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TITLE: Visible and Near-IR Reflectance Spectra of Smectite Acquired Under Dry Conditions for Interpretation of Martian Surface Mineralogy

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ABSTRACT BODY: Visible and near-IR (VNIR) spectra from the MEx OMEGA and the MRO CRISM hyper-spectral imaging instruments have spectral features associated with the H2O molecule and M OH functional groups (M = Mg, Fe, Al, and Si). Mineralogical assignments of martian spectral features are made on the basis of laboratory VNIR spectra, which were often acquired under ambient (humid) conditions. Smectites like nontronite, saponite, and montmorillionite have interlayer H2O that is exchangeable with their environment, and we have acquired smectite reflectance spectra under dry environmental conditions for interpretation of martian surface mineralogy. We also obtained chemical, Moessbauer (MB), powder X-ray diffraction (XRD), and thermogravimetric (TG) data to understand variations in spectral properties. VNIR spectra were recorded in humid lab air at 25-35C, in a dynamic dry N2 atmosphere (50-150 ppmv H2O) after exposing the smectite samples (5 nontronites, 3 montmorillionites, and 1 saponite) to that atmosphere for up to ~l000 hr each at 25-35C, ~105C, and ~215C, and after re-exposure to humid lab air. Heating at 105C and 215C for ~1000 hr is taken as a surrogate for geologic time scales at lower temperatures. Upon exposure to dry N2, the position and intensity of spectral features associated with M-OH were relatively insensitive to the dry environment, and the spectral features associated with H2O (e.g., ~1.90 um) decreased in intensity and are sometimes not detectable by the end of the 215C heating step. The position and intensity of H2O spectral features recovered upon re-exposure to lab air. XRD data show interlayer collapse for the nontronites and Na-montmorillionites, with the interlayer remaining collapsed for the latter after re-exposure to lab air. The interlayer did not collapse for the saponite and Ca-montmorillionite. TG data show that the concentration of H2O derived from structural OH was invariant to the dry N2 treatment for saponite and the montmorillionites, but the nontronites had additional structural OH after treatment. Upon exposure to dry N2, the VNIR spectra also acquired a red slope with decreasing albedo between ~0.4 and ~2.0 um. The magnitude of the effects covaries with exposure time to dry N2 and heating temperature. Upon re-exposure to lab air, the slope and albedo do not completely recover to pre-exposure values. MB data show that these effects do not result from partial reduction of ferric to ferrous iron, and TG data show they do not result from loss of structural OH. Possible explanations include formation of small clusters of (superparamagnetic) ferric oxide and reduced smectite crystallainity. The difference in spectral properties between spectra acquired in humid lab air and under dry conditions are consequential for interpretation of CRISM and OMEGA spectra. For example, nontronite by itself and not nontronite plus ferrihydrite can account for the red spectral slope in martian spectra where nontronite is indicated by the Fe-OH spectral features.

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