EVIDENCE FOR INTERLAYER COLLAPSE OF NONTRONITE ON MARS FROM LABORATORY VISIBLE AND NEAR-IR REFLECTANCE SPECTRA. R. V. Morris[1], D. W. Ming[1], D. C. Golden[2], T. G. Graff[2], and C. N. Achilles[2], [1]ARES NASA Johnson Space Center, Houston, TX 77058, richard.v.morris@nasa.gov and [2]Jacobs Engineering, ESCG, Houston, TX.

Introduction: Dioctahedral smectites (e.g., nontronite and montmorillionite) are interpreted to occupy the optical surface of Mars at a number of locations on the basis of spectral features derived from interlayer H_2O and MOH (M=Fe^{3+}_2, Fe^{3+}Al, Al_2, 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 H_2O occur at ~1.4 and 1.9 μm from $2\nu_1$ and $\nu_1+\nu_2$, respectively, where ν_1 and ν_2 are the fundamental stretching and bending vibrations of the H_2O 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 H_2O can exchange with the martian environment [e.g., 6], a number of studies have examined the strength of the interlayer H_2O 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 H_2O 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 H_2O.

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

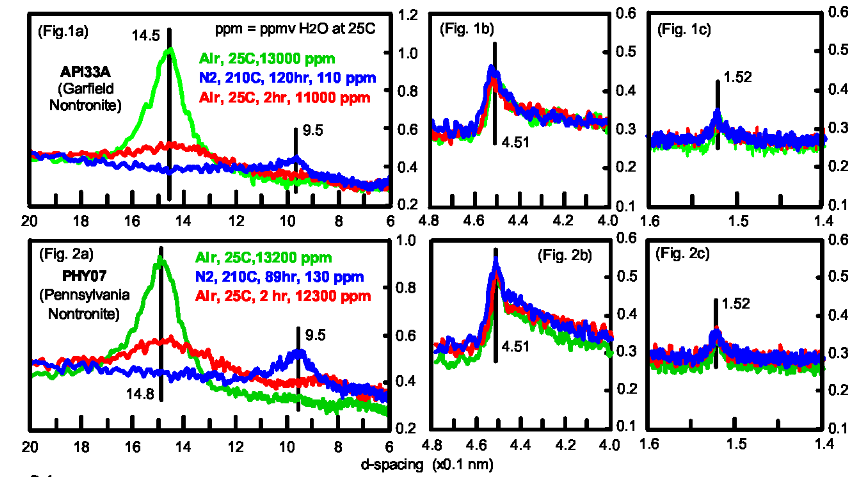
VNIR reflectivity spectra (0.35-2.50 μm) were acquired with an Analytical Spectral Devices (ASD) FieldSpec3 fiber optic spectrometer configured with a Mug light. The instrument was co-located with a hot plate, dewpoint meter (Vaisala DRYCAP DM70), and an IR thermometer (Fluke Model 66) in a 1-atm. glove box that can be kept under continuous purge by dry-N_2. 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.

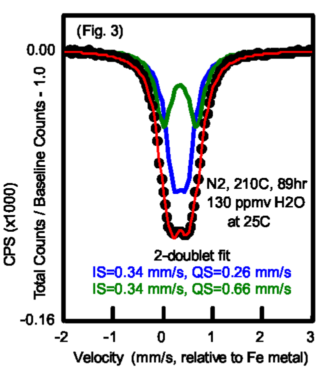
Results: The XRD patterns for API33A and PHY07 (Figs. 1 and 2) show that heating at ~210°C and a final concentration of 100-130 ppmv H_2O in the glove box resulted in full interlayer collapse (blue traces) as indicated by the (001) basal diffraction peak at 9.5 Å [e.g., 11]. After ~2 hr in air (red traces), the nontronites acquired interlayer H_2O as indicated by the basal diffration 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.

