**AQUEOUS SULFATE FLUXES IN BASALTIC CATCHMENTS: AN ANALOG INVESTIGATION OF SULFATE DEPOSITION IN MERIDIANI PLANUM, MARS.** R. D. Moore, A. Szynkiewicz, University of Tennessee, Knoxville (rmoore84@vols.utk.edu)

**Introduction:** The Meridiani Planum region on Mars has extensive sulfate-rich sedimentary deposits, typically containing up to 25-50 wt.% $SO_4^{2-}$ [1, 2]. Many hypotheses have been proposed to explain how this sulfate was formed and transported to this region, including groundwater evaporation in a playa setting with subsequent eolian transport [3], aqueous transport through adjacent valley network systems [4], in situ acidic alteration of primary minerals [5], direct volcanic sulfur gas emission [6], and/or hydrothermal circulation [7]. Generally, it is accepted that water played a key role in the formation of the sulfate minerals in the Meridiani sediments. This area is adjacent to equatorial valley networks and shows distinctive mineralogical (hematite, sulfates, chlorides) and sedimentological (layered strata) evidence for past aqueous activity via both surface water and groundwater flows. Therefore, water-rock interaction and aqueous transport of $SO_4^{2-}$, as opposed to deposition by atmospheric and volcanic degassing processes [3-5], may better explain the origin of these large $SO_4^{2-}$ deposits in Meridiani Planum.

However, none of the previous models can account for the total mass of $SO_4^{2-}$ present in Meridiani Planum (~5 x $10^{13}$ tons) [4, 8]. One process that has yet to be considered is chemical weathering of primary S-bearing minerals (e.g., sulfates, sulfides, elemental S) present in the basaltic bedrock, which is an important source of $SO_4^{2-}$ in aqueous systems on Earth. Therefore, our goal is to study the importance of secondary, low-temperature alterations related to aqueous weathering of basaltic bedrock to assess mechanisms by which $SO_4^{2-}$ is formed and cycled in terrestrial environments. This knowledge can be then used to characterize similar processes that may have occurred in Meridiani Planum.

Additionally, previous studies have mainly considered one sole source for sulfate deposition (i.e., groundwater, surface runoff, or atmospheric deposition) in Meridiani Planum. However, the sheer volume of $SO_4^{2-}$ present, over an area of ~$3.1 \times 10^5$ $km^2$, suggests that sulfate deposition would have operated under a complex hydrological system [8-10] with active regional recharge influencing surface stream (e.g., valley networks) and groundwater flows. Based on knowledge from terrestrial analogs, it can be expected that a hydrological system interacting with volcanic bedrock (typically abundant in S-bearing minerals from hydrothermal S emissions) might have been the important source of $SO_4^{2-}$ for Meridiani.

To determine if water-rock interaction and aqueous transport of $SO_4^{2-}$ via surface runoff and groundwater could have been a sulfate source for Meridiani Planum, we investigated $SO_4^{2-}$ fluxes [tons/yr] in the watersheds of basaltic islands on Earth. Hawaii and Iceland were used as Mars analogs due to their comparable basaltic composition to Mars and spatially constrained hydrologic systems. The calculated $SO_4^{2-}$ fluxes were normalized relative to watershed sizes [tons/yr/$km^2$], which allowed for estimation of the total mass of $SO_4^{2-}$ that could have been transported on Mars based on direct comparisons with the total drainage area of Meridiani. In the end, the timescale of aqueous transport was estimated for Meridiani Planum in order to better constrain the timing of liquid water on the surface of Mars during the Hesperian.

**Methods:** Modern aqueous $SO_4^{2-}$ fluxes were quantified in the terrestrial basaltic islands of Hawaii (Kauai and the Big Island) and Iceland for selected catchments with historical records (up to ~50 years) of stream discharges and $SO_4^{2-}$ concentrations. The data were obtained from the United States Geological Survey (USGS) and the Global Runoff Data Centre (GRDC).

*Calculating $SO_4^{2-}$ flux.* To estimate ion flux within the terrestrial hydrological systems, both $SO_4^{2-}$ concentration and flow discharge were used (Eq. 1):

$$SO_4 \text{ flux [mg/s]} = \text{discharge [L/s]} \cdot SO_4 \text{ conc. [mg/L]} \quad (1)$$

Additionally, annual water budgets proposed by Schopka and Derry [11] were used to calculate the $SO_4^{2-}$ flux associated with groundwater flows and surface runoff in the Hawaiian islands. For example, in older basaltic terrains, like the island of Kauai, ~85% of the total discharge sourced by meteoric precipitation typically occurs as runoff and 15% as groundwater. Conversely, younger terrains, like that of the Big Island, experience more groundwater transport of meteoric precipitation (~80%) as a result of higher bedrock permeability related to unfilled vesicles and lava tubes. Therefore, in our study the total annual $SO_4^{2-}$ flux for basaltic terrains was also determined based on these previously determined groundwater and surface water flows in the Kauai and Big Island.

