

**EVIDENCE FOR INTERLAYER COLLAPSE OF NONTRONITE ON MARS FROM LABORATORY VISIBLE AND NEAR-IR REFLECTANCE SPECTRA.** R. V. Morris<sup>1</sup>, D. W. Ming<sup>1</sup>, D. C. Golden<sup>2</sup>, T. G. Graff<sup>2</sup>, and C. N. Achilles<sup>2</sup>, <sup>1</sup>ARES NASA Johnson Space Center, Houston, TX 77058, [richard.v.morris@nasa.gov](mailto:richard.v.morris@nasa.gov) and <sup>2</sup>Jacobs 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 H<sub>2</sub>O and MOH (M=Fe<sup>3+</sup><sub>2</sub>, Fe<sup>3+</sup>Al, Al<sub>2</sub>, 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<sub>2</sub>O occur at ~1.4 and 1.9 μm from 2ν<sub>1</sub> and ν<sub>1</sub>+ν<sub>2</sub>, respectively, where ν<sub>1</sub> and ν<sub>2</sub> are the fundamental stretching and bending vibrations of the H<sub>2</sub>O 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<sub>2</sub>O can exchange with the martian environment [e.g., 6], a number of studies have examined the strength of the interlayer H<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O.

**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-N<sub>2</sub>. 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.

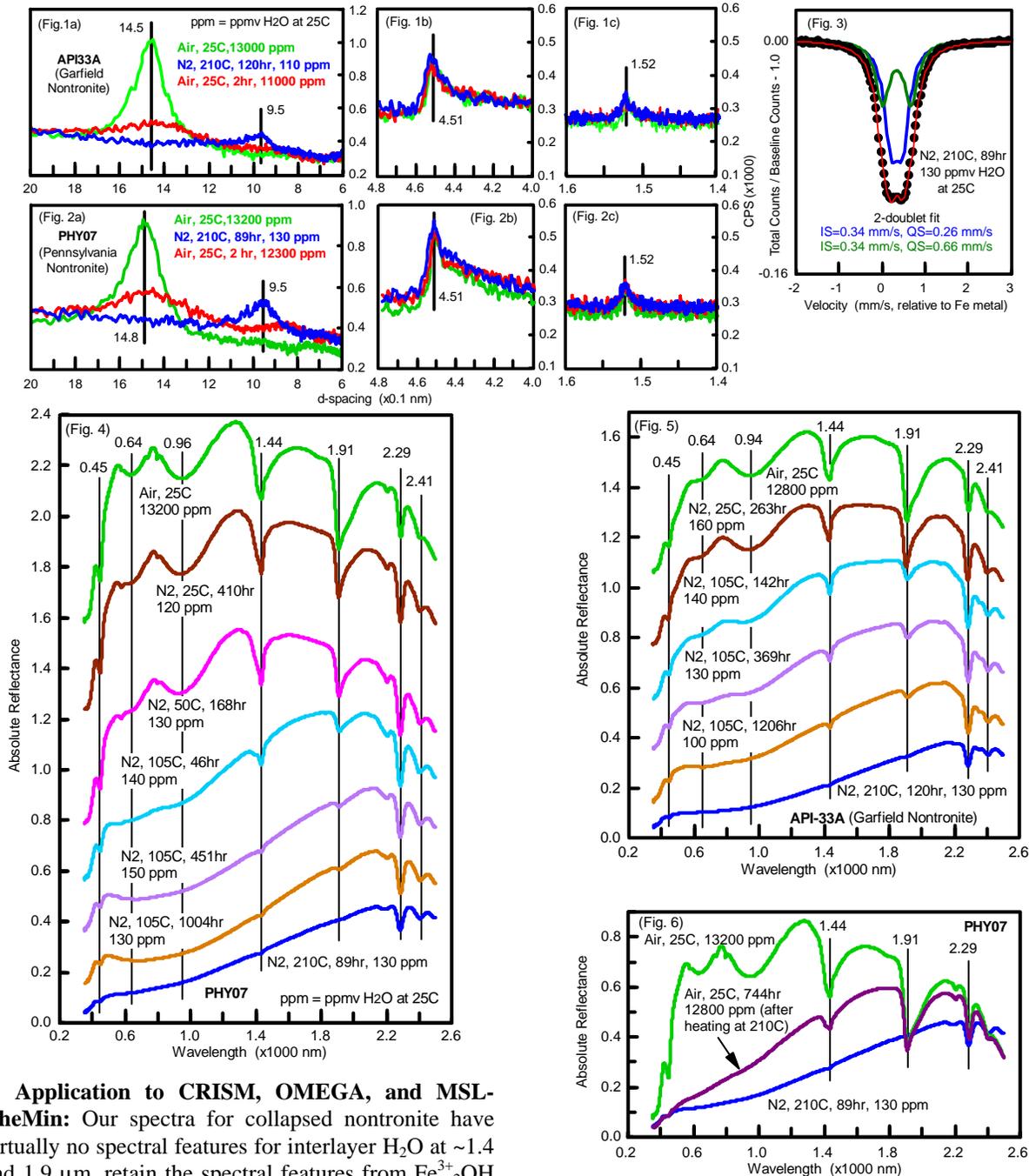
XRD patterns were obtained in ambient air within 7 min after their removal from the glove box.

