

GEOCHEMICAL MODELING OF AQUEOUS ALTERATION PROCESSES WITHIN THE BURNS FORMATION, MERIDIANI PLANUM, MARS. C. D. Cino¹, E. Dehouck¹, and S. M. McLennan¹, ¹Department of Geosciences, Stony Brook University, Stony Brook NY, 11794-2100, USA (christie.cino@stonybrook.edu; erwin.dehouck@stonybrook.edu; scott.mclennan@stonybrook.edu).

Introduction: The Martian paleoenvironment may have evolved from an aqueous, clay-bearing environment to a more desiccated, low pH and sulfate-rich setting, with the boundary sometime in the late Noachian (~3.7 billion years ago) [1]. Sandstones found in the Burns formation, preserved at Meridiani Planum and containing abundant sulfates, are considered to be representative of the later sulfate-rich setting. Current models of aqueous alteration that gave rise to the Burns involve acidic alteration resulting in dissolution of Fe- and Mg-silicates (e.g., olivine) and re-deposition (and diagenetic alteration) of Fe-, Mg- and Ca-sulfates as cements [2,3]. Formation of well-crystallized clay minerals may be inhibited in such acidic environments, and neither Mössbauer nor Mini-TES provided unambiguous evidence for phyllosilicates. The chemical composition of any residual silicate component could provide insight into the possible presence of clays or their poorly crystalline or non-crystalline equivalents and this study is an attempt to explore this question.

The Burns formation represents a "wetting-upward" eolian succession in which ground water and localized surface water played a significant role [2]. Preserved mineralogy (summarized in [3]), determined by Mössbauer, Mini-TES and Pancam and further constrained by APXS elemental correlations, include, in decreasing abundance: amorphous silica, Mg-sulfate, jarosite, Ca-sulfate, plagioclase, hematite, pyroxene, olivine and possibly chlorides. Also present is 23±10% (on average) of poorly characterized igneous, altered igneous (possibly including phyllosilicates) and Mössbauer Fe3D3 components [4].

In our original modeling reported in [5], available chemical and mineralogical data were used to evaluate the possibility of clay minerals (or chemical equivalents) in residual materials that exclude chemically precipitated minerals and their diagenetic products [5]. A continuation to this work has been underway that incorporates available uncertainties on mineralogical abundances to better constrain any potential phyllosilicate mineralogy. To achieve this, we adapted a mass balance algorithm that was developed to determine the possible range of bulk compositions and amounts of amorphous materials in rocks and soils examined by the *Curiosity* rover XRD instrument [6]. This program was developed in Scilab 5.4.1 [7], and details are summarized in [6].

Methods: In our original modeling, APXS data for Burns formation targets abraded by the RAT (Rock Abrasion Tool), and for which there are Mössbauer data quantitatively constraining iron mineralogy, were used to systematically "subtract" chemically precipitated constituents to evaluate the composition of the residue [5] (similar to approach in [8]). For minerals detected by Mössbauer, sample-by-sample subtractions were carried out, but for minerals determined by Mini-TES [9], it was only possible to subtract formation averages from individual samples.

In the revised modeling approach, results from our original subtraction model were used to carry out a mass balance calculation on a sample-by-sample basis, incorporating estimated uncertainties in mineral abundances. These calculations require: bulk chemical composition, ratio of chemical constituents to residue, Fe³⁺/Fe²⁺ ratio from Mössbauer [4], mineral oxide compositions in weight percent, mineral abundances in weight percent, and finally, estimated uncertainties (here estimated to be ±10%). The calculations thus result in a range of allowable compositions for each RAT target (one example is shown in Fig. 1 center).

Results and Discussion: The initial procedure required two successive calculations: (1) removing amorphous silica and those components thought to be associated with sedimentary sulfates (CaSO₄, MgSO₄, jarosite, schwertmannite) and (2) then removing hematite and possible chlorides. For these two cases, the average amount of residual material remaining, respectively, was 35% and 28% of the rocks [5]. Residues remaining after subtracting the assigned chemical constituents are plotted on A-CN-K ternary diagrams (Fig. 1 left) along with starting bulk compositions and the average compositions of the chemical constituents that were removed. A shift from igneous and volcanic compositions to compositions suggestive of a secondary mineral assemblage, including a possible clay mineral component [8], are observed, consistent with alteration that produced Al-rich residues [10].

