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of stream SO<sub>4</sub> showed greater variation in the Sulphur Creek catchment, which has active fumaroles and elevated emission of hydrothermal H<sub>2</sub>S into stream



**Figure 1.** Variations of  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of stream  $\text{SO}_4$  in the Valles Caldera watershed.

water (-8 to +3 ‰ and -5 to +5 ‰, respectively). Other catchments with no  $\text{H}_2\text{S}$  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  $\text{SO}_4$  at Sulphur Springs (-5 to -3 ‰) is indicative of prevailing oxidation of  $\text{H}_2\text{S}$  to  $\text{SO}_4$  with water oxygen (-9 ‰) rather than atmospheric  $\text{O}_2$  (+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  $\text{H}_2\text{S}$  from fumarolic emissions (5-13%). Additionally, atmospheric deposition of  $\text{SO}_4$  from fumarolic emissions in the snow cover appears to be negligible compared to the  $\text{SO}_4$  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  $\text{SO}_4$  originating from oxidation of hydrothermal  $\text{H}_2\text{S}$  gas appears to be sourced by water oxygen. Although

atmospheric  $\text{O}_2$  is present, it does not appear to significantly contribute to  $\text{H}_2\text{S}$  oxidation. Given that Mars probably never had an  $\text{O}_2$ -rich atmosphere, this finding may provide important insight regarding plausible oxidation pathways of S gases in Martian surface environments.

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