

OXIDATIVE WEATHERING ON MARS AND IMPLICATIONS FOR CHEMICAL ALTERATION DURING THE AMAZONIAN EPOCH. M. R. Salvatore¹, J. F. Mustard¹, J. W. Head¹, R. F. Cooper¹, D. R. Marchant², and M. B. Wyatt¹, ¹Department of Geological Sciences, Brown University, Providence, RI, USA, Mark_Salvatore@brown.edu, ²Department of Earth Sciences, Boston University, Boston, MA, USA.

Introduction: Martian low albedo terrains exhibit a variety of visible/near-infrared (VNIR) and thermal infrared (TIR) spectral properties. This diversity has been attributed to variations in both the primary (unaltered) and secondary (altered) mineral phases. However, these proposed compositional variations are often incongruous between wavelength regions, which are sensitive to different physical and compositional properties of the materials under investigation. Ideally, both the VNIR and TIR spectral regions should be in accordance when investigating the composition of the martian surface.

Characterization of oxidative weathering processes in Beacon Valley of the McMurdo Dry Valleys (MDV) of Antarctica [1] reveals VNIR and TIR spectral signatures that are consistent with spectral signatures observed across the martian surface [2]. This alteration process yields diagnostic morphological, chemical, and spectral signatures that represent the oxidation of ferrous iron as a result of an outward migration of divalent cations [3]. The alteration process is driven by the presence of an oxidation gradient between the rock interiors and the surrounding oxidizing environment.

In this study, we report the initial results from modified TIR unmixing models of martian low albedo terrains using a customized endmember library that is consistent with regional VNIR spectroscopy. We first summarize the pioneering spectral investigations that established our current understanding of martian surface compositions. We show how these new results provide a consistent interpretation of VNIR and TIR data, and we conclude with the implications of these results and the outstanding questions that remain.

Summary of Previous Studies: Global TIR spectroscopic studies using the Thermal Emission Spectrometer (TES) instrument identified two unique spectral shapes: Surface Type 1 (ST1) and 2 (ST2). They were interpreted to represent basaltic and andesitic surfaces, respectively [4]. Since this initial identification, the conclusion that ST1 spectral features are due to largely unaltered basalts has remained the preferred interpretation, while the nature of ST2 has been widely debated. Weathered basalt was first proposed as an alternate hypothesis by [5], who demonstrated that the TIR spectra of smectites are similar to the high-Si andesites. Other critical work demonstrated that similar spectral shapes could be produced through the presence of micron-thick amorphous silica coatings [6], palagonite [7], zeolites [8], Al- or Fe-rich opaline silica [9], Si-rich mineraloids [9], and allophane [10], showing that a variety of materials can fit these TIR spectral signatures. However, difficulty arose

in matching these TIR spectral analogs with comparable VNIR measurements. Additionally, each proposed alteration phase requires unique environmental conditions that are often at odds with our current understanding of martian climatic evolution [e.g., 11].

The first high-resolution global VNIR surface observations were made by the Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité (OMEGA) instrument onboard Mars Express. These data were used to identify a range of both primary and secondary mineral phases [12], and regional low albedo terrains were shown to exhibit only variations in primary mineral composition and in spectral slope [13]. Notably, regions defined as ST2 by the TES instrument lack the molecular vibrations associated with hydrated mineral phases, raising questions about the nature of the alteration phases put forward to explain ST2.

Oxidative Weathering Analog: The products of oxidative weathering represent the initial stages of chemical alteration. Due to the hyper-arid and hypo-thermal conditions [14] present in Beacon Valley, Antarctica, this early stage of chemical alteration is uniquely preserved in a metastable state. Spectrally, oxidative weathering tends to slightly weaken mineral signatures in the VNIR while sometimes imposing a negative spectral slope (Fig. 1a). In the TIR, these products mimic the spectral shape of some mature alteration products and high-Si phases previously identified on the martian surface [1,5-10] (Fig. 1b). Accordingly, oxidative weathering products are soundly consistent with martian spectral datasets in both the VNIR and TIR spectral ranges. This consistency, as well as the oxidizing, hyper-arid, and hypo-thermal conditions that characterize Mars during the Amazonian [11], makes oxidative weathering a viable analog process that warrants further consideration and investigation.

TIR Linear Unmixing: TES TIR emission spectra for nine classic martian low albedo regions [15] were studied using a customized spectral endmember library. Excluded from this library are secondary mineral phases that, while appropriate for fitting and modeling in the TIR, are not detected in VNIR data over the same spatial extents (e.g., zeolites, high-Si hydrated glasses, and smectites). Instead, a TIR spectrum of Antarctic oxidation products is included in the library because its consistency between both the VNIR and TIR spectral ranges.

TES data were unmixed over the spectral range of 350–1300 cm^{-1} , excluding the opaque atmospheric CO_2 region centered near 670 cm^{-1} . These new unmixing models exhibit good spectral fits (average root-mean-square (RMS) error of 0.122%) and the oxidative altera-

tion component is modeled with abundances between 14–37% (average modeled abundance of 27.9%). Other modeled mineral constituents are in good agreement with previous VNIR [13] and TIR [15] analyses.

Complete linkage hierarchical clustering (Table 1) of the modeled clinopyroxene (CPX), orthopyroxene (OPX), olivine (OLV), plagioclase (PLG), and alteration rind (RIND) abundances of these nine spectral shapes yields similar clusters to those originally reported in [15]. While proportions of the other modeled minerals are somewhat variable, RIND is largely substituted for high-Si phases, indicating that different compositional interpretations are required. The distribution of these different spectral classes across the martian surface (Fig. 2) provides new insight into both the primary surface composition as well as the abundance of oxidative alteration products present on the surface.

