Optical Effects Due to Hydration and Dehydration of Salts: Laboratory Measurements with Applications to Ceres.
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Introduction: Photometric measurements from the Dawn mission's Framing Camera revealed more than 130 bright patches of varying size and albedo on the generally dark background of dwarf planet Ceres [1]. In particular, the brightest area, the central portion of Occator crater (19.8N, 239.3 E), has a measured geometric albedo of ~0.5, compared with ~0.09 for Ceres average surface reflectance [2], and a spectral shape in the visible (0.4-1.0 μm) that is consistent with water-ice, Fe-poor clay minerals, and salts [1]. Interestingly, Occator's albedo appears to darken with distance from the bright central crater feature; however the source of this darkening is unknown and the interpretation of the bright material is complex (Jaumann et al. 2016) [3]. The similar spectral color and geological settings of most bright patches [1] and their wide range of albedos (from 2× up to 5× Ceres average) raise questions about the darkening mechanism, which contains clues to the composition of the bright patches and the regolith alteration processes on Ceres. Nathues et al. [1] hypothesize that the darkening may result from either mixing with the (darker) native soil or from the dehydration of magnesium sulfate hexahydrite, the best match for the photometric spectral slope.

Laboratory experiments to determine the effects of hydration and dehydration, as a function of temperature and pressure, for varied grain size fractions on the optical spectra for several salts, including $MgSO_4 \bullet 6H_2O$ and KBr, are in progress to compare with observations of Ceres' bright spots, including Occator crater.

Experiment: A Perkin Elmer UV/Vis/NIR spectrometer (Lamba 1050, wavelength range: 0.17–3.3 μm) with a diffuse reflection accessory (Harrick Praying Mantis) has been used to measure the reflectance of KBr (a standard) and $MgSO_4$ of varied hydration (heptahydrate, -hexahydrate, -monohydrate, and anhydrous). The Perkin Elmer spectrometer can be switched to a Thermo Nicolet Nexus 670 Fourier Transform Infrared spectrometer to perfom identical measurements for wavelength region of 0.6 – 15 μm. Salts were prepared by sieving into three size fractions of <45 microns, 45-125 microns, and 250-500 microns either in atmosphere or in dry-nitrogen as appropriate. An aluminum cup (13 mm dia, 0.5 mm depth) was filled with the sample powder and seated within a small vacuum chamber (Harrick Low-Temperature Reaction Chamber), within the Praying Mantis. The chamber pressure may be varied from 10^{-6} torr to 2.3 ktorr. Gases (such as H_2O, CO_2, NH_3) can be introduced into the chamber in a controlled flux, and sample temperature can be varied from 120°K to 850°K. *In situ* spectral measurements to ascertain the optical effect of hydration/dehydration may be made as a function of time, pressure, temperature, and varied gases exposure.

For the first results presented here, KBr powder of varied grain size fraction was sieved at room temperature in ambient atmosphere. The diffuse spectrum was taken in the range of 0.9–2.4 μm, at spectral resolution set to 2.5nm and a detector response time of 0.08s. This abbreviated spectrum was used to minimize spectral acquisition time, with each spectrum taking ~2.5 min.

For measurements investigating the effect of hydration on albedo, a slurry of KBr and water ($KBr:H_2O$) sample was prepared by adding 45-125 micron KBr powder to 0.03 ml liquid water (HPLC grade) in the Al cup. We observed the optical response due to dehydration as a function of time at ambient conditions. To obtain absolute diffuse reflectance of the samples, raw spectra were divided by that of dry-KBr powder (grain size: 45 −125 μm).

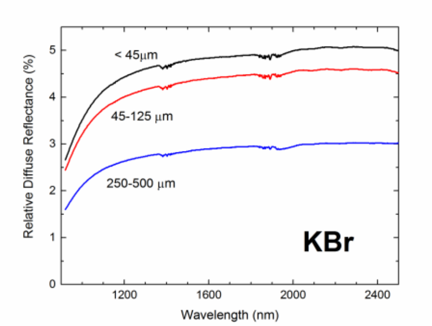

Figure 1. Relative diffuse reflectance of KB as a function of particle size; smaller particles increase absolute spectra reflectance. Small absorptions (~1.4 & ~1.9 microns) due to atmosphere do not appear in absolute reflectance spectra.

