

SURFICIAL CHEMICAL ALTERATION OF ANTARCTIC SEDIMENTARY ROCKS AS AN ANALOG FOR MODERN WEATHERING ON MARS. K. Truitt¹, K. Roszell¹, M. Salvatore¹, N. Lanza², E. Rampe³, N. Mangold⁴, E. Dehouck⁵, R. Wiens², and S. Clegg². ¹University of Michigan-Dearborn, msalva@umich.edu, ²Los Alamos National Laboratory, ³NASA Johnson Space Center, ⁴LPG-Nantes, Université de Nantes, France, ⁵IRAP, UPS-OMP, Université de Toulouse, France.

Introduction: Early in Mars' history, evidence suggests that warmer and wetter environments resulted in the aqueous alteration of the dominantly basaltic martian crust [1]. However, since ~3.5 Ga, Mars has been subjected to primarily cold and dry environmental conditions [1]. The most analogous geologic terrestrial environments to "modern" martian conditions are present throughout the Transantarctic Mountains (TAM), where mean annual temperatures approach -50° C and where most snowfall on ice-free landscapes sublimates prior to accumulation [2]. Previous studies have shown that oxidative weathering processes are the primary mode of surface weathering of fine-grained basaltic clasts under these unique environmental conditions [3]. With the exception of a single sandstone [4], however, the effects of oxidative weathering processes on sedimentary rocks in Antarctica has not been thoroughly investigated, despite the dominance of sedimentary lithologies at both the *Curiosity* and the *Opportunity* rover landing sites. Unlike the fine-grained basalts studied in [3], sedimentary rocks in the TAM vary significantly in terms of their composition, grain size, hardness, and porosity and permeability, all of which likely play a significant role in the production and preservation of alteration products at the rock surfaces. Here, we test the hypothesis that oxidative weathering is the dominant weathering process of sedimentary rocks in the TAM, and how Mars-relevant analytical techniques can be used to investigate these processes in situ.

Previous Work: The majority of research on chemical weathering on both Earth and Mars has been focused on aqueous alteration processes and products, as this alteration regime is most pervasive on Earth [e.g., 5-9]. The influence of predominantly anhydrous alteration processes on fine-grained basalts in the TAM was discussed by [3] and applied to remote investigations of the martian surface by [10]. In short, a strong oxidation gradient between the atmosphere and a rock interior results in the preferential migration of divalent cations to a rock's surface, where they can be easily destroyed by physical erosion [3,11]. This leads to a preferential depletion of divalent cations (CaO and MgO) and an accompanying relative enrichment in monovalent cations (Na₂O and K₂O) in alteration rinds, which is not commonly observed in aqueous alteration regimes. The work of [4] on an immature Antarctic sandstone showed similar results, with an oxidation rind penetrating several millimeters into the sample and minor chemical variations that are consistent with the preferential removal of divalent cations.

Samples: Samples were obtained from the NSF-funded Polar Rock. Samples were selected based on visual evidence for oxidative weathering and by accompanying documentation of their locations and sampling methods. In total, 178 samples were collected for analysis, including 32 mudstones, 30 sandstones, 33 tuffs, and 26 conglomerates.

Analytical Techniques: Samples were subset into small chips with both altered and unaltered faces. Powders of sample interiors and surfaces were also created using a diamond-tipped rotary drill in a method identical to [3], which has been shown to sample to a depth of ~500 μm. Major element chemistry was derived for interior and surface powders using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and the flux fusion preparation and dilution techniques described in [3,4]. Laser-induced breakdown spectroscopy (LIBS) analyses were performed at Los Alamos National Laboratory on the ChemCam engineering model. Fourteen interior and surface sample pairs were measured at three different locations using 150 pulses per location in an effort to identify compositional trends with depth. X-ray diffraction (XRD) analyses were performed at the University of Michigan using a Rigaku Ultima IV powder diffractometer on <63μm powders using a Cu- α source over a two-theta range of 3° to 65°. Visible/Near-infrared (VNIR) reflectance spectra were acquired between 0.35 and 2.50 μm using an ASD FieldSpec4 portable field spectrometer.

Results: Current analyses and results are unable to support the hypothesis that oxidative weathering is the dominant alteration mechanism acting upon the surfaces of sedimentary rocks in the TAM. Bulk chemical measurements confirm that, with few exceptions, divalent cations are more depleted than monovalent cations in sample surfaces relative to their interiors. However, some samples exhibit compositional trends that are consistent with traditional (near-neutral) aqueous alteration processes, while others show more complex relationships between their interiors and surfaces (Fig. 1).

Analyzed sedimentary rocks can be classified into three broad classes. Samples belonging to Class 1 are most consistent with oxidative weathering being the dominant alteration process acting upon sample surfaces. These rocks show minimal mineralogical variability between surfaces and interiors and minor chemical variability that is largely consistent with that observed in previous oxidative weathering studies [3,4]. Samples in Class 2 show surface alteration that is more consistent with aqueous alteration of rock surfaces, including mineralogical evidence for hydrated phases in sample sur-

faces (relative to their interiors), chemical compositions that trend in the general direction of more aqueously modified compositions, and/or spectral signatures indicative of hydrated mineral phases at the rock surfaces. Lastly, samples in Class 3 appear to have undergone unique alteration processes that are not prevalent in other studied samples. For example, PRR-25633 (welded tuff) shows significant enrichment of FeO_T and depletion of SiO_2 at its surface, while VNIR spectra confirm the presence of goethite at the surface but not in the interior. Sample PRR-12393 (mudstone) shows a unique spectral and compositional trend that indicates an enrichment of gypsum in the rock's interior and depletion at the rock's surface. The "bleached" appearance at the sample's surface is consistent with previous studies [12] and may indicate the combined effects of oxidative weathering and ultraviolet radiation.

