SULFUR CYCLING AND MASS BALANCE AT MERIDIANI, MARS. B. M. Hynek[1,2], T. M. McCollom[1], and A. Szynkiewicz[3], [1]Laboratory for Atmospheric and Space Physics, University of Colorado Boulder, [2]Dept. of Geological Sciences, University of Colorado Boulder, [3]Dept. of Earth and Planetary Sciences, University of Tennessee-Knoxville. hynek@lasp.colorado.edu

Introduction: Unlike Earth's carbon cycle, Mars' history has been dominated by a sulfur cycle. This has likely had a large impact on geophysical (core composition), geological (sulfur sources-to-sinks), and even climatic conditions (potentially warming the planet). Sulfur enrichment is evident in the Mars meteorites (enrichment up to ~22 wt%), global martian soil (2.5 wt%), global dust (2.7 wt%), and bedrocks investigated by rovers (>30 wt% in cases) [e.g., 1]. It is thought that Mars accreted sulfur-rich, and through extensive volcanism it outgassed significant sulfur to the surface-atmosphere environments. Thus, sulfur is perhaps the key element for understanding the geochemical evolution of Mars.

One of the largest concentrations of sulfur-rich bedrocks occurs in Meridiani Planum; the site of the Opportunity rover investigations. These bedrocks are thought to have been subjected to acid-sulfate weathering that resulted in sulfate cemented sandstones (e.g., [2]). However, the source of the sediments and sulfur for these acidic groundwater fluids remains unclear.

Multiple Working Hypothesis Testing: Here, we test the varied hypotheses regarding emplacement of the *sediments* and *sulfur* at Meridiani Planum. The Opportunity rover investigated >10 m of Burns formation stratigraphy that was consistently sulfur-rich, averaging about 20 wt% (e.g., [2]). Underlying the Burns formation is the Grasberg formation, which was also sampled by Opportunity with a sulfur content around 10 wt% [3]. Orbital data and geologic mapping indicate the Burns formation (or at least associated layered stratigraphy) is up to 800 m thick and sulfate rich (e.g., [4]). Recent geological mapping by Hynek and di Achille [5] has provided broader context for the local in situ rover observations and extended them over a large area (Fig 1). Here we address the question, what was the source of the sediments and sulfur required to result in the extensive (4 $\times 10^5$ km^2) deposits of sulfate-rich bedrocks, with a volume of ~1 $\times 10^5$ km^3?

Groundwater upwelling

The canonical model proposes basaltic rock that was weathered in a "dirty evaporite" and transported to Meridiani (e.g., [6]). The source of sediment for this scenario is unconstrained. The sulfur would have come from later groundwater upwellings of acidic fluids. (e.g., [3,6,7]). If the acid-sulfate fluids were of pH 3 (based on detections of jarosite), then .001 mol/L H_2SO_4, or 0.001 mol/L * 98 g/mol leads to ~0.1 g/L of H_2SO_4 available for deposition in the bedrocks. 1 m^3 of Burns bedrock likely has a mass of ~2400 kg. 20 wt% SO_3 requires 480 kg SO_3/m^3, or ~480 kg H_2SO_4/m^3. Therefore, 4.8 × 10^6 L of fluid would be required to deposit enough S (SO_3 mass divided by 0.1 g/L) per m^3. However, more S is deposited in the total Meridiani layered sulfate-rich geologic units (volume = 1 × 10^{14} m^3), thus 4.8 × 10^{20} L of fluid would be required to impart enough sulfur. This volume of 4.8 × 10^8 km^3 is almost half of Earth's entire ocean volume (or a >3.3 km global equivalent layer) and is probably well above Mars' planetary water budget.

Volcanic Airfall/Ashflow

McCollom and Hynek ([8]; also this conference) proposed the source of the sediments and sulfur was from local to distal volcanic eruptions through time. In this case, the S would be indigenous to the ash deposits. S-rich ash deposits can be common on Earth, owing to the oxidation, condensation, and nucleation of S gas species in the eruption plume onto the airborne ash, eventually becoming part of the ash deposited on the ground. The 1982 El Chichón (Mexico) eruption yielded 2.6 wt% S in the ash deposits [9], which is still well below the 20 wt% S in the Burns formation. The sediment volume of 1 × 10^5 km^3 would require roughly 40 Yellowstone-sized eruptions to account for the amount of materials. If these were from distal sources, more eruptions would be required.

