GEOCHEMICAL TRENDS IN THE LAYERED SULFATE DEPOSITS AT MERDIANI PLANUM AND IMPLICATIONS FOR THEIR ORIGIN. T. M. McCollom, Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309 (mccollom@lasp.colorado.edu).

Introduction: A number of different scenarios have been proposed to explain the formation of the layered sulfate deposits at Meridiani Planum observed by the Opportunity rover, each of which has substantially different implications for the geologic history and astrobiological potential of the deposits [1-7]. Most of the proposed scenarios invoke the addition of an oxidized sulfur source (S_{ox}) to a basaltic precursor, but the scenarios disagree on whether the system was open or closed to other elements during this process. The Opportunity science team has proposed that the deposits formed through addition of salts from evaporation of sulfate-bearing groundwater to an altered basaltic presursor, followed by transport and further post-depositional chemical alteration [1,2,8,9]. Alternative scenarios suggest that SO_2 from atmospheric or volcanic sources was added to the basalt under conditions where other all elements were immobile [3-5] (referred to here as closed-system models).

Conceptually, these two types of models should produce very different trends when the measured abundances of elements are examined as a function of SO_3 (Fig. 1). Elements that are immobile during S_{ox} addition should follow a trend of decreasing abundance with increasing SO_3 owing to dilution by the added S_{ox} component. The slope and intercept of the dilution trendline depend on the initial abundance of the element. Conversely, elements precipitated from the fluid along with S_{ox} will exhibit increasing abundance with increasing SO_3, with the slope reflecting the ratio of the element to S_{ox} in the precipitates. Of course, both trends can potentially be modified by secondary mobilization of elements following the S_{ox} influx process.

Results: To investigate mobility of elements during formation of the Meridiani deposits, trends of ele-
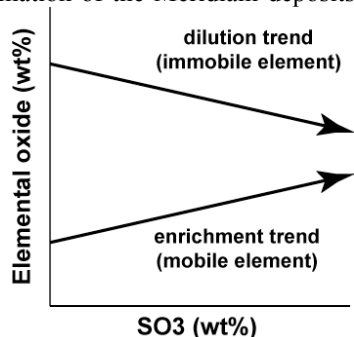

Figure 1. Schematic diagram illustrating expected trends for dilution of an immobile element during addition of an oxidized S-bearing component and for enrichment of a mobile element along with SO_3 under open-system conditions.

ment oxides as a function of SO_3 were assessed. The analysis included all sulfate-bearing bedrock samples analyzed by APXS following preparation with the RAT through sol 2515 except for Penrhyn, which showed anomalous data for many elements.

Many of the major elements including Al, Na, K, Ti, P, and Cr exhibit trends of decreasing abundance with SO_3 that are consistent with dilution (Fig. 2), indicating these elements were immobile during addition of S_{ox}. Si also shows a decreasing trend, but measured values deviate slightly from the trend expected for dilution alone, suggesting other factors contribute to the
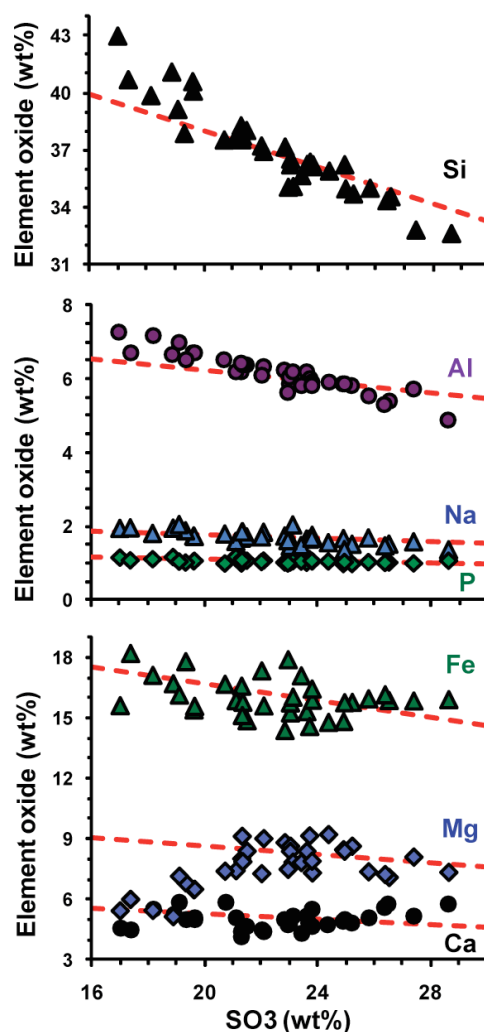

Figure 2. Measured abundances of selected elements as a function of SO_3. Red dashed lines are dilution trends based on average oxide contents for Meridiani deposits on an SO_3-free Meridiani, and are similar to typical Martian basalt compositions.

measured abundances. Mg shows a discontinuous distribution, with different trends above and below ~21 wt% SO_3 (Fig. 2). It has been observed that Mg and SO_3 decrease in abundance with depth in the deposits, leading to suggestions that Mg-sulfate salts were mobilized out of the deposits after initial deposition [8,9]. Assuming this to be the case, the original composition of the deposits prior to Mg-sulfate loss can be calculated (Fig. 3). Once this is done, Mg abundances conform to the expected dilution trend, albeit with some scatter that is likely attributable to post-depositional process. Much of the deviation of the Si is also accounted for, indicating that both Mg and Si were probably immobile during S_{ox} addition.