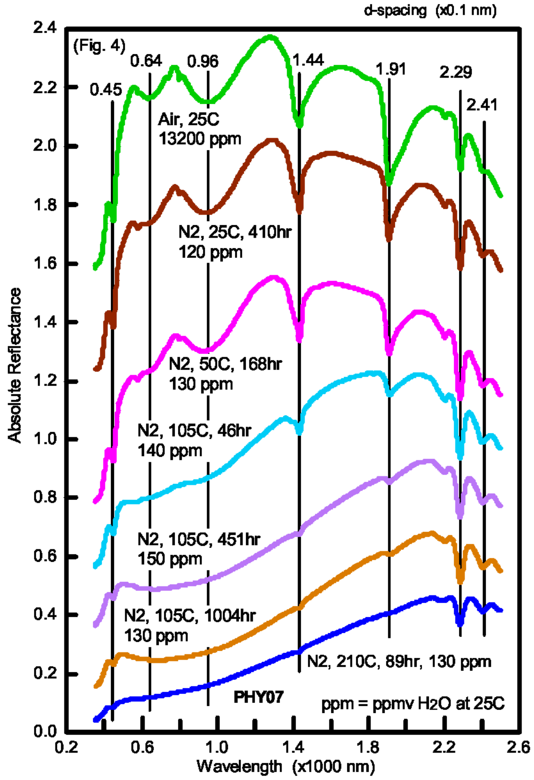
The MB spectrum for PHY07 heated to 210°C shows no detectable Fe^{2+} (Fig. 3). The spectrum is well fit by two octahedral Fe^{3+} doublets (from [e.g., 12]) and no tetrahedral Fe^{3+} doublet.

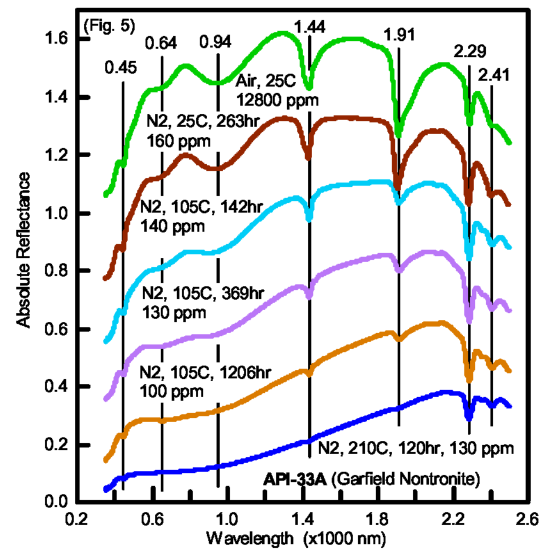
The nontronite VNIR spectra are dramatically effected by interlayer collapse (Figs. 4 and 5). With increasing temperature and time at low environmental H_2O concentration, the intensity of the 1.4 and 1.9 μm bands from interlayer H_2O decrease (in agreement with [1-4]) and, after heating at 210°C, are virtually not detectable. The spectral features at 2.29 μm and 2.40 μm associated with Fe^{3+}_2-OH do not change position and are better resolved as interlayer H_2O is lost. The band at 1.44 μm is the overtone for the Fe^{3+}_2OH stretching vibration.

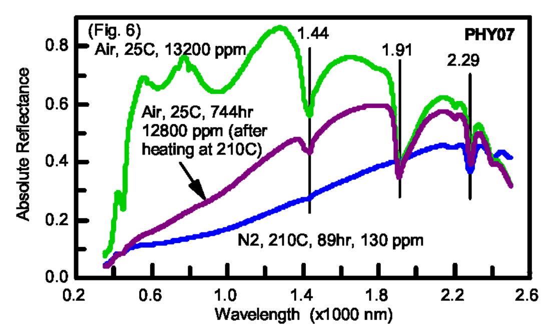
The well-defined Fe^{3+} electronic bands at ~0.45, 0.63, and 0.95 μm for the unheated nontronites broaden and increase in intensity (surface darkens) with increasing time/temperature until, with complete interlayer collapse, a positive, featureless slope is present between ~0.5 and 2.2 μm. We interpret progressive darkening of the surface in part to progressive removal of interlayer H_2O 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 H_2O is acquired as evidenced by the 1.4 and 1.9 μm bands, but the Fe^{3+} spectral features still closely resemble those for the collapsed nontronites even after 744 hr of exposure to air for PHY07 after heating in dry N_2 at 210°C (Fig. 6).











Application to CRISM, OMEGA, and MSL-CheMin: Our spectra for collapsed nontronite have virtually no spectral features for interlayer H_2O at ~1.4 and 1.9 µm, retain the spectral features from $Fe^{3+}{}_2OH$ 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 Fe^{3+} between ~0.5 and 2.0 µm. Thus, the low relative intensity of H_2O bands compared to $Fe^{3+}{}_2OH$ bands and the absence of well-defined Fe^{3+} bands (e.g., at 0.96 µm) for martian nontronite are evidence for significant loss of interlayer H_2O 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.

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