Atmospheric Source

Niles and Michalski [10] and Michalski and Niles [11] proposed an atmospheric source for the S and sediments. They envisaged the sediments could represent a sublimation residue from a large-scale deposit consisting of dust and ice emplaced during times of high obliquity or true polar wander. In this case, the sulfur would be derived from sulfate-rich aerosols from the atmosphere that acid weathered the silicate dust within the ice deposits. Craddock and Greeley [12] estimated volcanic outgassing totals during Late Noachian/Early Hesperian and found that 1.23 × 10^{17} kg of S would have been deposited planetwide during these times. The Meridiani layered units make up 0.35% of the planet, yielding 4.24 × 10^{14} kg S deposited in this region, which is 100× less than the 4.8 x 10^{16} kg actual S estimate in these bedrocks. In terms of the sediment volume, modern polar ice deposits on Mars have dust contents <<10% and perhaps <0.01%. Using 1% dust in the ice, that requires a 50 km total thickness of ice through time to account for the sediment volume.

Fluvial Input

Large valley networks are found uphill from the Meridiani deposits and these could also be a source for the S and sediments. These fluvial systems appear to have been active before, and also during, the incipient emplacement of the sulfate-rich bedrocks [13,5]. Sediment transport modeling by Hoke et al. [14] detailed the volume of material removed, and the timescales to form the valleys. The valleys feeding into Meridiani have a volume of ~1.1×10^3 km^3, which is only about ~1% of the volume of the Meridiani sedimentary package. Using the valleys' excavated volume and the global average of 2.5% S on the surface of Mars yields 5×10^{16} kg total S that could have been deposited in Meridiani from this process. Additional S likely came from groundwater inflow across the watershed, but the above estimate is ~1000× too little S.

Conclusions: Given the above attempts to explain the volume of materials and their S content, the sources of the sediment and sulfur for Meridiani remains entirely unknown. None of the proposed hypotheses can account for either the S mass or sediment volume, even when considering the less S-rich Grasberg formation as representative of the broader stratigraphy. The groundwater upwelling model requires half of Earth's ocean volume to impart enough S and no source for the sediments has been proposed. The volcanic airfall/ashflow model requires copious sulfur in the ash and unidentified volcanic sources. Meanwhile, the atmospheric model comes up short on the mass of the sulfur that outgassed during deposition of these sediments and requires a net total of ~50 km thickness of ice through time. The fluvial model also cannot account for the mass of the S or the volume of materials present. Thus, a new model is required to explain the sources for both the S and sediment in these exceedingly voluminous sulfate-rich layered materials.

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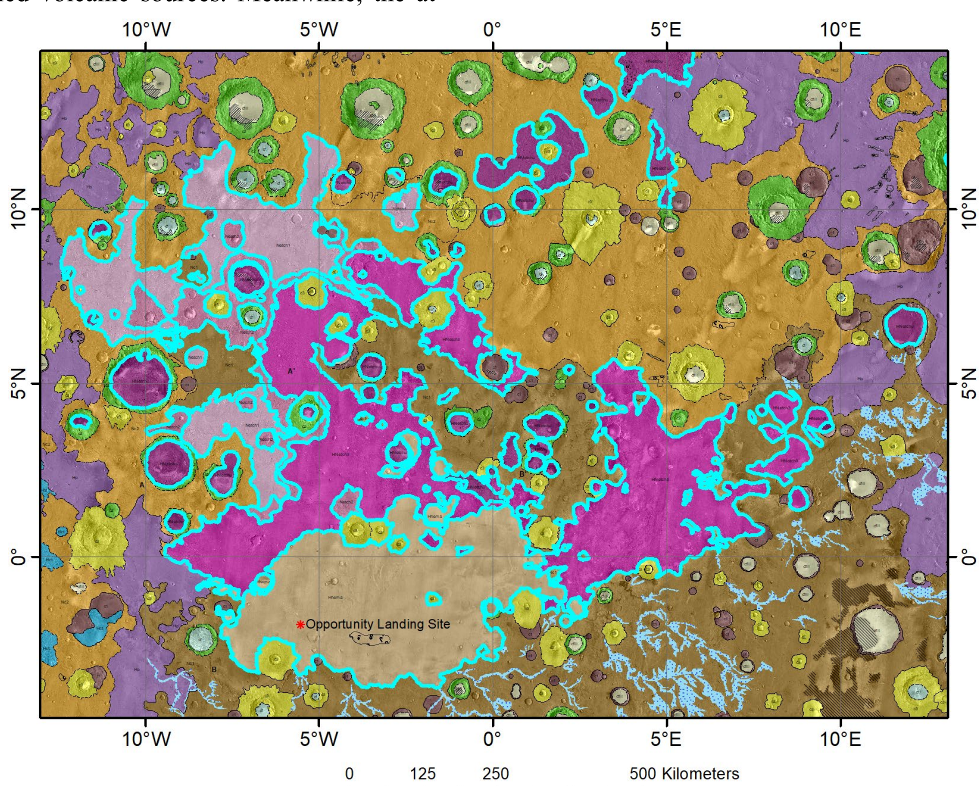

Figure 1. Geologic map of the Meridiani region [5] with sulfate-rich layered sedimentary units highlighted in blue. Valley networks to the south and west are also mapped.