VISIBLE AND NEAR-IR REFLECTANCE SPECTRA FOR SMECTITE, SULFATE AND PERCHLORATE UNDER DRY CONDITIONS FOR INTERPRETATION OF MARTIAN SURFACE MINERALOGY. R. V. Morris[1], D. C. Golden[2], D. W. Ming[1], T. G. Graff[2], R. E. Arvidson[3], S. M. Wiseman[3], K. A. Lichtenberg[3], and S. Cull[3]. [1]ARES NASA Johnson Space Center, Houston TX 77058 (richard.v.morris@nasa.gov), [2]ESCG-JW23, Houston, TX, [3]Washington University, St. Louis, MO.

Introduction: Visible and near-IR (VNIR) spectral data for the martian surface obtained from orbit by the MRO-CRISM and OMEGA instruments are interpreted as having spectral signatures of H_2O/OH-bearing phases, including smectites and other phyllosilicates, sulfates, and high-SiO_2 phases [e.g., 1-4]. Interpretations of martian spectral signatures are based on and constrained by spectra that are obtained in the laboratory on samples with known mineralogical compositions and other physicochemical characteristics under, as appropriate, Mars-like environmental conditions (e.g., temperature, pressure, and humidity). With respect to environmental conditions, differences in the absolute concentration of atmospheric H_2O can effect the hydration state and therefore the spectra signatures of smectite phyllosilicates (solvation H_2O) and certain sulfates (hydration H_2O) [e.g., 5-7].

We report VNIR spectral data acquired under humid (laboratory air) and dry (dry N_2 gas) environments for two natural smectites (nontronite API-33A and saponite SapCa-1) to characterize the effect of solvation H_2O on spectral properties. We also report spectral data for the thermal dehydration products of (1) melanterite ($FeSO_4.7H_2O$) in both air and dry N_2 gas and (2) Mg-perchlorate ($Mg(ClO_4)_2.6H_2O$) in dry N_2 environments. Spectral measurements for samples dehydrated in dry N_2 were made without exposing them to humid laboratory air.

Methods: VNIR reflectivity spectra (0.35-2.50 µm) were acquired with Analytical Spectral Devices (ASD) fiberoptic spectrometers configured with Mug lights. A FieldSpec3 Hi-Res spectrometer was used for measurements in laboratory air at ~25°C. A FieldSpec3 spectrometer, a hot plate (ambient to 400°C), and a dewpoint meter (Vaisala DRYCAP DM70) were co-located in a one-atmosphere glove box that can be kept under continuous purge using dry N_2 gas (from liquid N_2) to provide a dry atmosphere. Spectral measurements on samples in the glove box were made in air (8000-12000 ppm H_2O by volume) prior to starting the N_2 purge, after purging 24-650 hr at ~25°C (150-400 ppm H_2O or 0.5-2.0% relative humidity), and, depending on the sample, after heating to 50-330°C on the hot plate and cooling to ~25°C. Because H_2O evolves during heating, the time at temperature was governed by the time required for the H_2O content of the gas atmosphere to return to <400 ppm.

Powder X-ray diffraction spectra (PANalytical X'Pert PRO) were obtained under ambient conditions for all samples within 5-10 min and ~1 hr after their removal from the glove box or after thermal treatment in air to determine mineralogical composition and phase stability.

Results and Discussion:

Nontronite and Saponite. Dehydration of nontronite and saponite under hyper-arid conditions results in a dramatic decrease in intensity of spectral features that require the presence of only the H_2O molecule (e.g., at ~1.9 µm) relative to those that require the presence of only M-OH (e.g., at 2.29 and 2.31 µm for nontronite (M = Fe) and saponite (M = Mg), respectively (Fig. 1)). All M-OH spectral features between 2.0 and 2.5 µm are also better resolved with increasing loss of solvation H_2O. Spectral features that are composites of H_2O-only and M-OH-only absorptions will also decrease in intensity and can shift in position if the individual peaks occur at different wavelenghts. Saponite is an example, where a broad band centered near 1.41 µm (Fig. 1b, blue) under humid conditions is sharp and centered at 1.39 µm for measurements under hyper-arid conditions (red).

The enhancement of M-OH relative to H_2O spectral features in Fig. 1 is in agreement with previous studies of smectites [e.g., 6-8]. The magnitude of the enhancements cannot be directly compared, however, because environmental H_2O concentrations are not reported in all the earlier work.

If climatic conditions on Mars favor loss of solvation H_2O over geologic time, these results imply that spectral features for M-OH should dominate over those for H_2O for smectites and other phases that can exchange H_2O with the martian atmosphere. We suggest that dehydration of solvation H_2O from smectites by heating at ~110°C for laboratory timescales is a reasonable surrogate for dehydration of solvation H_2O over geologic timescales at lower temperatures.

