

A MINERALOGIC AND GEOCHEMICAL MODEL FOR FORMATION OF LAYERED SULFATE DEPOSITS AT MERIDIANI PLANUM BY ACID-SULFATE ALTERATION. T. M. McCollom¹ and B. M. Hynek^{1,2}, ¹Laboratory for Atmospheric and Space Physics and ²Department of Geological Sciences, University of Colorado, Boulder, CO 80309 (mccollom@lasp.colorado.edu).

Introduction: The Mars Exploration Rover (MER) Opportunity spent several years making detailed observations of the morphology, chemical composition, and mineralogy of sulfate-rich layered deposits in the Burns Formation at Meridiani Planum on Mars [1,2]. The MER science team has interpreted the layered sulfate deposits to have formed through a sequence of events that involved basalt weathering, precipitation of sulfate minerals by evaporation of infiltrating groundwater, transport of elements both into and out of the rocks, erosion, and transport [1-4]. Although this model has been widely accepted by the Mars science community, a detailed, comprehensive model of bedrock formation by these processes has never been presented, and some aspects of the geochemistry appear to be incompatible with the proposed scenario [5-7]. Consequently, alternative hypotheses should be seriously considered. Several alternative scenarios for formation of the deposits have been proposed over the years, including acid-fog weathering of basalt, weathering of glacial deposits, impacts, alteration of sulfide minerals, and acid-sulfate alteration of volcanic deposits [5-10]. Here, we further explore the possibility that the Meridiani deposits formed through alteration of Martian pyroclastic basalt by SO₂-bearing steam in a fumarole-like setting.

Geochemistry of Meridiani Deposits: Measurements made by Opportunity have led to two fundamental conclusions in regard to the chemical composition of Meridiani bedrocks [1,2,5,6]. First, the elemental composition of the rocks closely resembles the composition of pristine Martian basalt with the addition of sulfur. This is evident, for instance, in Fig. 1, which shows that the compositions of Meridiani bedrocks after S is removed is essentially identical to that of typical Martian basalts. Similarly, the ternary plot in Fig. 2a shows that the compositions of the bedrocks fall very close to a mixing line between pristine basalt and a S-bearing endmember. Although the oxygen content of the rocks was not directly measured by Opportunity, the rocks are highly enriched in Fe(III) relative to pristine basalt, indicating that substantial O has been added to the rocks in addition to S. Second, the compositions of bedrocks in the Burns Formation are nearly uniform, with only minor variations in Mg, Si, and S among sampling points (Figs. 1 & 2a). Any scenario for formation of the deposits must first and foremost be able to explain these basic observations.

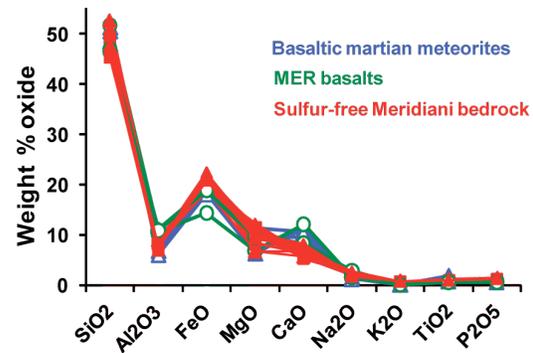


Figure 1. Compositions of bedrocks in the Burns Formation at Meridiani Planum measured by the Opportunity rover. Compositions have been re-calculated to a sulfur-free basis to facilitate comparison with Martian basalt.

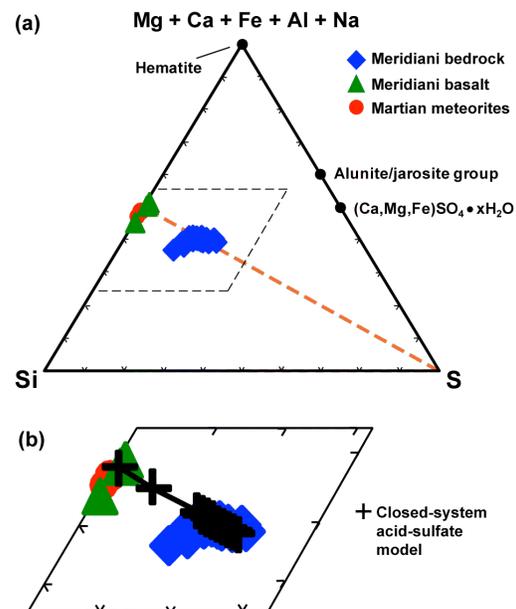


Figure 2. (a) Ternary diagram showing relative molar proportions of major rock-forming elements in bedrocks from the Burns Formation. (b) Expanded view of area outlined with dashed line in (a), focusing on evolution of rock composition during simulated acid-sulfate alteration in the reaction path model (Fig. 3).

Model for formation of Meridiani deposits:

The most simple and straightforward way to explain the chemical composition of the Meridiani bedrocks would be addition of S and O to Martian basalt under conditions where other elements are essentially immobile. One scenario where this could occur is through acid-sulfate alteration of basalt by SO₂-bearing steam,

as occurs in volcanic fumaroles [e.g., 11,12]. In terrestrial fumaroles, soluble elements are commonly transported out of the system by rainfall and groundwater flow. However, under conditions of more limited water availability like those that likely prevailed on early Mars, alteration may have occurred under conditions where elements were much less mobile. To test this possibility, we developed a reaction path model to simulate the reaction of Martian basalt with a solution of sulfuric acid created by condensation of SO_2 -bearing steam. The simulation was conducted under low water:rock conditions, restricting mobilization of elements into the fluid. Because the rocks at Meridiani are highly oxidized, the model assumed equilibrium with atmospheric O_2 at present day levels (10^{-5} bar).

