

**CHARACTERIZING WIDESPREAD OXIDATION PROCESSES ON MARS: ALTERATION RIND DEVELOPMENT AND EFFECTS ON SPECTROSCOPIC INVESTIGATIONS.** M. R. Salvatore<sup>1</sup>, J. F. Mustard<sup>1</sup>, J. W. Head<sup>1</sup>, R. F. Cooper<sup>1</sup>, D. R. Marchant<sup>2</sup>, and M. B. Wyatt<sup>1</sup>. <sup>1</sup>Brown University, Dept. of Geol. Sci., Providence, RI, USA, Mark\_Salvatore@brown.edu, <sup>2</sup>Boston University, Dept. of Earth Sci., Boston, MA, USA.

**Introduction:** The martian surface is composed largely of minimally altered basalts that have been exposed to predominantly hyper-arid, hypo-thermal, and oxidizing conditions. The physical and chemical interaction between basalts and this environment has not been fully explored in the past. What is the specific process of alteration and its resulting products and how might they be identified and studied on the martian surface? In this study, we investigate the hyper-arid and hypo-thermal alteration processes in the McMurdo Dry Valleys (MDV) of Antarctica, where a “Mars-like” lithology (the Ferrar Dolerite) [1] has been weathering under “Mars-like” conditions [2] for millions of years. As a result of this process, alteration rinds and oxide coatings are predicted to form and can influence the interpretation of rock surfaces using remote spectral datasets. The identification of alteration rinds and coatings on rocks across the martian surface [e.g., 3-5] may indicate the widespread occurrence of such processes.

**Antarctic Field Work and Laboratory Analyses:**

*Sample Collection and Preparation.* Fourteen samples were collected along an age transect through central Beacon Valley [6]. Rock chips were created for spectroscopic and morphologic investigations. Powders of sample interiors and rinds were created for mineralogical and chemical analyses using a diamond-tipped rotary drill; depth of rind sampling was confined to the uppermost 200  $\mu\text{m}$  of the sample surface. Morphological investigations include optical microscopy, transmission electron microscopy, and scanning electron microscopy. Mineralogical investigations include visible/near-infrared (VNIR) reflectance and mid-infrared (MIR) emission spectroscopy, X-ray diffraction, and Mössbauer spectroscopy. Chemical investigations include inductively coupled plasma atomic emission spectroscopy via flux fusion and electron microprobe analyses.

*Signatures of Alteration.* Alteration rinds were observed on all fourteen dolerite samples. These rinds are defined as an oxidized outer layer that seamlessly transition into the unaltered rock interiors with the original crystal structure still largely preserved. None of the rinds appear as depositional coatings, confirming that they are not the result of simple chemical precipitation but represent the products of an internal reaction.

Mineralogical and chemical analyses along transects from the unaltered interiors to the exterior rinds document little change in bulk chemistry and mineralogy. The largest observed change is a  $\sim 10\%$  increase in  $\text{Fe}^{3+}/\text{Fe}_{\text{Total}}$ . This is clearly observed in visible/near-

infrared spectroscopy and quantified using Mössbauer spectroscopy.  $\text{Fe}^{3+}$  is either present as a nanophase component or in the primary crystal structures. MIR emission spectroscopy also suggests an increase in amorphous aluminosilicate components in the rinds relative to their interiors with increasing rind development.

VNIR spectroscopy shows considerable variation between rock surfaces and interiors that include an increase in overall albedo and a deep absorption feature in the visible wavelengths caused by the presence of optically significant  $\text{Fe}^{3+}$ . MIR spectroscopy shows a weakening of spectral signatures associated with primary mafic minerals (plagioclase, pyroxene) and a strengthening of narrow absorptions centered near  $1100\text{ cm}^{-1}$  and  $470\text{ cm}^{-1}$  that are associated with amorphous aluminosilicates. These strong spectral signatures associated with oxidation-driven alteration are intriguing in that they are not representative of significant chemical or mineralogical changes but are diagnostic of alteration in cold and dry environments. Consequently, this becomes an indicator for interpreting surface compositions using VNIR through MIR spectroscopy. Additional work focused around transmission electron microscopy is underway to investigate the relationship between these observed spectral signatures and the alteration processes.

*Alteration Process Characterization.* Given the oxidation-potential difference between the dolerite interiors and the terrestrial atmosphere, oxidation can be effected by the migration of relatively mobile cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) to the free surface, where they react with atmospheric  $\text{O}_2$  to form soluble oxide species; this ion flux is compensated by a concurrent flux of electrons, which is manifested in the local conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (Fig. 1). These electrons, too, provide the charge necessary for ionization of the atmospheric  $\text{O}_2$  [7]. This process most efficiently dissipates the Gibbs energy despite causing significant and distinctly metastable textural changes in the process.

The present internal reaction fronts represent distinct metastable reactions that occur due to a surplus of  $\text{Fe}^{3+}$  caused by the inward migration of electron holes. Multiple oxidation fronts can form as a function of locally exceeding an  $\text{Fe}^{3+}$  oxidation buffer within the rock and relative cation mobility (Fig. 1). The lack of preserved soluble oxide species on sample surfaces throughout Beacon Valley is likely due to a combination of aeolian abrasion and aqueous dissolution, mobilization, and deposition in the regolith during transient episodes

when liquid water is present [2]. Additionally, very little cation leaching is required to produce the observed spectral and chemical variations; the precise amount necessary is a topic of current investigation.

