

Geochemical Constraints on the Presence of Clay Minerals in the Burns Formation, Meridiani Planum, Mars. C. D. Cino¹ and S. M. McLennan¹, ¹Department of Geosciences, Stony Brook University, Stony Brook NY, 11794-2100, USA (christie.cino@stonybrook.edu; scott.mclennan@stonybrook.edu).

Introduction: Current paradigms for the paleoenvironmental evolution of early Mars involve a surface that evolved from a clay-bearing, water-rich environment to a more desiccated, low pH and sulfate-rich setting, with the boundary in the late Noachian [1]. Burns formation sandstones, 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]. In such acidic environments, formation of clay minerals is thought to be inhibited and neither Mössbauer nor Mini-TES provided unambiguous evidence for phyllosilicates. On the other hand, the chemical composition of any residual silicates 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 on average is 23±10% of poorly characterized igneous, altered igneous (possibly including phyllosilicates) and the Mössbauer Fe3D3 component [4]. Here we use available chemical and mineralogical data to evaluate the possibility of clay minerals (or equivalents) in the residual materials that exclude chemically precipitated minerals (and their diagenetic products).

Methods: We used APXS data for Burns formation targets abraded by the RAT (Rock Abrasion Tool), and for which there were associated Mössbauer data quantitatively constraining iron mineralogy. The approach is to systematically "subtract" constituents interpreted to be chemically precipitated (which in some cases have been diagenetically altered) and then evaluate residual chemical compositions to constrain the potential for the presence of clay minerals (similar to approach in [5]). For minerals detected by Mössbauer, we were able to carry out subtractions on a sample-by-sample basis but for minerals determined by Mini-TES

[6], it was only possible to subtract formation averages from individual samples.

Removing Iron Minerals: Mössbauer provides constraints on Fe²⁺/Fe³⁺ ratios and abundances of iron-bearing minerals [3]. Accordingly, iron not associated with silicate minerals, is present as hematite, jarosite, and the so-called Fe3D3 phase [4]. Both hematite and jarosite are considered to be diagenetic products of chemically precipitated minerals [3,7]. However, Fe3D3 is poorly characterized, more complicated, and may include various Fe-oxides/hydroxides, superparamagnetic hematite or goethite, schwertmannite or iddingsite. We arbitrarily assigned half of the Fe3D3 to the sulfate mineral schwertmannite, a likely diagenetic product of ferrous sulfate oxidation [7], in order to satisfy the sulfur mass balance of the samples.

Removing Silica: Combined APXS and Mini-TES data suggest the presence of excess SiO₂ in the form of amorphous silica [6], on average making up about 25% abundance by weight. Removal of this amount of amorphous silica left residual SiO₂ of ~33-43 wt%.

Removing Sulfates: Mössbauer data provide direct information only about the amount and composition of Fe-bearing sulfates. Constraints on the amount and composition of non-Fe-bearing sulfates come from Mini-TES formation averages [6]. Accordingly, a portion of sulfur was removed as natrojarosite and half of the Fe3D3 (assuming schwertmannite; see above). Due to mass balance constraints and Mössbauer peak positions, K-jarosite was ruled out [4]. Remaining sulfur was subtracted out as Ca- and Mg-sulfates with the distribution between magnesium and calcium being 0.65:0.35, consistent with Mini-TES [6].

Removing Chlorine: Mineralogical controls on Cl abundances are poorly understood. Morris et al. [4] suggested that Cl⁻ may substitute for OH⁻ in jarosite but such that OH⁻>Cl⁻. Accordingly we assigned a small amount of Cl to jarosite (ratio of Cl⁻:OH⁻≤1:9.1). Remaining Cl was subtracted out as halide salts, sylvite and halite, with the distribution between Na- and K-chlorides being 0.85:0.15.

