**SPECTROSCOPIC DETECTIBILITY OF SULFATES IN DUST AND DURICRUST ON MARS.** Christopher D. Cooper and John F. Mustard, Department of Geological Science, Box 1846, Brown University, Providence RI, 02912. (Christopher\_Cooper@brown.edu).

**Introduction:** Abundant sulfur was detected in the Martian surface material by the Viking Landers, with higher concentrations occurring in crusts and clods [1,2]. Cementation by sulfate salts has been proposed to explain the higher sulfate abundance in the more cohesive materials, with magnesium as the likely cation [1,3]. In addition, there are a number of regions on Mars with a dark red color, intermediate albedo, and intermediate thermal inertia [4,5,6] that appear to have a unique mineral composition [7] and are thought to consist of regionally extensive cemented material analogous to the smaller clods found at the landing sites. The high sulfur concentration and its apparent mobility have important implications for understanding surface compositions and pedogenic processes on Mars.

A weak 4.5  $\mu$ m band attributed to sulfate has been observed in some telescopic spectra [8]. However, it did not appear to have the same pattern of absorptions seen in pure MgSO<sub>4</sub>, gypsum, or anhydrite. A fundamental question thus arises: what are the detection limits of sulfates on Mars? Furthermore, how does the physical form (e.g. powders vs. crusts) affect detection?

In a previous work [9] we showed that anhydrous  $MgSO_4$  in dry powder mixtures with palagonite was observable using laboratory reflectance spectroscopy from bands in the 4.5 µm and 9.8 µm regions, although absolute contrast on these bands was less than 1% reflectance. Cemented crusts formed from these mixtures had very different spectral properties and are more likely to be detectable with using TES. Our current work with these samples is aimed at distinguishing between textural and compositional sources for the changes in the spectral properties of powder and cemented mixtures of palagonite and sulfates. A suite of mixtures was prepared as analogs to Martian duricrust and dust and measured in the laboratory to investigate the spectral detectibility of sulfates on Mars.

**Samples:** Some palagonites (amorphous or weakly crystalline weathering products of basaltic glass) are good spectral analogs for the Martian soil [10,11]. The JSC Mars-1 palagonite is a well characterized material [12] that is a useful medium for these experiments. The objective to simulate processes in the Martian soil requires fine-grained materials and thus the 25-45  $\mu$ m fraction of JSC Mars-1 was dry sieved to produce particles from 15-20  $\mu$ m in size. This size fraction was mixed in five different proportions with reagent grade anhydrous magnesium sulfate to create analogs to the Martian soil. The chemical composi-

tions of the palagonite mixtures were calculated from the composition of JSC Mars-1 [12] and are compared with Viking measurements in Table I. Biconical reflectance from 0.9 to 26  $\mu$ m was measured in a Nicolet FTIR spectrometer and tied to visible to near-infrared spectra measured by the RELAB bidirectional spectrometer [13]. Powders were also measured after being packed to form a dense, compressed surface.

After measuring the dry powder mixtures, water was added to each powder to form a paste which was then dried in a sample dish to create a brick of cohesive, cemented material. The bricks were hard and resistant to breaking. The color and texture were uni-



**Figure 1.** Mid-infrared reflectance spectra of powder (dotted) and cemented (solid) mixtures of JSC Mars-1 palagonite and  $MgSO_4$ .



**Figure 2.** Spectra of endmembers and 10% MgSO<sub>4</sub> mixture showing effects of texture. Loose powders (dashed) are darkest, followed by packed powders (dotted) and cemented mixtures (solid).

