

A LABORATORY TECHNIQUE FOR THERMAL INFRARED MEASUREMENT OF HYDRATED MINERALS. A. M. Baldridge¹ and P. R. Christensen¹, ¹School of Earth and Space Exploration, Arizona State University, MC 6305, Tempe, AZ, 85287-6305 alice.baldridge@asu.edu.

Introduction: Laboratory thermal infrared spectroscopy has been utilized for comparison to remotely sensed data from planetary surfaces. The laboratory techniques for measurements using the Nicolet Nexus 670 E.S.P FTIR interferometer at Arizona State University's Mars Space Flight Facility (MSFF) are described by [1, 2]. Emission spectroscopy using an interferometric spectrometer measures the energy of the sample, of reflection and of background sources. The measured voltage varies as a function of wavelength and temperature of the sample by the following equation [2]:

$$V_{\text{meas}}(\lambda, T) = [\varepsilon_{\text{samp}}(\lambda)B_{\text{samp}}(\lambda, T) + R_{\text{samp}}(\lambda)\varepsilon_{\text{env}}(\lambda) \bullet B_{\text{env}}(\lambda, T) - \varepsilon_{\text{inst}}(\lambda)B_{\text{inst}}(\lambda, T)]F^*$$

* $V_{\text{meas}}(\lambda, T)$ – measured voltage as a function of wavelength and temperature

$\varepsilon_{\text{samp}}(\lambda)$ – emissivity of the sample as a function of wavelength

$B_{\text{samp}}(\lambda, T)$ – the radiance of the sample as a function of wavelength and temperature

$R_{\text{samp}}(\lambda)\varepsilon_{\text{env}}(\lambda)B_{\text{env}}(\lambda, T)$ – energy that is emitted by the environment and reflected off sample

$\varepsilon_{\text{inst}}(\lambda)B_{\text{inst}}(\lambda, T)$ – instrument energy

F – response function of the spectrometer

The sample target is illuminated by thermal energy from both the instrument and the environment. The total energy measured is therefore a combination of the energy from the sample and the energy reflected off the sample from these sources. [3] describe a technique for accounting for environmental illumination. However, this method assumes a cooled detector. The detector at the MSFF is uncooled, at ambient temperature, which produces a very low signal when measuring the energy from a sample that has a temperature close to its own. For this reason the sample is usually heated well above room temperature (~80C). Additionally, heating of the sample allows the first part of the above equation to dominate the reflected component.

Most of the emissivity spectra measured in the MSFF are heated to temperatures between 60-80C for at least several hours prior to measurement. Particulate samples are often actively heated during measurement to maintain constant temperature. While this method is acceptable for most rock and mineral samples, some samples (specifically hydrated samples) change composition quickly at temperatures even

slightly above room temperature. This change in composition is evident in both the physical appearance of the sample and in the position of the absorptions [4, 5]. Instead of heating, the samples can be cooled by placing the sample in a container with CO₂ ice. This study describes for which minerals it is important to consider dehydration and the methods used to measure the emissivity spectra of these samples avoiding dehydration.

Ca-Sulfates: During measurement of the thermal infrared spectral of sulfate-cemented materials [6], the surface of gypsum (CaSO₄•2H₂O) crystals rapidly dehydrated upon heating. The surface of a smooth, transparent gypsum crystal became white and flakey. SEM analysis of the crystal revealed that the crystal surface was disaggregated and consisted of dust-sized particles indicative of dehydration and the release of bound water Figure 1. Because thermal infrared spectroscopy (TIR) measures only the upper few micrometers of the sample, the spectrometer was most likely only measuring the emission of the white surface rather than of the bulk gypsum crystal. A separate unheated gypsum crystal was cooled to ~ -20C and the TIR spectrum measured. The TIR spectra of both the heated and cooled gypsum are shown in Figure 2. The position of the S-O absorption near 1200cm⁻¹ is shifted to longer wavenumbers and a doublet is present in the heated sample indicative of bassanite or anhydrite. The cold spectrum has slightly decreased signal to noise, however the spectral contrast is similar and all expected absorptions are present. Additionally the heated sample exhibits absorption associated with water in particulate samples near 1600cm⁻¹.