**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<sub>2</sub>O 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<sub>2</sub>O 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 Fe<sup>2+</sup> (Fig. 3). The spectrum is well fit by two octahedral Fe<sup>3+</sup> doublets (from [e.g., 12]) and no tetrahedral Fe<sup>3+</sup> doublet.

The nontronite VNIR spectra are dramatically affected by interlayer collapse (Figs. 4 and 5). With increasing temperature and time at low environmental H<sub>2</sub>O concentration, the intensity of the 1.4 and 1.9 μm bands from interlayer H<sub>2</sub>O 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<sup>3+</sup><sub>2</sub>-OH do not change position and are better resolved as interlayer H<sub>2</sub>O is lost. The band at 1.44 μm is the overtone for the Fe<sup>3+</sup><sub>2</sub>OH stretching vibration.

The well-defined Fe<sup>3+</sup> 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<sub>2</sub>O 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<sub>2</sub>O is acquired as evidenced by the 1.4 and 1.9 μm bands, but the Fe<sup>3+</sup> 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<sub>2</sub> 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<sub>2</sub>O at ~1.4 and 1.9 μm, retain the spectral features from Fe<sup>3+</sup><sub>2</sub>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 Fe<sup>3+</sup> between ~0.5 and 2.0 μm. Thus, the low relative intensity of H<sub>2</sub>O bands compared to Fe<sup>3+</sup><sub>2</sub>OH bands and the absence of well-defined Fe<sup>3+</sup> bands (e.g., at 0.96 μm) for martian nontronite are evidence for significant loss of interlayer H<sub>2</sub>O 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.

**References:** [1] Bibring *et al.* (2006) *Science*, 312, 400. [2] Poulet *et al.* (2005) *Nature*, 438, 623. [3] Mustard *et al.* (2008) *Nature*, doi:10.1038/nature07097, 305. [4] Ehlmann *et al.* (2009) *JGR*, 114, doi:10.1029/2009JE003339. [5] Farmer (1974) *The Infrared Spectra of Minerals*. [6] Bish *et al.* (2003) *Icarus*, 164, 96. [7] Bishop *et al.* (1994) *Clays Clay Min.*, 42, 702. [8] Milliken and Mustard (2005) *JGR*, 110, E12001, doi:10.1029/2005JE002534. [9] Cloutis *et al.* (2008) *Icarus*, 195, 140. [10] Singer (1982) *JGR*, 87, 10159. [11] Brindley and Brown (1980) *Crystal Structures of Clay Minerals and Their X-Ray Identification*. [12] Sherman and Vergo (1988) *Am. Min.*, 73, 1346.