

**CHARACTERIZATION OF SYNTHETIC AND NATURAL MANGANESE OXIDES AS MARTIAN ANALOGUES.** V.K. Fox<sup>1</sup>, R.E. Arvidson<sup>1</sup>, B.L. Jolliff<sup>1</sup>, P.K. Carpenter<sup>1</sup>, J.G. Catalano<sup>1</sup>, M.A.G. Hinkle<sup>1</sup>, and R.V. Morris<sup>2</sup> <sup>1</sup>Washington University, Saint Louis, Missouri (foxv@levee.wustl.edu) <sup>2</sup>NASA Johnson Space Center, Houston, TX

**Introduction:** Recent discoveries of highly concentrated manganese oxides in Gale Crater [1,2] and on the rim of Endeavour Crater [3] by the Mars Science Laboratory Curiosity and Mars Exploration Rover Opportunity, respectively, imply more highly oxidizing aqueous conditions than previously recognized. Manganese oxides are a significant environmental indicator about ancient aqueous conditions, provided the phases can be characterized reliably. Manganese oxides are typically fine-grained and poorly crystalline, making the mineral structures difficult to determine, and they generally have very low visible reflectance with few distinctive spectral features in the visible to near infrared, making them a challenge for interpretation from remote sensing data [4]. Therefore, these recent discoveries motivate better characterization using methods available on Mars, particularly visible to near infrared (VNIR) spectroscopy, X-ray diffractometry (XRD), and compositional measurements. Both rovers have complementary instruments in this regard. Opportunity is equipped with its multispectral visible imager, Pancam, and an Alpha Particle X-ray Spectrometer (APXS), and Curiosity has the multispectral Mastcam, ChemCam (laser-induced breakdown spectroscopy and passive spectroscopy), and APXS for in situ characterization, and ChemMin (XRD) for collected samples.

**Characterization Methods:** This study presents initial detailed laboratory analyses of a variety of manganese oxide minerals, including synthesized pure specimens and naturally occurring mixed-phase samples. VNIR spectra were collected on silt-sized powders using an ASD field spectrometer from 0.4 to 2.5 micrometers. X-ray diffraction measurements were acquired for these samples using a Bruker D8 Advance powder diffractometer and the ICDD XRD pattern database to confirm or determine mineral phases. Preliminary measurements were collected on a subset of the natural samples using an Edax Orbis Micro X-ray fluorescence spectrometer to obtain elemental chemistry and spatial variations therein.

**Natural Samples.** Traditionally, manganese mineral samples have been called “Pyrolusite” or “Psilomelane” on the basis of physical appearance rather than actual mineralogical composition, because these dark and poorly crystalline minerals are difficult to identify visually. Therefore, labels, particularly those predating modern analytical techniques, are generally less informative or accurate than desired. Samples from Washington University’s reference mineral collection were selected for in-depth characterization

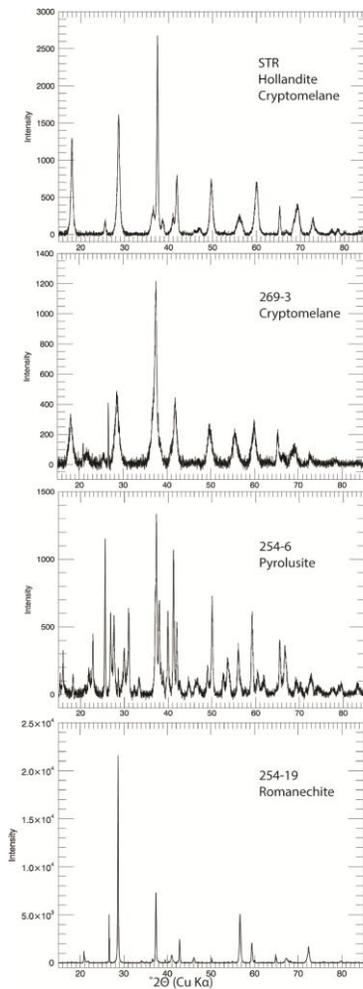
and were chosen to characterize a range of naturally occurring phases and provide data to complement the spectral reflectance measurements. Both “pyrolusite” and “psilomelane” samples were selected for characterization, and included crystalline growths, botryoidal masses and dendritic coatings, as well as amorphous coatings or masses. Results presented here are examples of relatively pure phases as determined by XRD measurements (Figure 1), although most are best characterized as mixed-phase. Characteristically dark VNIR spectra are shown in Figure 2.

**Synthetic Samples.** The naturally occurring samples were also compared to synthetically generated manganese oxide phases to establish expected spectral behavior of pure end members. These phases include pyrolusite ( $\beta\text{-Mn}^{4+}\text{O}_2$ ), bixbyite ( $\alpha\text{-Mn}^{3+}_2\text{O}_3$ ), hausmannite ( $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$ ), vernadite ( $\text{Na}_{0.2}\text{Mn}^{4+}_{0.95}\text{O}_2 \cdot n\text{H}_2\text{O}$ ) and both triclinic and hexagonal birnessite ( $(\text{Na,Ca,K})_x(\text{Mn}^{4+},\text{Mn}^{3+})_2\text{O}_4 \cdot n\text{H}_2\text{O}$ ) [5]. These minerals represent a range of Mn mineral structures, oxidation states, and common formation environments. XRD measurements confirmed mineral phases (Figure 3), and VNIR spectra are shown in Figure 4. The powders are all dark black to dark grey, although hausmannite is dark reddish-brown. The phyllo-manganates (birnessite and vernadite) have absorption features at 1.9 micrometers that are characteristic of water within the mineral structure.

