

**CONSTRAINTS ON THE MODE AND EXTENT OF SEDIMENTARY ROCK ALTERATION IN HYPER-ARID AND HYPO-THERMAL ENVIRONMENTS.** M. Salvatore<sup>1</sup>, K. Truitt<sup>2</sup>, K. Roszell<sup>2</sup>, N. Lanza<sup>3</sup>, E. Rampe<sup>4</sup>, N. Mangold<sup>5</sup>, E. Dehouck<sup>6</sup>, R. Wiens<sup>3</sup>, and S. Clegg<sup>3</sup>. <sup>1</sup>Northern Arizona University, mark.salvatore@nau.edu, <sup>2</sup>University of Michigan-Dearborn, <sup>3</sup>Los Alamos National Laboratory, <sup>4</sup>NASA Johnson Space Center, <sup>5</sup>LPG-Nantes, Université de Nantes, France, <sup>6</sup>LGL-TPE, Université de Lyon, France.

**Introduction:** Geologic evidence suggests that the surface of Mars has been dominated by cold, dry, and relatively stable environmental conditions over the past ~3.5 Ga [1]. These conditions differ from those presumed to be present prior to ~3.5 Ga, when observations indicate that the martian surface was at least intermittently able to support the prolonged flow of liquid water. Despite the more than 75% of martian history dominated by cold, dry, and stable conditions, few investigations have studied weathering and alteration processes that may influence the martian surface during this time.

[2] investigated the role of surface alteration on dolerites in the McMurdo Dry Valleys (MDV) of Antarctica (the most Mars-relevant environment on Earth), demonstrating that immature oxidative weathering products can be uniquely preserved on erosion-resistant lithologies under these cold, dry, and stable environmental conditions. However, this study did not consider the role of similar weathering processes on sedimentary lithologies, which vary significantly in their parental composition and physical properties (e.g., porosity, induration). While [3] analyzed potential oxidative weathering trends in a single sandstone from the Transantarctic Mountains, variations in alteration products or processes in different sedimentary lithologies were not considered in detail.

Might oxidative weathering be hindering our ability to determine the true chemistry and mineralogy of martian sedimentary surfaces? Is it possible that measurements of the geochemistry of brushed rock surfaces by the Mars Science Laboratory (MSL) Curiosity rover in Gale crater do not represent the true composition of the inherent rocks, but instead the products of hypo-thermal and hyper-arid oxidative weathering? To test whether such processes might be influencing sedimentary rock surfaces, we conducted a suite of chemical and mineralogical analyses on sedimentary rocks from throughout the Transantarctic Mountains [4]. Should oxidative weathering signatures significantly mask the underlying composition of these sedimentary rocks, these processes must be taken into consideration when deciphering the formation environments of sedimentary rocks on Mars. If these processes do not dominate sedimentary rock surfaces in Antarctica, however, then it is unlikely that our interpretation of martian sedimentary surface compositions are to be significantly influenced by such processes potentially occurring on Mars.

**Methods:** We collected a suite of Antarctic sedimentary rock samples from the Polar Rock Repository at the Ohio State University. In total, 178 samples were collected, which include 32 mudstones, 30 sandstones, 33 tuffs, and 26 conglomerates.

Visible/near-infrared (VNIR, 0.35 - 2.50  $\mu\text{m}$ ) and thermal infrared (TIR, ~8 - 50  $\mu\text{m}$ ) spectra were acquired from surface and interior rock fragments. VNIR data are relevant to both martian orbital (e.g., OMEGA, CRISM) and surface (e.g., Mastcam) observations, as are the acquired TIR data (e.g., THEMIS, TES, Mini-TES). Rock fragments were also analyzed using laser-induced breakdown spectroscopy (LIBS) at Los Alamos National Laboratory on the ChemCam engineering model to derive sample chemistry. Major element chemistry was also derived from powdered samples using inductively coupled plasma-optical emission spectroscopy (ICP-OES) on samples prepared using the flux fusion methodology. X-ray diffraction (XRD) was also used on both surface and interior powders to determine bulk mineralogy.

All performed analyses are directly relevant to martian orbital and surface measurements, as the purpose of this investigation is to identify significant alteration processes and products associated with cold, dry, and stable environmental conditions.

**Results:** We assess the chemical alteration of rock surfaces relative to their interiors using the Weathering Intensity Scale (WIS), which compares the behavior of monovalent cations, divalent cations, and silica [5]. This method includes the ability to identify trends in Si, which is absent from most other weathering indices (e.g., Chemical Index of Alteration, CIA). The WIS compares  $M^+$  ( $\text{Na}^+ + \text{K}^+ + 2\text{Ca}^{2+}$ ),  $R^{2+}$  ( $\text{Fe}^{2+} + \text{Mg}^{2+}$ ), and  $4\text{Si}$  ( $\text{Si}/4$ ) in a ternary diagram, where trends away/towards different apices indicate different modes of alteration.

The WIS requires knowledge of the abundance of  $\text{Fe}^{2+}/\text{Fe}_{\text{Total}}$ , which has not yet been derived for the sedimentary samples measured in this study. As a result, we refer to the work of [2], who found that igneous rocks that underwent oxidative weathering processes in the MDV have 14% more  $\text{Fe}^{3+}$  at their surfaces relative to their unaltered interiors. We assumed the same relative enrichment in  $\text{Fe}^{3+}$  at the surfaces of the sedimentary samples and assumed that, on average, the sedimentary rocks contain ~75%  $\text{Fe}^{3+}$ . These assumptions allow us to plot the WIS on a ternary diagram, where the sedimentary rocks in this study are plotted against the igneous rocks from [2] (**Fig. 1**). Mössbauer spec-

troscopy is underway to better quantify the  $\text{Fe}^{2+}/\text{Fe}_{\text{Total}}$  in these sedimentary samples.

