

**Temperature Dependence of Calcium and Sodium Montmorillonite at 2.6 $\mu$ m** M.M. McAdam<sup>1</sup> and C.A. Hibbitts<sup>1, 1</sup> Johns Hopkins University Applied Physics Laboratory (e-mail: maggiemmcadam@gmail.com).

**Introduction:** While the changes in montmorillonite spectra due to heating have been investigated for some time [e.g. 1] spectral changes at cryogenic temperatures have not been extensively studied. In laboratory experiments simulating airless bodies using an Ultra High Vacuum (UHV) chamber, we observed changes in the spectra of calcium montmorillonite and sodium montmorillonite upon desiccation and subsequently upon cooling. The chemical compositions of these two phyllosilicates are  $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , structurally falling into the category of expansive clays that can adsorb significant water [2]. This research has broad implications for missions such as Dawn to airless potentially clay-rich bodies [3-5].

**Data Collection:** A Bruker Equinox55 FTIR (Fourier transform infrared) spectrometer utilizing an external liquid-nitrogen cooled MCT detector is used to investigate the 1.5 – 5.5- $\mu$ m biconical reflectance characteristics of the clays, as either a loose powder or a pressed pellet. Each spectrum is an average of 100 scans, at a resolution of 4  $\text{cm}^{-1}$ . The illumination geometry is determined by the port positions on the chamber, with the incident angle set at 20° and emission angle 40°. Each spectrum presented is itself an average of groups of at least four (usually between 5 – 10 but sometimes more) spectra obtained under similar temperature and vacuum conditions.

**Results and Discussion:** The unnormalized spectra are affected by both hydration and temperature. Figure 1a (calcium montmorillonite) and 1b (sodium montmorillonite) show that hydration makes a significant difference in the spectra. The blue spectra in figure 1a and 1b are averages of spectra taken under near-ambient conditions at temperatures of 24-39° Celsius (C), either at atmospheric pressure or upon initial pump down and thus are significantly hydrated. The green spectra in figures 1a and 1b are taken after desiccating for hours or days under high vacuum ( $P \leq 1 \times 10^{-6}$  Torr) at temperatures of 5-36° C. Significant brightness differences exist between these two spectra at 3 and 4 $\mu$ m, and the 3- $\mu$ m hydration band is narrowed on its short-wavelength shoulder. The brightness change ( $\Delta R$ ) between the ambient and desiccated are: for calcium montmorillonite  $\Delta R = 0.161 \pm 0.002$

reflectance units and for sodium montmorillonite,  $\Delta R = 0.0194 \pm 0.009$  reflectance units. There also are the changes near 2.5 - 2.7 $\mu$ m. As the clay desiccates, the brightness in this area increases allowing features between 2.45 and 2.55  $\mu$ m (calcium montmorillonite) and 2.56 and 2.6  $\mu$ m (sodium montmorillonite) to appear, as see in figures 3a and 3b. The change in spectral shape around 2.6  $\mu$ m is focused upon as there is evidence is temperature-dependent as opposed to hydration dependent.

Invariance in hydration at varying temperatures is demonstrated via analysis of the 3- $\mu$ m hydration band. The depth and width of the 3  $\mu$ m band is a proxy measurement of the hydration of clay [6]. Using averaged normalized spectra, we calculate the area of this absorption feature from 2.5  $\mu$ m to 3.9  $\mu$ m (calcium montmorillonite) and from 2.5  $\mu$ m to 3.78  $\mu$ m (sodium montmorillonite). Figure 2 shows the 3- $\mu$ m band areas for spectra in specific temperature ranges. The slopes of the trend line fit to these band areas are very close to zero, indicating that there is negligible hydration change with temperature while under high vacuum. Thus, the 2.6  $\mu$ m band changes are likely only due to temperature.

Figures 3a and 3b show averaged, normalized calcium montmorillonite and sodium montmorillonite spectra at different temperatures. The spectral dependency is characterized with the spectral slope ( $\delta R/d\lambda$ ) that is calculated between 2.54  $\mu$ m and 2.65  $\mu$ m for calcium montmorillonite and 2.55  $\mu$ m and 2.58  $\mu$ m for sodium montmorillonite. Both clays exhibit a temperature dependency, with sodium montmorillonite having a stronger dependency.

**Conclusions:** Hydration state affects the infrared spectra of sodium and calcium montmorillonite. Once desiccated, both clays exhibit temperature dependent changes near 2.6  $\mu$ m. We hypothesize this effect may be related to the size of the calcium and sodium ions and the strength of cation-OH bond, which affects the position and shape of the shortwave side of the 3  $\mu$ m hydration feature. Sodium, having a smaller charge but a similar ionic radius (0.95 Å) to calcium (0.99 Å) [7], will likely have a weaker bond to the structural OH and behave differently than the more tightly bound calcium montmorillonite structure.