Results and Discussion: We carried out successive calculations: (1) removing amorphous silica and those components thought to be associated with sedimentary sulfates (CaSO₄, MgSO₄, jarosite, schwertmannite) and (2) removing silica, sulfates, hematite and chlorides. For these two cases, the average amount of residual material remaining, respectively, was 35% and 28% of

the rocks. Residues remaining after subtracting the assigned chemical constituents are plotted on ACNK and ACNKFM ternary diagrams (Figs. 1 and 2) along with starting compositions. A shift from igneous-like compositions to compositions suggestive of a secondary mineral assemblage, including a possible clay mineral component [5], is observed on both diagrams. The ACNK diagram (Fig. 1) includes the Chemical Index of Alteration (CIA) scale, with values mostly ranging between 75-95, consistent with alteration that produced Al-rich residues [8]. Phyllosilicates, such as kaolinite and chlorite, have CIA of 95-100 and other clays, such as smectites and illites, have values of ~75-85 [8]. In the ACNKFM diagram (Fig. 2) residual components also plot in the field consistent with the presence of secondary clay minerals [9,10]. On this diagram, clay minerals that plot closest to the residual field are natural montmorillonites [10] but could also represent a mixture of various Mg/Fe rich phyllosilicates, such as nontronite or saponite, and other Al-rich minerals, similar to those inferred from APXS data at Matijevec Hills in Endeavour crater [10].

The Burns formation is broadly interpreted to have formed in an acidic groundwater environment [e.g., 3,11,12] due mainly to the presence of the ferric sulfate mineral jarosite, which forms at pH of <4 [7,11]. Such environments are thought to inhibit formation of aluminous or ferric iron clay minerals [13] although examples are known where clays co-exist with low pH settings [14]. In addition, when clays encounter low pH settings, they can lose crystallinity and become amorphous to X-rays (but not to IR) [15]. Glotch et al. [6] 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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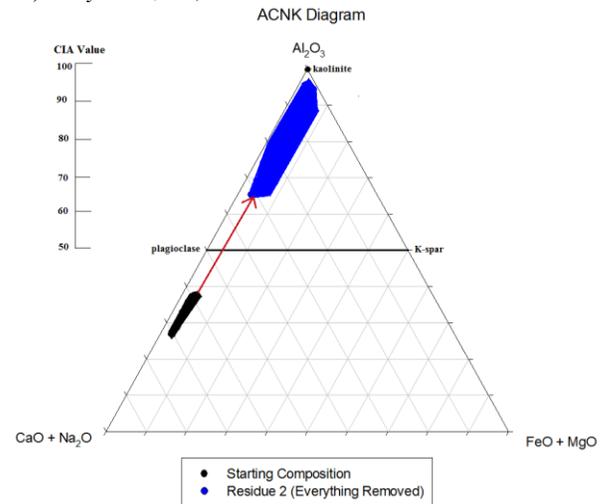


Figure 1 - Ternary diagram (ACNK) with end members Al_2O_3 , $\text{CaO} + \text{Na}_2\text{O}$, and K_2O for starting and residual compositions plotted in mole percent. $100 \cdot \text{Al} / (\text{Al} + \text{Ca} + \text{Na} + \text{K})$ represents CIA values, with Al_2O_3 apex being 100 and $(\text{CaO} + \text{Na}_2\text{O}) - \text{K}_2\text{O}$ - tie line being zero. Note the field for the sulfate-only removal is obscured behind the "Everything Removed" field. After removing known chemically precipitated minerals compositions shift to higher CIA suggesting the possibility of residual clays [6].

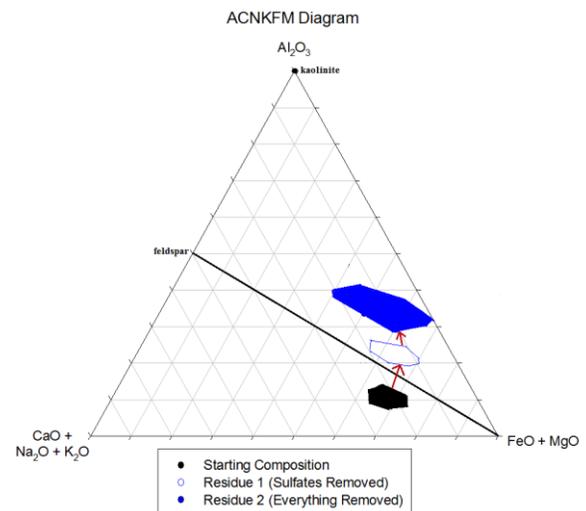


Figure 2 - Ternary diagram (ACNKFM) with end members Al_2O_3 , $\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$, and $\text{FeO}_T + \text{MgO}$ for initial, intermediate, and final residual compositions plotted in mole percent. The "unmixing" paths shift compositions to an area where secondary materials, including phyllosilicates, plot [8].