Building upon our earlier study [4], we now recognize at least three different weathering processes occurring at the surfaces of the samples analyzed to test the hypothesis that oxidative weathering dominates the surfaces of sedimentary rocks throughout the Transantarctic Mountains (**Fig. 1**).

**Aqueous Alteration.** Traditional aqueous weathering appears to influence several of the samples analyzed in this study. These samples exhibit a trend towards the 4Si apex from their original starting compositions, indicating a preferential leaching of mobile cations relative to less mobile silica.

**Oxidative Weathering.** Oxidative weathering, as identified in Antarctic basalts, is indicated by a minor shift away from the  $\text{R}^{2+}$  apex as the abundance of monovalent cations preferentially increases relative to divalent cations, and as  $\text{Fe}^{2+}$  transitions to  $\text{Fe}^{3+}$  [2]. While some of the sedimentary samples analyzed in this study show comparable chemical trends, these processes do not dominate our suite of samples.

**Coatings/Patinas.** Unlike the Antarctic basalts, which show no evidence for coatings preserved on their surfaces, several samples analyzed in this investigation exhibit coatings or patinas that are dominated by widely different compositions than their interiors.

For example, sample PRR-25633 exhibits a significant increase (~15 wt.%) in  $\text{FeO}_T$  and an associated decrease (~13 wt.%) in  $\text{SiO}_2$  at its surface relative to its interior. LIBS measurements also show that the geochemistry measured at the rock's surface rapidly decreases with increasing depth into the sample, indicating the presence of a relatively thin surface coating. Lastly, XRD and VNIR analyses confirm the presence of goethite on the surface of this sample, which is absent from the sample interior. In **Figure 1**, this sample appears to trend significantly towards the  $\text{R}^{2+}$  apex, although this trend is almost certainly the result of the assumed  $\text{Fe}^{3+}/\text{Fe}_{\text{Total}}$  and not a representation of the actual geochemical behavior.

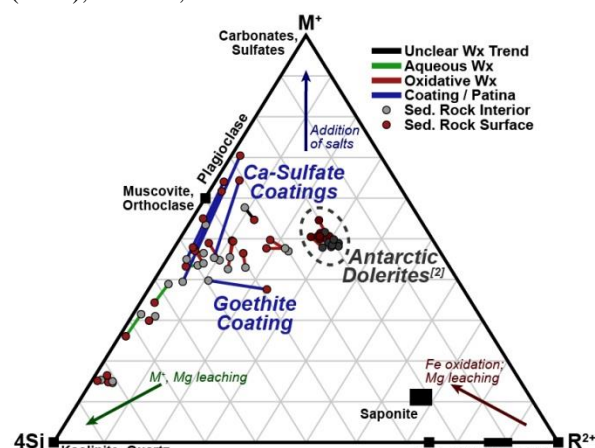
Similarly, four tuff samples show evidence for Ca-sulfate at their surfaces, as indicated by a ~4-10 wt.% increase in CaO. Although sulfur was not directly measured in our chemical analyses, the corresponding decrease in silica, the observed trend towards the  $\text{M}^+$  apex in **Figure 1**, and VNIR signatures consistent with gypsum on the surfaces of these samples support the presence of a Ca-sulfate phase.

**Discussion:** Our hypothesis that sedimentary rocks throughout the Transantarctic Mountains should be dominated by oxidative weathering processes can be confidently rejected based on the analyses performed in this investigation. It is apparent that the wide range of starting compositions, the diversity of weathering environments, and the range of rock porosity and indu-

ration all contribute to the type and extent of alteration at work on these samples, as is highlighted in **Figure 1**. Despite these different types of chemical alteration, nearly all of the measured samples (with the exception of those with coatings or patinas) do not show significantly different compositional signatures between rock surfaces and interiors, indicating that chemical weathering in cold, dry, and stable environments is limited.

These results also suggest that oxidative weathering processes are unlikely to be significant contributors to the observed spectral and compositional signatures of regions of Mars dominated by sedimentary lithologies. While surface alteration under hyper-arid and hypo-thermal conditions may be possible, it is unlikely that such alteration would complicate our interpretation of the bulk composition, or significantly alter our understanding of martian surface processes. A notable exception would be the presence of coatings or patinas, as observed in some of the Antarctic samples. While evidence for these features have been noted on the martian surface [6,7], they appear to be the exception rather than the rule, and can be successfully identified using equipment common to most Mars rovers.

**References:** [1] Bibring, J.-P., et al. (2006) *Science* **312**, 400. [2] Salvatore, M.R., et al. (2013) *GCA* **115**, 137. [3] Cannon, K.M., et al. (2015) *EPSL* **417**, 78. [4] Truitt, K., et al. (2017) *LPSC* **48**, 1243. [5] Meunier, A., et al. (2013) *AmJSci* **313**, 113. [6] Haskin, L.A., et al. (2005), *Nature* **436**, 66. [7] Lanza, N.L., et al. (2016), *GRL* **43**, 7398.



**Figure 1.** A WIS ( $\text{M}^+ - \text{R}^{2+} - 4\text{Si}$ ) ternary diagram highlighting different weathering trends in Antarctic sedimentary rock surfaces (red circles) relative to their interiors (grey circles). Interiors and surfaces of the same rock are linked, and the colors of these links represent different dominant alteration processes (see legend). Igneous dolerites from [2] are also plotted on this diagram as a reference for oxidative weathering trends. See [5] for more detailed discussions on  $\text{M}^+ - \text{R}^{2+} - 4\text{Si}$  ternary diagrams and the WIS.