**Martian Observations and Implications:** The oxidation potential between martian basalts [8] and the martian atmosphere creates a similar dynamic response to that observed in Beacon Valley, resulting in widespread oxidation. VNIR reflectance spectroscopy of martian low albedo terrain confirms the ubiquity of nanophase iron oxides and minimally altered basaltic terrains [9,10]. Similarly, MIR emission spectroscopy of low albedo surfaces are best modeled as largely unaltered basalts with variable contributions of amorphous aluminosilicate materials, particularly at high latitudes [11]. These spectral signatures are analogous to the altered dolerite surfaces found in Beacon Valley, which imply that oxidation-driven alteration processes may be an important contributor to many of the spectral signatures observed on Mars.

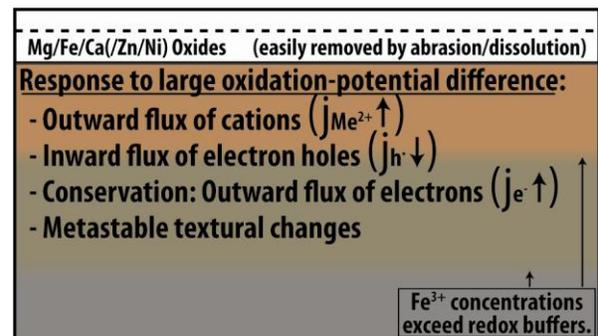
Alteration rinds of varying morphology were directly observed on both Humphrey and Mazatzal, two picritic basalts in the plains of Gusev Crater analyzed by the Mars Exploration Rover *Spirit* [12]. The alteration rind on Mazatzal appears to be a complex depositional rind that completely masks the underlying lithology, while the rind on Humphrey is more analogous to those observed in Antarctica where soluble coatings may have been remobilized by environmental processes. Observations of both rocks, however, are largely consistent with products of oxidation-driven alteration. The ventifacted nature of Mazatzal may have hindered aeolian abrasion during recent episodes of alteration, thus preserving these delicate layers. On the other hand, the upright nature of Humphrey may result in the effective scouring of deposited materials and preservation of solely the oxidized rind. VNIR spectra from the Pancam on *Spirit* also show a ferric iron absorption in the visible wavelengths and an increased albedo in the NIR on both rocks, consistent with our observations of altered dolerites in Beacon Valley.

As shown in Beacon Valley, oxidation-driven alteration and subsequent redistribution of weathered materials can dominate the observed spectral signatures. Additionally, subaerially altered materials on Mars were likely to have been subjected to oxidation processes prior to aqueous alteration. Such a scenario could substantially modify the starting compositions that were subsequently altered and could influence models of aqueous alteration.

**Future Work:** Investigating the link between spectroscopy and the oxidation-driven alteration processes observed in Beacon Valley is vital towards understanding the relationship between remote observations and physical, chemical, and mineralogical properties of pla-

netary surfaces. Additional laboratory measurements, including laser-induced breakdown spectroscopy and transmission electron microscopy will be utilized to detail the chemical and physical changes that occur within alteration rinds. Analyses of brushed and ground rock surfaces from the Mars Exploration Rovers may hold valuable information regarding the nature and extent of oxidation and alteration, and future work will utilize these data to investigate such processes. Ultimately, upon landing in Gale Crater, the Mars Science Laboratory will be well equipped to investigate alteration processes and products using its scientific payload. The preservation of these alteration products on the martian surface can provide valuable information regarding the rate of oxidation, the antiquity and stability of the surface, the erosive nature of the current martian atmosphere, and the composition of the underlying materials.

**References:** [1] Harvey, R. P. (2001), *Martian Highlands & Mojave Desert Wkshp.*, 25-26. [2] Marchant, D. R. & J. W. Head (2007), *Icarus*, 192, 187-222. [3] McSween, H. Y. et al. (1999), *JGR*, 104, 8679-8716. [4] Knoll, A. H. et al. (2008), *JGR*, 113, doi:10.1029/2005JE002477. [5] Haskin, L. A. et al. (2005), *Nature*, 436, 66-69. [6] Marchant, D. R. et al. (2007), *LPSC*, 38, abs. 1895. [7] Cooper, R. F. et al. (1996), *GCA*, 60, 3253-3265. [8] Herd, C. D. K. et al. (2002), *GCA*, 66, 2025-2036. [9] Bell, J. F. (1992), *Icarus*, 100, 575-597. [10] Morris, R. V. et al. (2000), *JGR*, 105, 1757-1817. [11] Wyatt, M. B. & H. Y. McSween Jr. (2002), *Nature*, 438, 623-627. [12] McSween, H. Y. et al. (2006), *JGR*, 111, doi:10.1029/2005JE002477.



**Fig. 1.** A sketch of the oxidation-driven alteration process. A layer of oxides is created as cations ( $Me^{2+}$ ) and electrons ( $e^-$ ) diffuse to the free surface in response to the large oxidation-potential difference. Electron holes ( $h^{\cdot}$ ), manifested as  $Fe^{3+}$ , diffuse into the rock to counter this cation flux. This process results in the local concentration of  $Fe^{3+}$  exceeding different redox buffers, creating the observed oxidation fronts. Environmental processes, including aeolian abrasion and aqueous dissolution, can easily remove the surficial oxide layers, as is observed in Beacon Valley.