

EFFECTS OF DEHYDRATION ON TIR SPECTRA OF CHLORIDES AND IMPLICATIONS FOR MARS.

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Introduction: The search for liquid water as a the requirement for life has driven Mars exploration. It is commonly accepted that liquid water was once pervasive at the surface [e.g. 1, 2, 3] but under current environmental conditions liquid water is not stable at the surface over large scales. As the past reservoir receded, it would have left behind evaporite minerals, possibly hydrated and capable of providing a transient source of liquid water. Therefore, to understand the extent and abundance of past water and potential reservoirs of current water, the detection of such minerals is key.

[4] identified a unique compositional unit in the southern highlands of Mars using spectral data collected by the Mars Global Surveyor Thermal Emission Spectrometer (TES) and Mars Odyssey Thermal Emission Imaging System (THEMIS). These units exhibit featureless, sloping emissivity spectra attributed to a material with non-unit emissivity such as chloride salts [5].

The spectral identification of chlorides is challenging because they are featureless over much of the thermal infrared (TIR) portion of the spectrum [e.g. 6, 7, 8, 9]. Anhydrous chlorides, like halite, are transparent from 5-20 μ m and their detection is often interpreted based on their effect on the spectra of co-occurring minerals. For example, minor amounts of sulfates and adsorbed water contaminants can have pronounced spectral features in a halite matrix (Figure

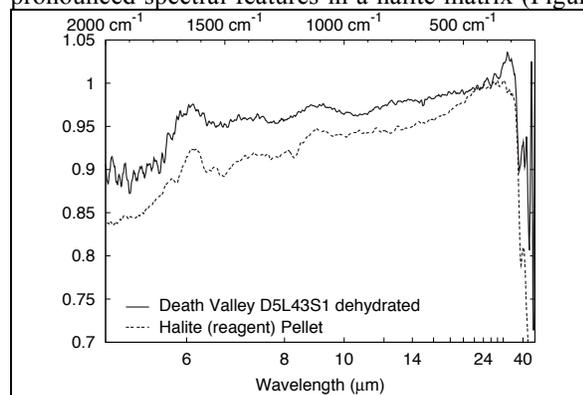


Figure 1. Emissivity spectra of halite and Death Valley sample D5L43S1 after one week of dehydration. These spectra are transparent at short wavelengths as evidenced by transmission features due to adsorbed water at $\sim 6\mu$ m and sulfate at $\sim 9\mu$ m. Both spectra exhibit a sharp decrease in emissivity at long wavelengths characteristic of the absorptions in anhydrous chlorides.

1) [8, 9, 10]. Hydrated chlorides, although also featureless through much of the TIR spectral range, are not transparent and have distinct spectral features at long wavelengths (Figure 2) [9].

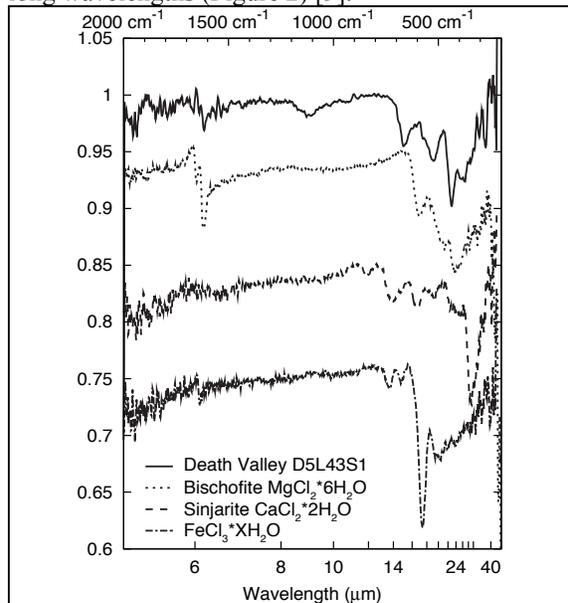


Figure 2. Hydrated chlorides: bischofite, sinjarite and an unknown ferric chloride. These three spectra have features associated with water at $\sim 6\mu$ m, most obvious in bischofite, and distinct features at wavelengths longer than 14μ m. Similarly, field sample D5L43S1 exhibits these characteristics and an additional feature at $\sim 9\mu$ m attributed to sulfate. Death Valley samples D5L42-D5L45 all exhibit the same emissivity features.

In an effort to better understand the spectral characteristics of chlorides as they occur in natural environments, especially the difference between hydrated and anhydrous chlorides in emissivity spectra, we have collected chloride-bearing evaporite deposits from Badwater Basin, Death Valley, CA. Here we report on the laboratory emissivity spectra for a representative subset of these samples. By comparing laboratory spectra with terrestrial remote sensing data, we hope to better constrain the mineralogy of the putative martian chlorides.