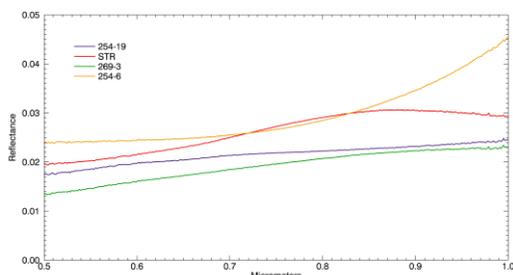
Comparisons of the spectra of the synthetic samples to Pancam multispectral data (13 bands from ~0.4 to 1.0 micrometers) collected by Opportunity of Mn oxide bearing rocks Pinnacle and Stuart Islands demonstrate that the dark coatings on these rocks are a mixed high valence Mn oxides. These discoveries bolster support for widespread aqueous activity throughout the rim of Endeavour crater, and may be components of widespread mineralization occurring as reduced groundwater contacted an oxidizing surface [3].

**Future Work:** The data generated by our laboratory measurements will be used to further inform interpretations of recent and future discoveries of high concentrations of Mn by both Opportunity and Curiosity. The Noachian crater rim that Opportunity continues to explore and the fluvial lacustrine deposits that Curiosity is investigating bear significant evidence for aqueous alteration. Better understanding the chemistry and mineralogy of observed deposits improves our understanding of the role of aqueous processes present on ancient Mars, strengthening our interpretations of the environmental conditions at the time and the poten-

tial for habitable environments.

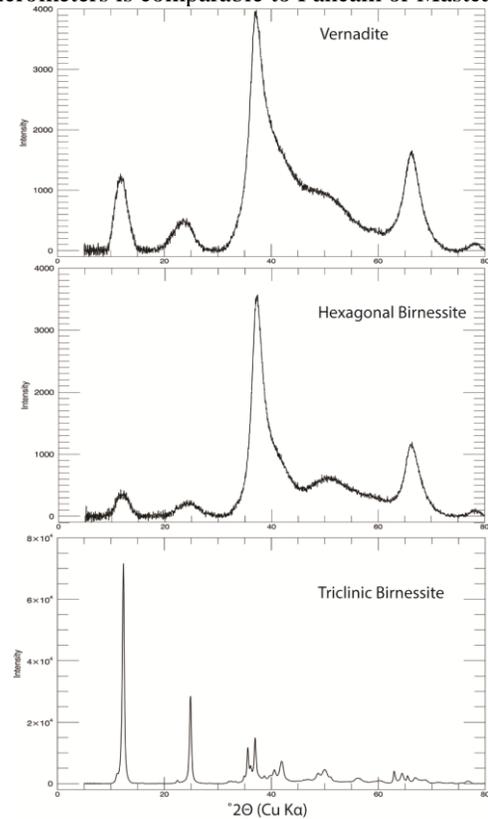


**Figure 1:** X-ray diffraction patterns from four naturally occurring manganese oxides. These samples are dominantly single phase, although all likely have minor secondary components. Sample STR matches with both hollandite ( $Ba_x(Mn^{4+}, Mn^{3+})_8O_{16}$ ) and cryptomelane ( $K_x(Mn^{3+}Mn^{4+})_8O_{16}$ ). Sample 269-3 matches cryptomelane. Sample 254-6 matches well with pyrolusite; Sample 254-19 matches with romanechite ( $Ba_{.66}(Mn^{4+}, Mn^{3+})_5O_{10} \cdot 1.34 H_2O$ ).

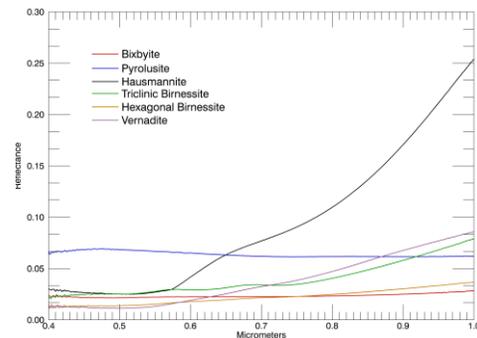


**Figure 2:** VNIR spectra of the same four naturally occurring samples as shown in Figure 1. All the pow-

ders are a very dark grey color, and very low visible reflectance. The wavelength range shown from 0.4 to 1.0 micrometers is comparable to Pancam or Mastcam.



**Figure 3:** XRD patterns of the laboratory synthesized phyllosilicates, also shown in Figure 4. Mixed valence phyllosilicates are considered a possible analogue for observations on Mars.



**Figure 4:** VNIR spectra of synthetic manganese oxides, representing a range of oxidation states, including mixed valences. In the visible wavelengths, all samples have very low reflectance, though hausmannite is reddish.

**References:**

- [1] Lanza, N. et al (2014) GRL. [2] Lanza, N. et al. (in review) Nature Geoscience. [3] Arvidson, R.E., et al (in review) Nature Geoscience. [4] Post, J.E., (1999) *Proc. Natl. Acad. Sci.* 96, 3447–3454. [5] Hinkle, M.A.G. (2014) PhD dissertation, Washington University in Saint Louis.