Given that the terrestrial data were compared with the whole regional watershed of Meridiani Planum, which is no longer hydrologically active, the relationships between catchment size and $SO_4^{2-}$ flux were also determined for the studied catchments in Hawaii (Fig. 1). This was done based on the estimated $SO_4^{2-}$ fluxes for individual catchments and their sizes measured upstream from the gauging stations, using ArcMap and in situ measurements from historical repositories. Generally, a positive relationship was seen

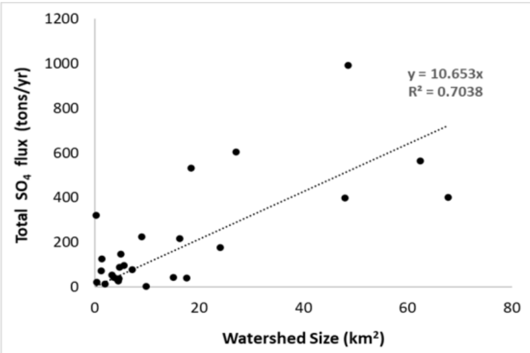


**Figure 1: Relationship between catchment sizes and $SO_4^{2-}$ fluxes in Kauai, HI.**

between larger catchments and higher $SO_4^{2-}$ fluxes (Fig. 1), which correlated with greater stream discharge in larger catchments.

This approach was then applied to the plausible hydrologic system of Meridiani Planum inferred based on orbital data (e.g., elevation, valleys). Using the aerial extent of the surrounding valley networks and topographic data as well as the relationship between $SO_4^{2-}$ flux and catchment size determined for terrestrial basaltic islands (Fig. 1), the maximum area of the theoretical Meridiani watershed was used (~3.1 x $10^5$ $km^2$, from Hynek et al., [4]) to calculate the possible $SO_4^{2-}$ flux for Meridiani Planum.

*Calculating timescales.* The timescale of aqueous activity needed to accumulate the mass of $SO_4^{2-}$ in Meridiani Planum was then determined using the following relationship:

$$\text{Time [yr]} = SO_4 \text{ mass [tons]} / SO_4 \text{ flux [tons/yr]} \quad (2)$$

In this calculation, the total mass of $SO_4^{2-}$ in Meridiani (~5 x $10^{13}$ tons) was adopted from Hynek and Di Achille (2017) [8]. This $SO_4^{2-}$ mass was then divided by the calculated $SO_4^{2-}$ flux for Meridiani based on the terrestrial data (Fig. 1).

**Initial Results:** The estimated terrestrial $SO_4^{2-}$ fluxes varied due to multiple variables in the analog sites (e.g., bedrock age, climate, active volcanism, etc.). For instance, Kauai is characterized by relatively low bedrock porosity, a wet climate, and no volcanic activity. As such, the annual $SO_4^{2-}$ flux for Kauai was ~11 tons/yr/$km^2$. Conversely, the Big Island of Hawaii has young, porous bedrock, less precipitation, and active volcanism with localized hydrothermal $H_2S$ emission, thus the estimated $SO_4^{2-}$ flux was higher, ~140 tons/yr/$km^2$. Applying these respective values to the theoretical watershed of Meridiani Planum (~3.1 x $10^5$ $km^2$), the possible $SO_4^{2-}$ fluxes could have ranged from ~3.3 x $10^6$ to ~4.4 x $10^7$ tons/yr when the water cycle was still active on the martian surface.

Using Equation 2 and the terrestrial $SO_4^{2-}$ fluxes, the amount of time to accumulate the mass of $SO_4^{2-}$ in Meridiani (~5 x $10^{13}$ tons [9, 10]) would be from ~15.1 million years (based on Kauai data) to ~1.1 million years (based on Big Island data). Note that similar estimates will be done in future work based on the $SO_4^{2-}$ fluxes in Iceland.

**Discussion:** Our results of $SO_4^{2-}$ fluxes in Kauai and the Big Island suggests that significant amounts of $SO_4^{2-}$ can be transported within basaltic terrains even under low S content in the bedrock and localized hydrothermal S emission. However, it should be kept in mind that many assumptions have been made in our model, and that factors such as climate, bedrock age, and volcanic S input can significantly influence the stream discharge and/or $SO_4^{2-}$ concentration within a hydrologic system. Nevertheless, the range of $SO_4^{2-}$ fluxes estimated in all our analog sites are reasonable, even when multiple environmental variables are accounted for.

The mass of $SO_4^{2-}$ deposited via this aqueous chemical weathering (with likely minor inputs from modern hydrothermal S emission on the Big Island of Hawaii) is more than enough to account for the amount of $SO_4^{2-}$ measured in Meridiani Planum. The calculated timescale of 15.1 million years using the data from Kauai with relatively low S content in the bedrock (<0.5 wt.% S) suggests that aqueous activity would not need lengthy periods of time to accumulate the measured mass of $SO_4^{2-}$ in Meridiani Planum. The even lower timescale estimated using data from the Big Island, more controlled by higher groundwater flow and increased volcanic activity, strengthens this argument. This new finding has implications for the timescale of water activity within Meridiani but potentially for the equatorial climate on Mars on a regional scale. Given that Hawaii is controlled by a tropical climate with relatively high annual precipitation, further comparisons with $SO_4^{2-}$ fluxes in Iceland, characterized by colder conditions, will make it possible to verify the role of climate on chemical weathering and aqueous $SO_4^{2-}$ transport to depositional environments.

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