-	Wt% MgSO <sub>4</sub> mixed with JSC Mars-1						VL	
Oxide	0%	5%	7%	10%	12%	18%	Fines	Clods
SiO <sub>2</sub>	43.5	41.3	40.3	39.2	38.1	35.7	43	42
$Al_2 \tilde{O}_3$	23.3	22.1	21.6	21.0	20.4	19.1	7.2	7
TiÕ <sub>2</sub>	3.8	3.6	3.5	3.4	3.3	3.1	0.61	0.59
$Fe_2O_3$	15.6	14.8	14.4	14.0	13.7	12.8	18.2	17.6
CaO	6.2	5.9	5.7	5.6	5.4	5.1	5.8	5.5
MgO	3.4	4.9	5.6	6.4	7.1	8.8	6	7
K,O	0.6	0.6	0.6	0.5	0.5	0.5	< 0.15	< 0.15
SÕ <sub>3</sub>	n.a.	3.4	4.9	6.6	8.2	11.9	7.4	9.2
Total	100	100	100	100	100	100	88.8	89.7
*JSC Mars-1 after removal of water from [12], VL from [2].								

**Table I.** Compositions of lab and Viking samples.

form throughout the interior of the bricks. Water was also added to the pure palagonite and  $MgSO_4$  endmembers and they were dried in the same manner. The sulfate formed a hard, solid mass while the palagonite control was only packed together. Finally, the pure sulfate crust was ground to produce a powder that was measured for reflectance with both loose and packed textures.

**Results:** The reflectance spectra of the mixtures and endmembers in both dry powder and cemented crust states are shown in Figure 1. All of the particulate spectra containing JSC Mars-1 palagonite are extremely dark and bland in reflectance longwards of 8.5  $\mu$ m. While the 9.8  $\mu$ m band due to sulfate (compare to 100% MgSO<sub>4</sub> spectrum) does reach a strength of 15% in the 18% MgSO<sub>4</sub> mixture [9], the absolute reflectance is less than 2% and detection may be difficult. As noted previously [9], at wavelengths longer than 8  $\mu$ m the reflectance is much higher in the cemented samples. Because the control "brick" of pure palagonite also also shows an increase reflectance beyond 10  $\mu$ m, this behavior is likely due to increased packing and decreased porosity in the sample, e.g. [14].

To further test this hypothesis, dry powder mixtures were packed into sample dishes forming a compressed surface. Figure 2 shows the differences due to texture in a representative group of the samples measured. All packed samples containing palagonite show the same strong slope upward from 8.5 to 9.5 µm that was exhibited by the control brick of pure palagonite. Notably, the sulfate mixtures do not exhibit an 8.6 µm reflectance peak like the cemented mixtures. To explore whether this is a consequence of physical or chemical effects of cementation, the 100% MgSO<sub>4</sub> brick was ground and measured as loose and packed powders. The loose material lacked most of the features of the anhydrous MgSO<sub>4</sub> powder as well as the 8.6 µm feature. The packed material was spectrally nearly identical to the cemented material. Crystallization of hydrated MgSO<sub>4</sub> (e.g. kieserite, epsomite) during cementation therefore leads to a different set of (weaker) spectral features, while textural changes cause the large peak at 8.6 µm and the rise in overall reflectance levels beyond 10 µm.



**Figure 3.** Comparison of predicted TES spectra of dust covered surfaces of Mars (10%  $MgSO_4$  powder, green) and region with 5% areal exposure of cemented duricrust (12%  $MgSO_4$  crust, red).

Implications: Given the textural and chemical contributions to the spectra of palagonite-sulfate mixtures, the potential exists to detect areas of sulfatecemented duricrust on the surface of Mars using the TES instrument. Although sulfate absorptions in loose dust are relatively weak, features in cemented materials are much stronger (similar to calcitepalagonite mixtures studied in [15]), and they are distinct from those observed in compacted soils. The peak at 8.6 µm is strong enough that even small areal abundances of duricrust should be detectable by the TES instrument. Linear mixtures of the spectra of dust and cemented materials were calculated to estimate the areal exposure of duricrust that would to create a 1% absorption within a TES spectrum. Figure 3 shows the calculated spectrum of a linear mixture of 95% loose powder (10% MgSO<sub>4</sub>) and 5% cemented material (12% MgSO<sub>4</sub>). The 8.6  $\mu$ m feature is readily visible (Fig. 3), which suggests that even a 5% exposure of duricrust from under mantling dust will result in a detectable TES spectrum.

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