Results of the model are shown in Fig. 3. The model predicts that acid-sulfate alteration of basalt will result in a secondary mineral assemblage composed of amorphous silica, anhydrite, kieserite, Fe-bearing natroalunite, and hematite. At intermediate stages, these alteration products may coexist with relict primary silicate phases including plagioclase, olivine, pyroxene, and glass. This mineral assemblage appears to be compatible with models of the mineralogy of Meridiani bedrock based on spectroscopic observations [13]. Although jarosite has been interpreted to be a component of the bedrock based on results from Mössbauer spectroscopy [14], the Fe-bearing natroalunite predicted by the models would also be consistent with the Mössbauer results [11,15].

The chemical composition of the predicted alteration assemblage in the models also appears to be compatible with observations from Opportunity (Fig. 2b). As alteration proceeds, the principal changes in elemental composition of the rocks include an increase in

SO_3 content through the precipitation of sulfate minerals and an increase in O content as Fe(II) is converted to Fe(III). Because the amount of sulfate minerals that form during alteration is limited by the amount of cations initially present in the rock (Fe, Mg, Ca, Al, etc.), the SO_3 content of the solids during alteration is restricted to the 22-27 wt% range, similar to the measured SO_3 contents of Meridiani bedrocks (Fig. 2b).

Conclusions: The model results indicate that the chemistry and mineralogy of the Burns Formation can be readily explained by acid-sulfate alteration of pyroclastic basalt, and the simplicity of the model suggests that it may be a more viable explanation than other more complex scenarios. Recent studies have potentially identified large volcanic structures that could be the source of pyroclastic deposits for Meridiani and other nearby areas [16]. Whether the acid-sulfate alteration might have occurred *in situ* at Meridiani or at the source area prior to explosive redistribution of the pyroclasts is a matter for further research.

References: [1] Squyres S. W. et al. (2004) *Science* 306, 1709-1714. [2] Squyres S. W. et al. (2006) *Science* 313, 1403-1407. [3] Grotzinger J. P. et al. (2005) *EPSL* 240, 95-121. [4] McLennan S. M. et al. (2005) *EPSL* 240, 95-121. [5] McCollom T. M. and Hynek B. M. (2005) *Nature* 438, 1129-1131. [6] McCollom T. M. and Hynek B. M. (2006) *Nature* 443, doi:10.1038/nature05213. [7] Niles P. B. and Michalski J. (2009) *Nat. Geosci.* 2, 215-220. [8] Berger G et al. (2009) *Amer. Mineral.*, 94, 1279-1282. [9] Zolotov M. Y. and Shock E. L. (2005) *GRL*, L21203. [10] Knauth L. P. et al. (2005) *Nature* 438, 1123-1128. [11] McCollom T. M. et al. (2014) *JGR*, 118, 1719-1751. [12] Hynek B. M. et al. (2014) *JGR*, 118, 2083-2104. [13] Glotch T. D. et al. (2006) *JGR*, E12S03. [14] Klingelhöfer G. et al. (2004) *Science*, 306, 1740-1745. [15] McCollom T. M. et al. (2014) *JGR*, 118, 1-38. [16] Michalski J. R. and Bleacher J. E. (2013) *Nature*, 502, 47-53.

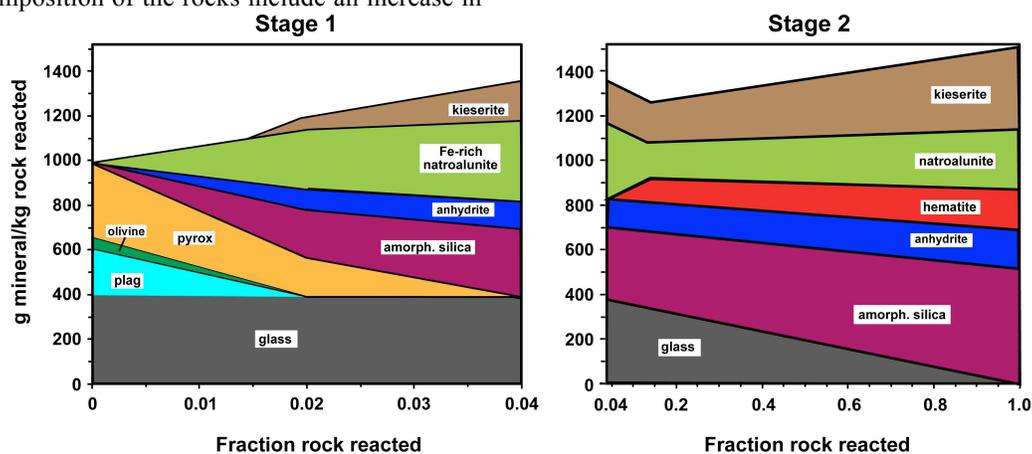


Figure 3. Predicted mineral composition during hydrothermal acid-sulfate alteration of basalt. Initial basalt is composed of 35 wt% pyroxene ($\text{En}_{50}\text{Wo}_{15}\text{Fs}_{35}$), 20 wt% plagioclase (An_{60}), 4 wt% olivine (Fo_{70}), and 40 wt% basaltic glass. Calculations are performed at 80 °C and a fluid:rock ratio of 0.2. Consistent with experimental and field observations [11,15], the models assume that primary silicates (plagioclase, pyroxene, olivine) react much faster than basalt glass. Stage 1 shows initial reaction where primary silicates dissolve, while Stage 2 involves more gradual dissolution of the glass (see [11] for more details).