The only major elements that do not conform to dilution trends are Ca, Fe, and Mn (Fig. 2). These elements show a considerable amount of scatter, although Ca exhibits a weak trend of increasing abundance with increasing SO_3. The textures of hematite nodules and occurrence of gypsum veins elsewhere in the formation [8,10] indicate that both Fe and Ca were subject to secondary mobilization, and post-depositional processes likely account for the scatter. As a result, the data for Ca and Fe show no clear trend and could be consistent with either open- or closed-system conditions.
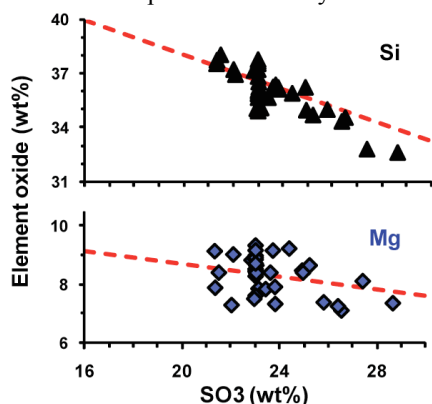

Figure 3. Oxide trends for Si and Mg after accounting for loss of Mg-sulfate salts for samples with SO_3 <21 wt%.

Implications: Although the geochemical trends could be compatible with the sedimentary-evaporite scenario proposed by the MER team, they place some very tight constraints on that scenario, including: (1) While Squyres et al. [2] have proposed that the sulfate salts were added to an altered basalt precursor depleted in $\Sigma(Fe+Mg+Ca)$ by 55%, the trends indicate that the presumed precursor could not have been depleted in these elements by more than 30%, or less if post-depositional removal of Mg is taken into account. (2) The slopes of the trendlines indicate that the molar cation:SO_4 ratio for elements deposited from the fluid would have to have been <0.3 and, since most sulfate salts have cation:SO_4 ratios $\geq$ 1, most of the cations

currently present as sulfate salts in the Meridiani deposits must have been leached from the altered basalt precursor rather than transported into the deposits by the fluid. (3) Since H^+ is the only feasible cation to achieve charge balance in the fluid, the trendlines also indicate that the fluids that deposited the sulfate were strongly acidic, which would seem to be incompatible with long-distance fluid transport through basaltic aquifers [11] (note that models invoking acid formation through conversion of Fe-sulfates to hematite [12] are relevant only to post-depostional processes).

The observed trends could also be compatible with closed-system scenarios, provided there was post-depositional mobilization of Mg, Fe, and Ca. Indeed, model calculations performed by assuming that Mg, Fe, and Ca were immobile during addition of a S_{ox} component and that deviations of these elements from dilution trends are accounted for by post-depositional transport closely reproduce the trends observed for all of the major elements (e.g., Fig. 4). While Squyres et al. [2] claimed that closed-system scenarios cannot account for the chemical compositions of Meridiani deposits, those authors did not consider potential contributions of post-depostional mobility in their arguments. Overall, the chemical composition of the Meridiani deposits is most accurately explained by scenarios that invoke addition of an oxidized sulfur source under otherwise closed-system conditions, followed by post-depositional mobilization of Mg, Fe, and Ca.
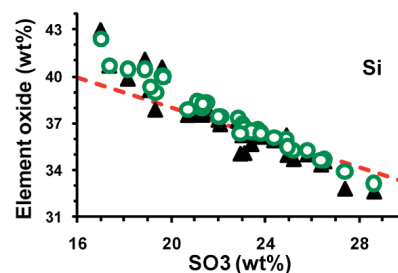

Figure 4. Measured abundance of SiO_2 as a function of SO_3 (triangles) compared with model values calculated for S_{ox} addition under closed-system conditions followed by post-depostion mobilization of Mg, Fe and Ca sulfates (circles). Models produce similar results for other elements.

References: [1] Squyres S. W. et al. (2004) *Science 306*, 1709-1714. [2] Squyres S. W. et al. (2006) *Science 313*, 1403-1407. [3] Berger G. et al. (2009) *Amer. Mineral., 94*, 1279-1282. [4] Niles P. B. and Michalski J. (2009) *Nat. Geosci. 2*, 215-220. [5] McCollom T. M. and Hynek B. M. (2005) *Nature 438,* 1129-1131. [6] Zolotov M. Y. and Shock E. L. (2005) *GRL,* L21203. [7] Knauth L. P. et al. (2005) *Nature 438,* 1123-1128. [8] McLennan S. M. et al. (2005) *EPSL 240*, 95-121. [9] Clark B. C. et al. (2005) *EPSL 240*, 73-94. [10] Arvidson R. E. et al. (2014) *Science 343*, DOI: 10.1126/science.1248097. [11] Andrews-Hanna J. C. et al. (2010) *JGR 115*, E06002. [12] Hurowitz J. A. et al. (2010) *Nat. Geosci. 3,* 323-326.