The Scilab-based modeling that incorporated estimated uncertainties is generally consistent with the simple mass balance model [5]. The ratio for Mg/Ca-sulfate and Na/K-chlorides required slight adjustment for a few samples, but stayed within the range of ratios estimated from Mini-TES data, i.e. 0.65/0.35 ± 0.02 and 0.85/0.15 ± 0.03, respectively [9]. The residual, crystalline, and bulk compositions are plotted on the

A-CNK-FM diagram in Fig. 1 (center, right). These results generally agree with the original diagram (Fig. 1 left), with only one outlier (Drammensjord). Drammensjord has 2% more calcium in the bulk composition and double the calcium in the residue than any other sample, which causes it to plot more left on the A-CNK-FM diagram. When uncertainties are also considered their compositions remain in the secondary mineral assemblage range (compare Fig. 1 center and right).

The Burns formation is broadly interpreted to have formed in an acidic groundwater environment [e.g., 3,11,12] based mainly on the presence of the ferric sulfate mineral jarosite, which forms at pH of <4 [12,13]. Such environments are thought to inhibit formation of aluminous or ferric iron clay minerals [14] although examples are known where clays co-exist with low pH settings [15]. In addition, when clays encounter low pH settings, they can lose crystallinity and become amorphous to X-rays (but not to IR) [16]. Glotch et al. [9] reported nontronite in the Burns formation but the identification is non-unique (T. Glotch, pers. comm.). Finally, non-silicate aluminous minerals such as Al-sulfates could also play a role but such minerals have not been detected.

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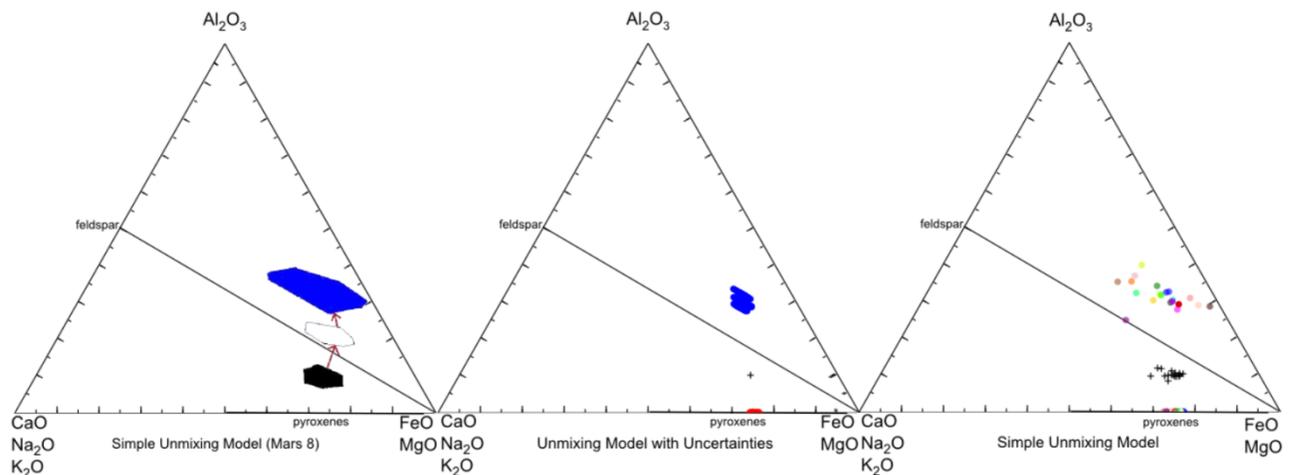


Figure 1 - Ternary diagrams (A-CNK-FM) with end members Al_2O_3 , $(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$, and $(\text{FeO}_{\text{total}} + \text{MgO})$ plotted in mole percent for initial and residual compositions. Left: Simple unmixing model where compositions shift to an area where secondary materials, including phyllosilicates, plot. Open field showing removal of sulfates and their diagenetic products only and blue field for removal of all potential chemical constituents). Taken from [5]. Center: unmixing model incorporating estimated uncertainties calculated on the individual sample Lionstone [6] using a program developed on Scilab [7]. Right: Scilab unmixing model for individual sample averages. Note that each calculated data point would have an uncertainty range comparable to that shown in the center figure.