

INSTABILITY OF MAGNESIUM SULFATE HEXAHYDRATE ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) ON CERES: LABORATORY MEASUREMENTS. C. Bu¹, G. Rodriguez Lopez¹, C.A. Dukes¹, L.A. McFadden², J-Y. Li³, and O. Ruesch² ¹University of Virginia (Laboratory for Astrophysics and Surface Physics, Materials Science & Engineering, Charlottesville, VA 22904; caixiabu@virginia.edu; gr3dw@virginia.edu; cdukes@virginia.edu), ²NASA Goddard (NASA/GSFC, Mail Code: 693, Greenbelt, MD 20771); lucyann.a.mcfadden@nasa.gov), ³Planetary Science Institute (1700 E. Ft. Lowell Rd., Suite106, Tucson, AZ 85719; jyli@psi.edu).

Introduction: Photometric measurements from the Dawn Framing Camera (FC) show more than 130 bright patches of varying size and albedo on the generally dark background of dwarf planet Ceres [1]. The largest and brightest region, Cerealia facula in the central portion of Occator crater (19.4°N, 239.0°E), has a geometric albedo of 0.4–0.5 in the visible wavelengths, ~5x brighter than the average Ceres geometric albedo of 0.09–0.10 [1–3]. On the basis of the absolute reflectance at 0.44–0.98 μm and the steep spectral-slope below 0.55 μm observed by Dawn’s FC, Nathues et al. [1] suggested that a combination of magnesium sulfate hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) and the average Ceres spectra best matched that of Cerealia facula and hypothesized that the systematic darkening with distance from Cerealia facula’s center may result from either the mixing of salt evaporates with increasingly larger quantities of the native soil or from progressive dehydration of the $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.

However, recent measurements by Dawn’s Visible and Infrared Imaging Spectrometer (VIR) throughout 0.40–5.0 μm show no strong H_2O absorption bands, expected for a hydrated MgSO_4 in any portion of Occator Crater [3]. Rather, within Cerealia facula VIR measured a composition consistent with Ceres’ dark material [4], but with a clear increase in the relative portion of carbonate, particularly sodium carbonate (Na_2CO_3) [3]. The prevalence of Na_2CO_3 , however, does not preclude the presence of a small percentage of hydrous MgSO_4 with attenuated water absorptions, or a larger percentage of anhydrous sulfate material which is featureless over VIR’s spectral range. Indeed, magnesium and sodium sulfates have been identified in aqueously-altered carbonaceous chondritic (CI & CM) meteorites, expected to be compositionally similar to Ceres, suggesting the existence of endogenous surficial sulfate on Ceres is plausible [5].

In this work, we determine the stability of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ on Ceres surface by quantifying the dehydration rate as a function of pressure and temperature.

Experiment: $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ powder samples of varied grain size fractions (<45, 45–83, and 250–500 μm) were prepared, and X-ray powder diffraction (XRD) measurements confirmed composition and structure of each specimen. Reflectance measurements were obtained using a Perkin Elmer Lambda-1050

spectrophotometer with Harrick Praying Mantis (PM) diffuse reflectance accessory and low-temperature reaction chamber (LT-RC). The sample powders were enclosed in the LT-RC; the PM directed the source light from the spectrophotometer onto the sample and collected the sample diffused reflectance to the spectrophotometer detectors. The LT-RC was evacuated to $\sim 10^{-3}$ – 10^{-5} Torr ($\approx 10^{-6}$ – 10^{-8} Earth atmosphere). As the powders were exposed to vacuum, *in-situ* time-sequenced spectra (wavelength $\lambda = 0.40$ – 2.50 μm ; resolution $\Delta\lambda = 4$ nm) were taken every 5 minutes. Spectral measurements were performed at 296, 200 and 147 K, approximating Ceres’ maximum, and typical equatorial daytime and nighttime surface temperatures, respectively [6]. For 200 and 147 K, a continuously flowing, dry nitrogen (N_2) gas was used during sample cooling prior to evacuation of the LT-RC to limit condensation of water vapor from the ambient atmosphere. Raw spectra of the samples were referenced to a PTFE (polytetrafluoroethylene) powder standard for measurements of relative reflectance.

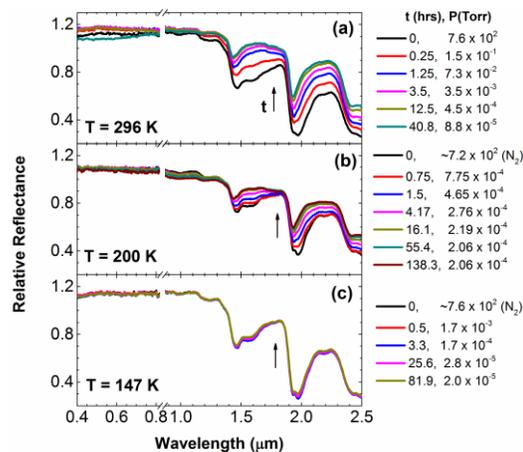


Figure 1. Temporal evolution of the relative reflectance for $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ powders (using grain size fraction of 45–83 μm) with vacuum-exposure time t , at (a) 296 K, (b) 200 K, and (c) 147 K. The evacuation started at $t = 0$ with ambient pressure $P \approx 760$ Torr of air or flowing nitrogen gas (N_2). Spectra at the representative conditions (t , P) are presented. Raw spectra of the samples were referenced to a PTFE (polytetrafluoroethylene) powder standard for measurements of relative reflectance.