Methods: Field samples were collected from the Badwater Basin, Death Valley, CA March 14-16, and October 19-21, 2011. Sampling sites were chosen based on classification of MODIS/ASTER airborne simulator (MASTER) TIR data. Salt crusts were carefully extracted from the surface and packaged to

avoid dehydration and disruption of the sample surface. Emissivity spectra were measured at Arizona State University's Mars Space Flight Facility using a Nicolet Nexus 670 E.S.P FTIR interferometer and the techniques of [11] for hydrated samples. Additionally, aliquots of a subset of the field samples were left exposed for 1 week and/or heated at 80C for several hours prior to measurement to induce dehydration of the sample.

Results and Discussion: A representative emissivity spectrum of one of our Badwater Basin evaporite samples is shown in Figures 2 and 3. This spectrum has emissivity minima at ~ 15 , 19 , and $23\mu\text{m}$ (666 , 526 , and 434 cm^{-1}) and is unique from common hydrated chlorides, such as bischofite, sinjarite or hydrated ferric chloride. The mineralogy of this sample will be confirmed with XRD, but we hypothesize that this is a Na-chloride that this sample is an unstable hydrated state, possibly hydrohalite ($\text{NaCl}\cdot 2(\text{H}_2\text{O})$). Hydrohalite is usually found in halite-saturated brines at temperatures below -5C [12] (not a likely temperature in Death Valley, CA). However, these samples were cooled to temperatures below freezing to avoid dehydration during emissivity measurements [10]. The presence of hydrohalite is therefore not unexpected. Additionally, the dehydrated sample aliquot has an emissivity minima at $\sim 38\mu\text{m}$ (264 cm^{-1}), matching that of halite (Figures 1 and 3), further indicating a Na-chloride.

Spectra extracted from the MASTER scene for the pixels corresponding to the sample sites D5L42-D5L45 show a difference in spectral contrast, but do have a similar shape, with an emissivity minimum near $9\mu\text{m}$, likely corresponding to sulfate contaminants (Figure 4). The laboratory spectra of dehydrated field

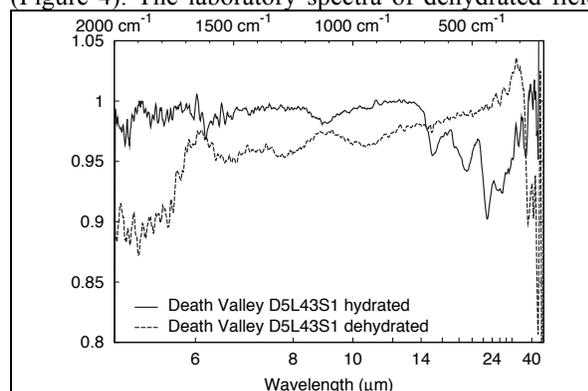


Figure 3. Death Valley sample D5L43S1 before and after dehydration. The dehydrated sample exhibits the transparency features and sharp emissivity minima at long wavelengths ($>25\mu\text{m}$) associated with anhydrous chlorides. The hydration state of the chloride has an obvious effect on the emissivity spectra.

samples appear inverted with an emissivity maximum at approximately $9\mu\text{m}$ corresponding to the transmission feature for sulfates. In previous studies of Death Valley using MASTER data [8], unique spectra from the usually wet central part of the basin were labeled "Damp" (due to their location). These spectra more closely resemble the shape of transparency features in the dehydrated field sample spectra.

In the remote sensing data from Badwater Basin, spectra that display an overall concave downward spectral shape between 8-12 microns tend to represent hydrated chlorides, whereas spectra with a relatively featureless or concave upward spectral shape tend to represent anhydrous chlorides. Spectra of the putative chloride deposits on Mars tend to be featureless, without transmission features and may therefore represent a hydrated chloride.

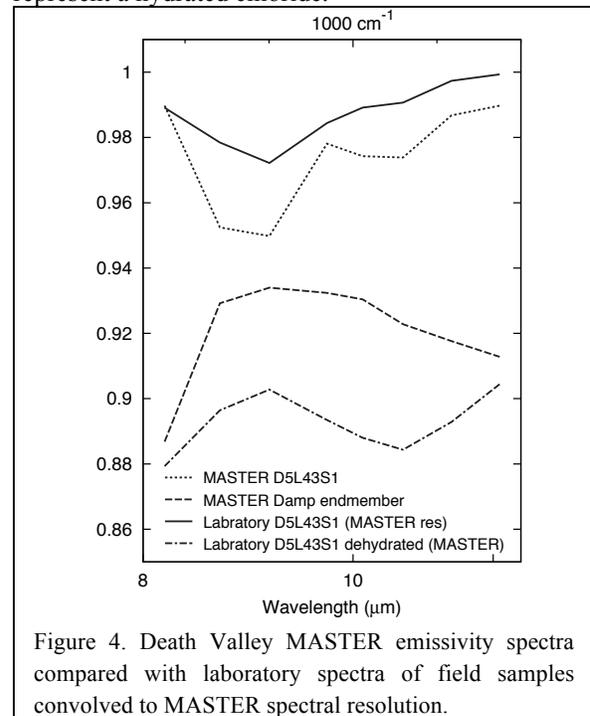


Figure 4. Death Valley MASTER emissivity spectra compared with laboratory spectra of field samples convolved to MASTER spectral resolution.

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