Discussion and Predictions: The identification of oxidative weathering processes and products in the MDV of Antarctica provides an appropriate analog for Amazonian alteration on the martian surface. This alteration produces spectral features that are consistent with both the VNIR and TIR spectral properties observed in martian low albedo terrains. A better understanding of these spectral features enables future studies to progress beyond this initial characterization to more definitively determine primary mineralogy and the distribution and nature of regional-scale alteration products. For instance, how does this new analog affect the modeled plagioclase/pyroxene ratio across the martian surface, and what are the resultant implications for volcanic evolution?

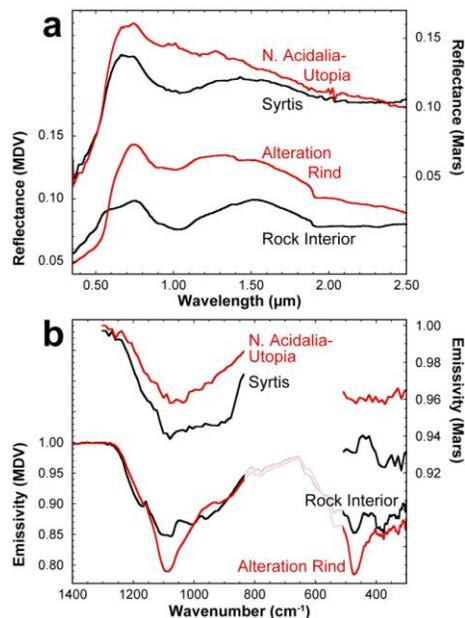


Fig. 1. (a) VNIR and (b) TIR spectra of representative martian terrains and unaltered (black) and altered (red) Antarctic rocks of basaltic composition.

Table 1. Modeled contributions of CPX, OLV, and RIND to the five clustered spectral classes derived in this study: Gr. 1 (N. Acidalia-Utopia, Aonium-Phrxi), Gr. 2 (Sirenum, Hesperia, Meridiani), Gr. 3 (Solis), Gr. 4 (Cimmeria-Iapygia, Tyrrhena), Gr. 5 (Syrtis).

	Gr. 1	Gr. 2	Gr. 3	Gr. 4	Gr. 5
CPX	Low	Mid	Mid	High	High
OLV	Low	Mid	Low	Mid	Low
RIND	High	Mid	Mid	Low	Low

Landed platforms, including the Mars Science Laboratory, can further test the hypothesis that oxidative alteration is widespread. Globally and regionally derived surface materials should consist primarily of unaltered igneous minerals, potentially large amounts of amorphous and poorly crystalline materials (primarily anhydrous), and Fe³⁺ dominating the iron-bearing materials. Hydrated alteration products not related to oxidation, however, are likely present in localized outcrops, particularly at the Gale Crater landing site, which was selected for investigation based on the orbital identification of these hydrated mineral species.

The substantial spectral contribution from oxidative weathering products across the martian surface suggests that Mars has been dominated by cold and dry environmental conditions throughout the Amazonian epoch. If warmer and wetter conditions were present for prolonged episodes since the exposure of these surfaces, more mature alteration phases would be expected. However, the absence of these phases at spectrally observable quantities (~10% areal abundance) verifies that warmer and wetter conditions were not sustained on the surface.

References: [1] Salvatore M. R. et al. (2013), *GCA*, under review. [2] Salvatore M. R. et al. (2012), *AGU Fall Mtg.*, abs. P11F-06. [3] Cooper R. F. et al. (1996), *GCA*, 60, 3253. [4] Bandfield J. L. et al. (2000), *Science*, 287, 1626. [5] Wyatt M. B. & McSween Jr. H. Y. (2002), *Nature*, 417, 263. [6] Kraft M. D. et al. (2003), *GRL*, 30, doi:10.1029/2003GL018848. [7] Morris R. V. et al. (2003), *LPSC XXXIV*, abs.#1874. [8] Minitti M. E. & V. E. Hamilton (2010), *Icarus*, 210, 135. [9] Michalski J. R. et al. (2005), *Icarus*, 174, 161. [10] Rampe E. B. et al. (2012), *Geology*, 40, 995. [11] Bibring J.-P. et al. (2006), *Science*, 312, 400. [12] Bibring J.-P. et al. (2005), *Science*, 307, 1576. [13] Mustard J. F. et al. (2005), *Science*, 307, 1594. [14] Marchant D. R. & Head J. W. (2007), *Icarus*, 192, 187. [15] Rogers A. D. & Christensen P. R. (2007), *JGR-P*, 112, doi:10.1029/2006JE002727.

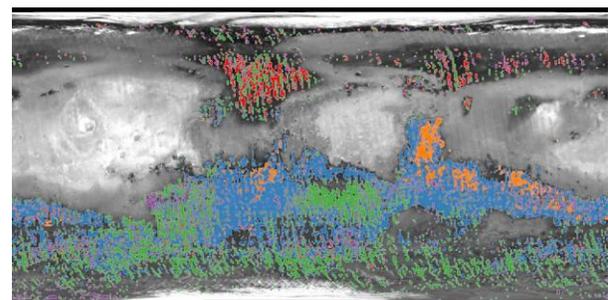


Fig. 2. The geographic distribution of the five spectral classes identified in this study: Gr. 1 (red), Gr. 2 (blue), Gr. 3 (green), Gr. 4 (purple), and Gr. 5 (orange).