While LIBS analyses of rock surface fragments relative to their interiors were generally consistent with the ICP-derived bulk surface and interior chemistries, we did not observe any definitive evidence for surface alteration (including rinds or coatings) that vary with depth. One sample (PRR-20642, broadly classified as a conglomerate) did show a potential Fe enrichment in the first ~10 LIBS spectra that is not reflected in the bulk chemical analyses (Fig. 2), but such observations are still being investigated in terms of their validity.

Discussion: Our preliminary results suggest that the alteration processes acting upon rocks in the cold and dry TAM can result in disparate patterns of compositional variability between sedimentary rock interiors and surfaces. These different patterns are likely the result of differing alteration histories, amounts of physical erosion, and inherent lithologic properties, including porosity, permeability, and hardness. The overall compositions of the clasts do not appear to have a systematic influence on the observed alteration trends.

Caution must be taken when comparing a range of analytical techniques, as each method is sensitive to a unique depth of sampling or penetration. In addition, there was no control over sample collection, as they were collected by numerous investigators for different investigations. It is unknown whether these samples represent archetypal weathering patterns or whether these samples represent anomalously weathered or unweathered endmembers. In all likelihood, the climatic stability of the TAM has likely prevented any sample from interacting with large quantities of liquid water.

Application to Mars: This work is part of a broader study to investigate the influence of "modern" martian climatic conditions on the observed composition and signatures of rocks in Gale crater by the *Curiosity* rover. Elemental trends consistent with oxidative weathering have been observed in the sedimentary landscape of Meridiani Planum [4,13], and understanding how LIBS, XRD, VNIR spectroscopy, and bulk chemistry measurements of sedimentary samples weathered in the Ant-

arctic environment have direct implications for measurements by the ChemCam, CheMin, Mastcam, and APXS instruments on *Curiosity*, respectively. Without this improved understanding, the ability to remotely assess the true compositional nature of rocks on Mars may be significantly hindered if oxidative weathering is not identified, characterized, and divorced from the underlying mineralogical and geochemical signatures.

References: [1] Bibring J.-P. et al. (2006) *Science*, 312, 400. [2] Faure G. and Mensing T.M. (2010) *The Transantarctic Mountains*, Springer. [3] Salvatore M.R. et al. (2013) *GCA*, 115, 137. [4] Cannon K.M. (2015) *EPSL*, 417, 78. [5] Harnois L. (1988) *Sed. Geol.*, 55, 319. [6] Nesbitt H.W. and Wilson R.E. (1992) *Am. J. Sci.*, 292, 740. [7] Lasaga A.C. et al. (1994) *GCA*, 58, 2361. [8] Hurowitz J.A. and McLennan S.M. (2007) *EPSL*, 260, 432. [9] McLennan S.M. (2012) *SEPM* 102, 119. [10] Salvatore M.R. et al. (2014) *EPSL*, 404, 261. [11] Cooper R.F. et al. (1996) *GCA*, 60, 3253. [12] Tasch P. and Gafford E.L. (1968) *J. Sed. Petrol.*, 39, 369. [13] Knoll A.H. et al. (2008) *JGR*, 113.

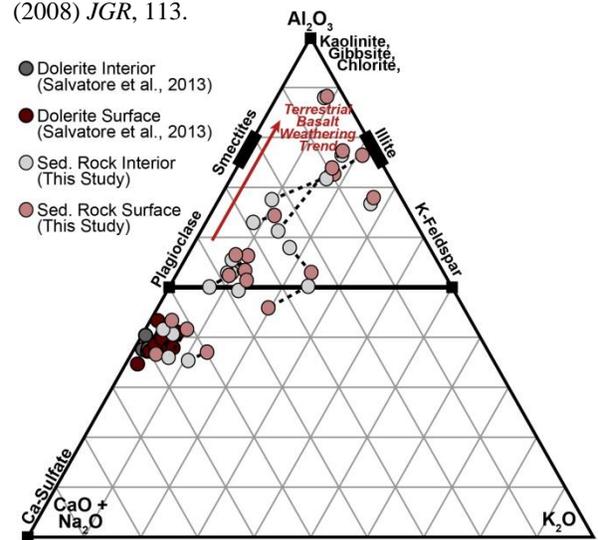


Fig. 1. Al_2O_3 - $\text{CaO}+\text{Na}_2\text{O}$ - K_2O (A-CN-K) diagram of the bulk chemistry of all sedimentary rock surface and interior pairs, and compared to trends in basalts (dolerites) from [3]. A typical terrestrial basaltic alteration pathway is indicated in maroon. The observed trends highlight the complexity of the alteration signatures.

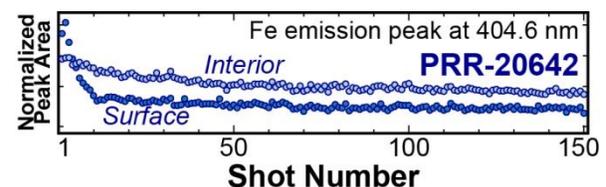


Fig. 2. Normalized peak area measurements of the 404.6 nm Fe peak for two sample interior and surface pairs. The greater peak areas for PRR-25633 are consistent with bulk chemical analyses, while the PRR-20642 LIBS data display an opposite relationship. LIBS sampling depths are <0.2 mm for 150 laser shots.