Results: The relative reflectance of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ at 296(± 1), 200(± 4), and 147(± 2) K as a function of vacuum-exposure time (t) are shown in **Figure 1 (a)–(c)**. The strong, diagnostic, asymmetric absorptions near 1.47 and 1.96 μm are from molecular water, due to the overtone(s) of the O-H stretching fundamental(s) and the superposition of the O-H stretching and the H-O-H bending fundamentals, respectively [7,8]. Sulfur oxides or sulfur allotropes are not directly observed as the S=O stretching modes have absorption features in the 7–8 μm region [9]. **Figure 1** shows that these absorption band depths attenuate with increasing vacuum-exposure time, accompanied with changes of the band shape, indicating the removal of the incorporated H_2O molecules. Complementary XRD analysis at 296 K show systematic attenuation of the $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ diffraction peaks with low-pressure-exposure, suggesting the structure transition from crystalline to amorphous.

We use the area of the OH/ H_2O absorption feature at $\sim 1.96 \mu\text{m}$ (A) as an indicator of total sample hydration. The A was calculated by converting each spectrum in **Figure 1** to optical depth units ($-\ln(R)$, where R is the relative reflectance), and then determining the integrated area of the absorption feature after subtraction of the non-linear background continuum. **Figure 2** shows the double logarithmic representation of hydration, $\ln\{-\ln(A)\}$ vs. $\ln(K) + n \times \ln(t)$.

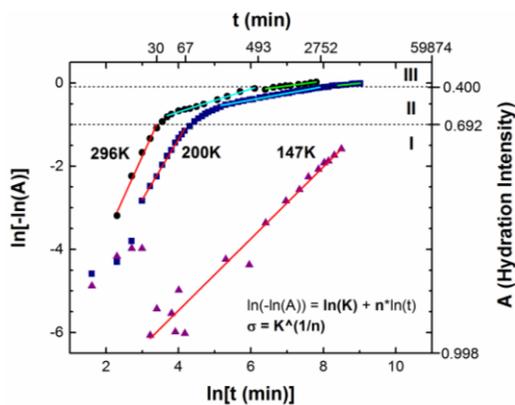


Figure 2. Double natural logarithm representation of the H_2O band area at $\sim 1.96 \mu\text{m}$ (A) of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ powders (grain size = 45–83 μm) as a function of vacuum-exposure time t (in units of minutes). Data were derived from the **Figure 1(a)–(c)** at 296, 200 and 147 K, respectively. The Avrami equation, $A = \exp(-Kt^n)$ is used to fit the linear regions (I, II, and III), with the slope and intercepts of the linear fits (solid lines) providing the Avrami parameter n and $\ln(K)$, respectively.

Discussion: The dehydration rate of hydrated sulfates depends on the bonding energy for each water molecule in the multiply-hydrated magnesium sulfate, as well as the rate of diffusion. We model the dehydration process using a simple Avrami equation [10], $A(t) = \exp(-Kt^n)$, where t is the vacuum-exposure time, K is

a temperature-dependent dehydration rate constant, and n is the Avrami exponent. Three linear regimes (I, II, and III) appear during dehydration of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ at 296 and 200 K (**Figure 2**), indicating three sequential, distinct phases. Plausible systematics for three-stage vacuum-dehydration are: (1) removal of interstitial, H-bonded water molecules, and/or physically absorbed water molecules, (2) the subsequent conversion or collapse of the crystal structure with H_2O loss, and (3) loss of final H_2O from an amorphous structure. We find the dehydration rate, $\sigma = K^{1/n}$, reduces as the stage processes from I to III, and also reduces as the temperature decrease.

Conclusion: Based on **Figure 2**, we derive the time it takes to dehydrate the $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ to a level of 1% (below instrument sensitivity) at each temperature. This is $\sim 10^3$ years (296 K), 0.5×10^5 years (200 K), and 10^{12} years (147 K).

Since the age of Occator crater is ~ 78 Ma ($\sim 10^8$ years) [1], and Ceres is $\sim 10^9$ years, our measured rates preclude $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ as a candidate material for Cerealia facula, or indeed anywhere on Ceres' surface.

These findings imply that hydrated MgSO_4 on any airless body may only exist in permanently shadowed regions where temperatures are always significantly lower than 147 K or where a water supply is always available.

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