Fe-Sulfates. The first thermal decomposition product of melanterite in both air and dry N_2 atmospheres is szomolnokite ($FeSO_4.H_2O$) (Fig. 2). The spectra are similar to literature szomolnokite spectra [e.g., 9], except that no spectral feature at ~0.43 µm from Fe^{3+} is present. In humid air at higher temperatures (~240°C),

Fe^{2+} oxidation occurs resulting in formation of a ferric sulfate hydroxide which is possibly hydrated (from XRD data). The spectral features from Fe^{3+}-OH are located at 1.49, 1.82, 2.23, and 2.37 µm. This phase may occur naturally on Mars [10]. Under hyper arid (and presumably low O_2) conditions, szomolnokite thermally altered to crystalline $FeSO_4$ (from XRD) (Fig. 2b). The broad bands centered near 0.99 and 1.53 µm are from Fe^{2+} electronic transitions.

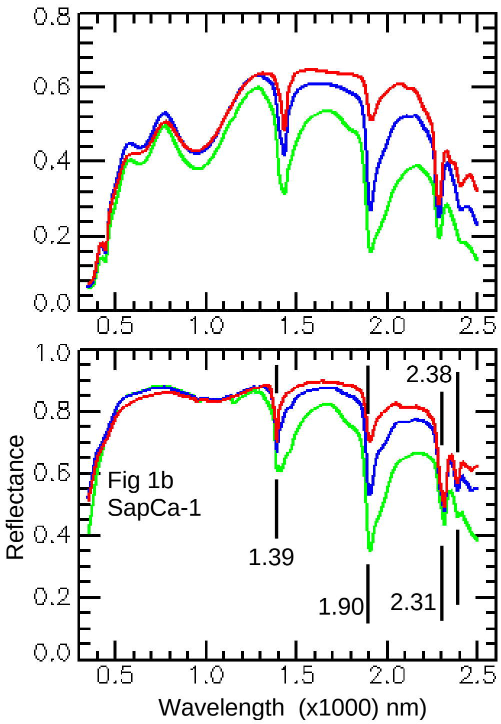

Fig. 1. (a) Nontronite (API-33A) spectra in air (**green**), after 24 hr N_2 purge at 25°C with final H_20 = 266 ppm (**blue**), and after 24 hr N_2 purge at 110°C with final H_2O = 200 ppm (**red**). (b). Saponite SapCa-1 spectra at at ambient conditions (**green**), after 24 hr N_2 purge at 25°C with final H_20 = 266 ppm (**blue**), and after 24 hr N_2 purge at 110°C with final H_2O = 200 ppm (**red**).

Mg-Perchlorate. The three most intense spectral features for fully and partially hydrated Mg-perchlorate are located at 1.42, 1.91, and 2.38 µm (Fig. 3). Because these positions approximate those for hydrous ferric sulfate, it is possible that locations previously interpreted as polyhydrated sulfates are actually mixed (and hydratedsulfate and perchlorate salts.

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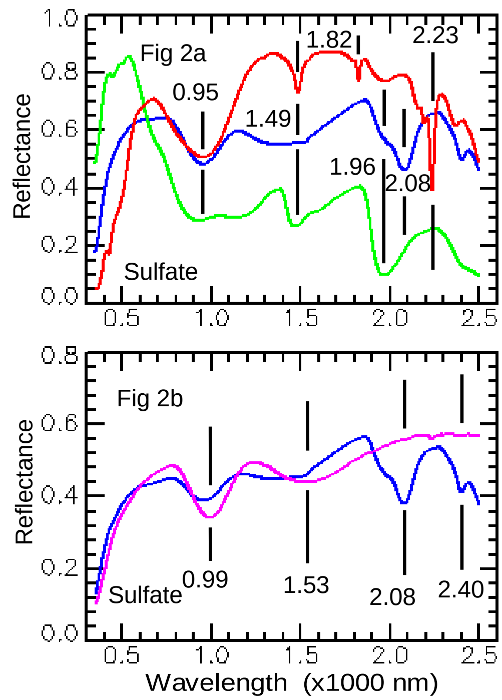

Fig. 2. (a) Spectra of melanterite ($FeSO_4.7H_2O$) (**green**) and szomolnokite ($FeSO_4.H_2O$) (**blue**) and ferric sulfate hydroxide (**red**) obtained by thermal dehydration in air. (b) Specta of szomolnokite (**blue**) and anhydrous $FeSO_4$ (**magenta**) obtained as thermal dehydration products of melanterite under dry conditions at 210°C and 310°C, respectively.

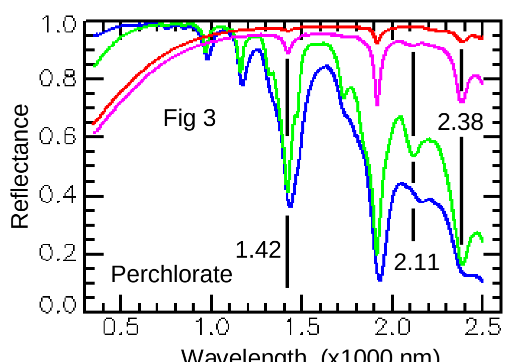

Fig 3. Spectra of unheated $Mg(ClO_4)_2.6H_2O$ (**blue**) and its thermal dehydration products in dry N_2 at 210°C (**green**) and 330°C (**red** and **magenta**).