**References:** [1] C Bruckenthal E.A. (1987) *Uni. of Hawaii* 90-96. [2] Clark R.N. et al (1990) *Geophys Res* 12653-12680. [3] Rivkin A.S. Volquardsen E.L. (2006) *Icarus* 563-576. [4] King T.V.V. Clark R.N. (1992) *Science* 1551-1553. [5] Rivkin A.S. Li J.Y. (2010) *Space Sci Rev.* [6] Miyamoto and Zolensky (1994) *Meteoritics* 29 849-853. [7] Geological Society of America Inc (2004) MCH092.

Figure 1a (Note: averages are not normalized)

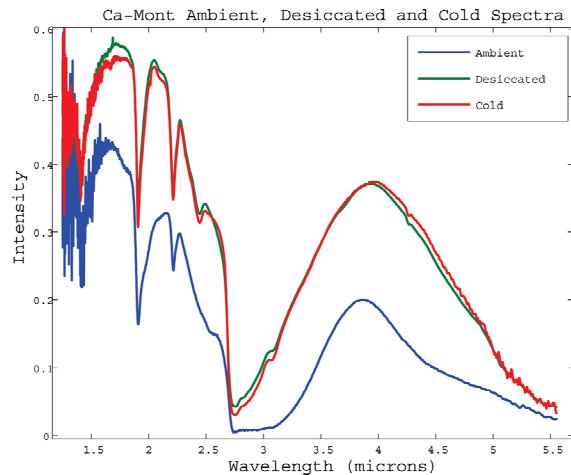


Figure 2

[5] Rivkin A.S. Li J.Y. (2010) *Space Sci Rev.* [6] Miyamoto and Zolensky (1994) *Meteoritics* 29 849-853. [7] Geological Society of America Inc (2004) MCH092.

Figure 1b

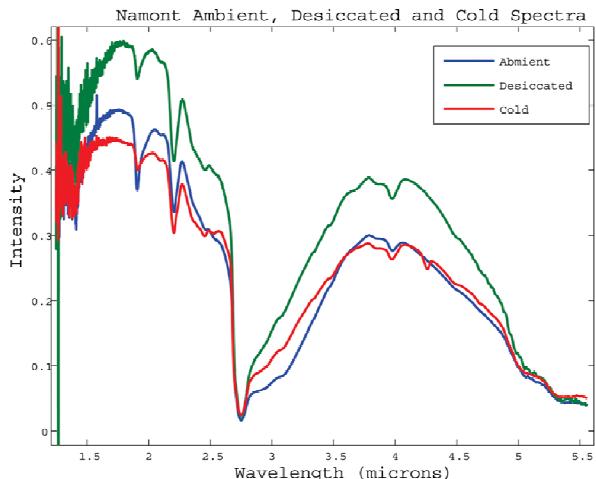


Figure 3a

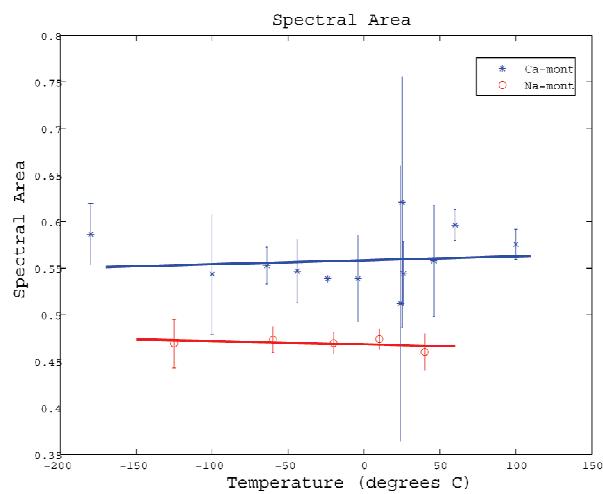


Figure 3b

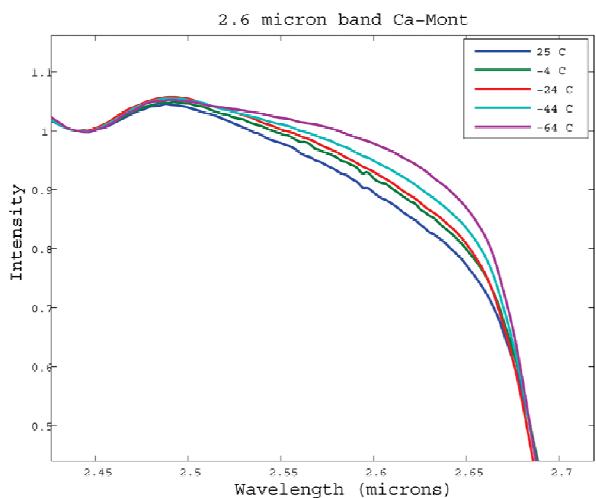


Figure 4