Results: As expected, the relative reflectance of KBr increases with decreasing particle size (Fig. 1) as more scattering of the incident light occurs. The small absorptions in the KBr spectra near 1.4 and 1.9 μm result from atmospheric humidity; they are observed because of the difference in pathlength between the reflected spectra and the transmitted reference beam in our dual beam spectrometer. These minor features are not apparent in absolute reflectance spectra.

Time-sequenced effects (step size ~10 minutes) of dehydration in the KBr:H_2O slurry are shown in Fig. 2. Two primary effects are apparent: 1) water absorption features at ~1.4 (1st overtone of O-H stretch) and ~1.9 (H-O-H bend in combination with O-H stretches) are diminished and 2) the absolute diffuse reflectance of the KBr:H_2O increases with time. Reduced water band absorption depth implies dehydration of the slurry with time, as the water evaporates. Since the density of KBr (~2.75 g cm^{-3}) is greater than water (~1 g cm^{-3}) we can be certain that the water is evaporating from the slurry, rather collecting at the bottom of the cup beyond the optical penetration depth. After 60 minutes, the depth of the water absorption bands approached that of the dry-KBr, consistent with visual inspection. Thus, the increase in overall reflectance with time can be correlated with dehydration.

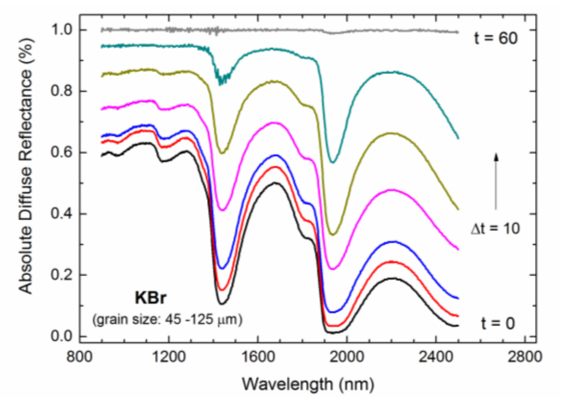

Figure 2. Absolute diffuse reflectance of the KBr:H_2O slurry. KBr powder was added to 0.03 ml water, and the first spectrum (t = 0) was taken in less than 2 mins after finishing the mixture. Time-sequenced raw spectra were taken every 10 minutes at room temperature and ambient atmosphere. The absolute diffuse reflectance is attained by referencing the raw spectra with that of a dry KBr sample.

Discussion: For the KBr:H_2O slurry we find that hydration decreases absolute reflectance in contrast to the proposed mechanism of darkening near the bright spots on Ceres [1]. Our result is similar to measurements by Prieto et al (1999) [4] for hydrated magnesium sulfate but in contrast to obervations of Dalton (2003) [5] who found little change in absolute reflectance for $MgSO_4$ with hydration levels below $6H_2O$ and darkening for magnesium heptahydrate [4, 5]. Our next measurements with hydrated $MgSO_4$ from 0.4-3.3 μm will better clarify changes in absolute spectral reflectance of this (and other) salts to inform interpretations of the cerian surface by Dawn.

Spectral measurements performed in a controlled environment for hydrated and anhydrous sulfates and perchlorates with regulated pressure and temperatures relevant to the diurnal temperature fluctuations at Ceres surface (~120 – 240 K) [6, 7] are currently underway. We will also measure changes in the UV-Vis spectral slope under these same conditions, as Jaumann et al. 2016 [3] suggest that variations in abundance of salts may affect the different slopes values in the UV-Vis.

Conclusion: Current laboratory measurements suggest that the effect of hydration on the absolute reflectance of salts is to darken the spectrum. We will present laboratory studies designed to understand the effects of hydration and dehydration on the optical spectra for several salts, including hydrated $MgSO_4$, to better inform Ceres' albedo near the bright spots.

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References: [1] A. Nathues et al. (2015) Nature 528, 237-239. [2] J.-Y. Li et al (2016) ApJL, under revision. [3] Jaumann et al. (2016) LPSC 47th Abstract. [4] O. Prieto et al. (1999) LPSC XXX, Abstract #1762. [5] J. B. Dalton (2003) Astrobiology 3 (4), 771-784. [6] O. Saint-Pé, et al. (2006) Icarus 105 (2), 271–281, [7] DeSanctis et al. (2015) Nature doi: 10.1038/nature16172 .