EVIDENCE FOR INTERLAYER COLLAPSE OF NONTRONITE ON MARS FROM LABORATORY VISIBLE AND NEAR-IR REFLECTANCE SPECTRA. R. V. Morris1, D. W. Ming1, D. C. Golden2, T. G. Graff2, and C. N. Achilles3, 1ARES NASA Johnson Space Center, Houston, TX 77058, richard.v.morris@nasa.gov and 2Jacobs Engineering, ESCG, Houston, TX.

Introduction: Dioctahedral smectites (e.g., nontronite and montmorillonite) are interpreted to occupy the optical surface of Mars at a number of locations on the basis of spectral features derived from interlayer H2O and MOH (M=Fe3+, Al3+, etc.) as observed by orbiting MRO-CRISM and MEx-OMEGA hyperspectral imaging spectrometers [e.g., 1-4]. At wavelengths shorter than ~2.7 µm, the strongest bands from interlayer H2O occur at ~1.4 and 1.9 µm from 2v1 and v1+v2, respectively, where v1 and v2 are the fundamental stretching and bending vibrations of the H2O molecule [5]. Smectite MOH vibrations occur near 1.4 µm (stretching overtone) and in the region between 2.1 and 2.7 µm (stretching + bending combination). Because interlayer H2O can exchange with the martian environment [e.g., 6], a number of studies have examined the strength of the interlayer H2O spectral features under Mars-like environmental conditions [7-9]. The relationship between spectral properties and the underlying crystal structure of the smectites was not determined, and the extent of interlayer H2O removal was not established.

We report combined visible and near-IR (VNIR), Mössbauer (MB), and powder X-ray diffraction (XRD) data for samples of the Fe-bearing smectite nontronite where the interlayer was collapsed by complete removal of interlayer H2O.

Samples and Methods: Pennsylvania nontronite (PHY07, <38 µm [10], courtesy of T. Roush) and the Garfield Washington nontronite (API33A, <150 µm) with their native exchangeable cations were used for our experiments.

VNIR reflectivity spectra (0.35-2.50 µm) were acquired with an Analytical Spectral Devices (ASD) FieldSpec3 fiber optic spectrometer configured with a Mug light. The instrument was co-located with a hot plate, dewpoint meter (Vaisala DRYCAP DM70), and an IR thermometer (Fluke Model 66) in a 1-atm. glove box that can be kept under continuous purge by dry-N2. The nontronites were heated stepwise at 50, 105, and 210°C for variable lengths of time. VNIR measurements were made at ~25°C within a few minutes after sample removal from the hot plate. MB measurements (Ranger Scientific MS-1200) were made at ~25°C on samples prepared by mixing with epoxy in the glove box before removal for measurement in lab air. Sample for XRD measurements (PANalytical X’Pert PRO) were made by depositing a small amount of material on a Si-metal substrate in the glove box. XRD patterns were obtained in ambient air within 7 min after their removal from the glove box.

Results: The XRD patterns for API33A and PHY07 (Figs. 1 and 2) show that heating at ~210°C and a final concentration of 100-130 ppmv H2O in the glove box resulted in full interlayer collapse (blue traces) as indicated by the (001) basal diffraction peak at 9.5 Å [e.g., 11]. After ~2 hr in air (red traces), the nontronites acquired interlayer H2O as indicated by the basal diffraction peak at ~14.6 Å, although the basal peaks are broad compared to unheated samples (green traces). The basic smectite crystal structure has not been altered, however, because non-basal diffraction peaks (020) and (060) at 4.51 Å and 1.52 Å [11], respectively, are essentially invariant with respect to position and width.

The MB spectrum for PHY07 heated to 210°C shows no detectable Fe2+ (Fig. 3). The spectrum is well fit by two octahedral Fe3+ doublets (from [e.g., 12]) and no tetrahedral Fe3+ doublet.

The nontronite VNIR spectra are dramatically effected by interlayer collapse (Figs. 4 and 5). With increasing temperature and time at low environmental H2O concentration, the intensity of the 1.4 and 1.9 µm bands from interlayer H2O decrease (in agreement with [1-4]) and, after heating at 210°C, are virtually not detectable. The spectral features at 2.29 µm and 2.40 µm associated with Fe3+-OH do not change position and are better resolved as interlayer H2O is lost. The band at 1.44 µm is the overtone for the Fe3+-OH stretching vibration.

The well-defined Fe3+ electronic bands at ~0.45, 0.63, and 0.95 µm for the unheated nontronites broaden and increase in intensity (surface darkens) with increasing time/temperature until, with complete interlayer collapse, a positive, featureless slope is present between ~0.5 and 2.2 µm. We interpret progressive darkening of the surface in part to progressive removal of interlayer H2O and in part to the transition of the dark layer from optically thin to optically thick. Upon exposure of the collapsed nontronites to lab air, interlayer H2O is acquired as evidenced by the 1.4 and 1.9 µm bands, but the Fe3+ spectral features still closely resemble those for the collapsed nontronites even after 744 hr of exposure to air for PHY07 after heating in dry N2 at 210°C (Fig. 6).
Application to CRISM, OMEGA, and MSL-CheMin: Our spectra for collapsed nontronite have virtually no spectral features for interlayer H₂O at ~1.4 and 1.9 µm, retain the spectral features from Fe³⁺OH with enhanced spectral contrast at the same locations (2.29 and 2.41 µm), and have a positive, low-albedo spectral slope instead of well-defined bands from Fe³⁺ between ~0.5 and 2.0 µm. Thus, the low relative intensity of H₂O bands compared to Fe³⁺OH bands and the absence of well-defined Fe³⁺ bands (e.g., at 0.96 µm) for martian nontronite are evidence for significant loss of interlayer H₂O if not interlayer collapse in response to arid environmental conditions. The detection of a 9.5-10 Å diffraction peak by MSL-CheMin might be in situ evidence for collapsed nontronite.