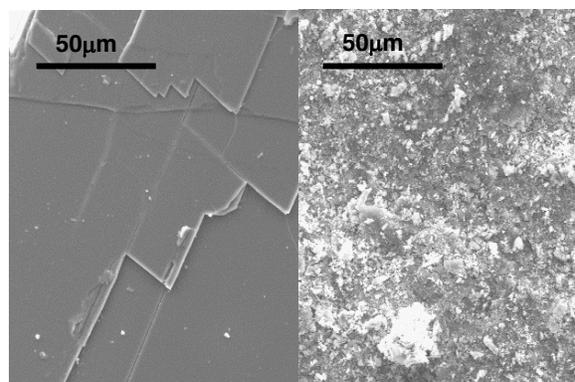


Figure 1. SEM image of gypsum crystal surface before and after heating

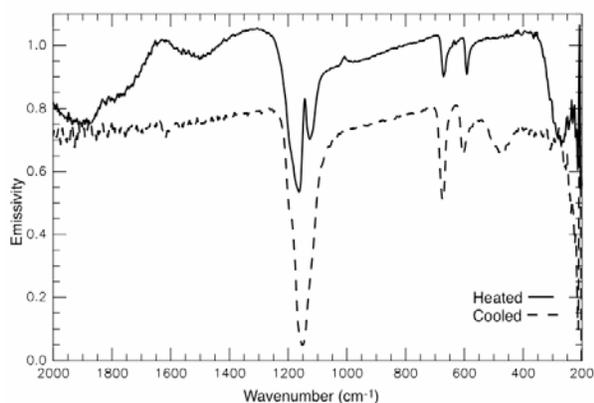


Figure 2. TIR spectra of heated and cooled gypsum

Mg- Sulfates: Similar effects on TIR spectra are seen in hydrated Mg-sulfate samples. Decreasing particle size has been shown to decrease spectral contrast [7-9]. $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ powder was pressed into pellets to increase the specular properties of the surface. The effect of heating the pellets is similar to that on the gypsum crystal: the surface of the pressed $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ pellet became dehydrated, changing the chemical structure of the material. [10-12] have shown that the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is not stable at 80C and rapidly dehydrates to pentahydrate ($\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$) or starkeyite ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$). The shift in S-O absorption can be quantified with hydration state [5]. A suite of MgSO_4 mineral of varying hydration were pressed into pellets and cooled to $\sim -20\text{C}$ for measurement. A spectral comparison of the heated and cooled MgSO_4 pellets is shown in Figure 3. Although the spectrum of the cooled pellet has a lower signal to noise, it represents a more accurate spectrum of the hydrated sulfate. The heated sample has lost water as indicated by the shift in S-O absorption position and the loss in spectral contrast.

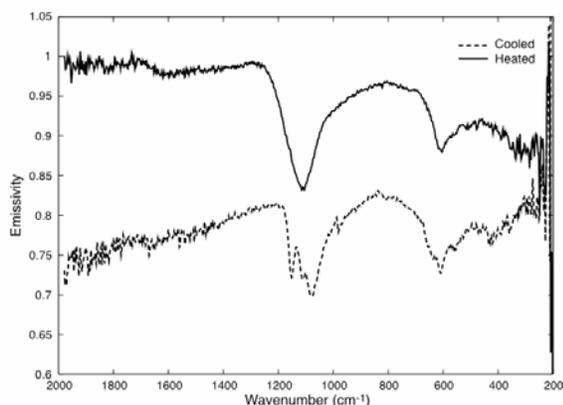


Figure 3. TIR spectra of cooled and heated $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Un-hydrated Samples: Changes in TIR optical properties are not expected over this temperature range. To confirm that this is the case, non-hydrated minerals were measured in a similar manner. The cooled and heated spectra of quartz, calcite and hematite are shown in Figure 4. There is no obvious shift in absorption position, nor is there a significant change in spectral contrast between the heated and cooled samples. The only difference is in the signal to noise, which is less in the cooled sample.

Discussion: Most natural samples are not hydrated and therefore, for the range of temperatures used in the MSFF, attention to temperature of the sample during TIR measurement is not necessary. When measuring hydrated samples important for the study of martian surface materials, such as Mg- and Ca-sulfates, the stability diagram for these minerals should be considered as increased temperature may alter the mineralogy of the sample. Other hydrated minerals for which this may be important include clays and zeolites [12-15], which will be investigated by this study.

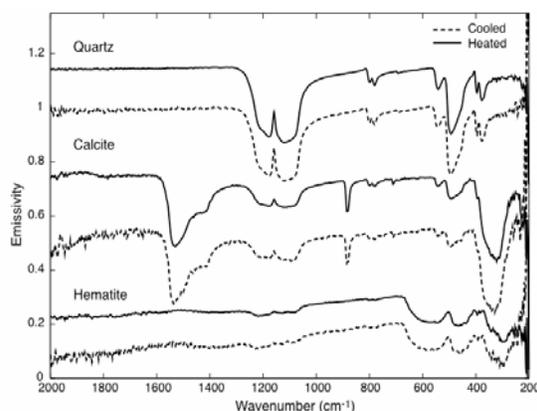


Figure 4. TIR spectral of cooled and heated un-hydrated minerals. Spectra scaled for plotting.

References: [1] Ruff, S.W., et al. (1997) *JGR*, 102(7), 14,899-14,913. [2] Christensen, P.R. and S.T. Harrison (1993) *JGR*, 98(11), 19,819-19,834. [3] Salisbury, J.W., et al. (1994) *JGR*, 99(B6), 11897-11911. [4] Lane, M.D. (2007) *Am. Miner.*, 921-18. [5] Baldrige, A.M. and P.R. Christensen (2006) *Workshop on Sulfates as Recorders of Atmospheric-Fluid-Rock Interactions* [6] Baldrige, A.M. and P.R. Christensen (2005) *AGU Fall Meeting Abstracts*, 210156. [7] Hunt, G.R. and R.K. Vincent (1968) *JGR*, 73(18), 6039-&. [8] Salisbury, J.W. and J.W. Eastes (1985) *Icarus*, 64(3), 586-588. [9] Salisbury, J.W. and A. Wald (1992) *Icarus*, 96(1), 121-128. [10] Bish, D.L., et al. (2003) *Icarus*, 164(1), 96-103. [11] Feldman, W.C., et al. (2004) *GRL*, 31(16), -. [12] Fialips, C.I., et al. (2005) *Icarus*, 178(1), 74-83. [13] Michalski, J.R., et al. (2006) *JGR*, 11103004. [14] Michalski, J.R., et al. (2006) *LPS*, XXXVII1146. [15] Ruff, S.W. (2004) *Icarus*, 168(1), 131-143.