

REFLECTANCE SPECTRA OF LOW-TEMPERATURE CHLORIDE AND PERCHLORATE HYDRATES RELEVANT TO PLANETARY REMOTE SENSING. J. Hanley¹, V. F. Chevrier¹, J. B. Dalton², C. S. Jamieson^{2,3}. ¹Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, USA, ²Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove, Pasadena CA 91011, ³NASA Postdoctoral Program Fellow; jhanley@uark.edu.

Introduction: Chlorides and perchlorates present on Mars can form aqueous solutions because of their low temperature eutectics and related lower evaporation rates [1]. Chlorides may be major constituents of some spectrally distinct units in Mars Odyssey THEMIS mid-infrared (MIR) observations [2], and along with other arguments for their existence in the martian regolith, the discovery of chlorides and perchlorates in subpolar latitudes by NASA's Phoenix Lander [3] suggests a global distribution of chlorides on Mars. On Europa, chlorides and perchlorates may be produced by radiolysis of Iogenic Na, Mg and Cl, or by aqueous geochemistry in the interior.

Neither chlorides nor perchlorates have been observed by near-infrared (NIR) spectrometers such as Mars Express OMEGA or MRO CRISM. This is partly because chloride spectra in databases lack NIR spectral absorption features [4] and most spectral libraries contain only high temperature "Earth-relevant" chlorides, e.g. NaCl or KCl. Similarly, little is known about perchlorate spectral features. At typical martian temperatures, hydrates of chlorides and perchlorates are more stable [1], though humidity will also affect hydration state. In addition, it has been demonstrated that spectra exhibit many temperature-dependent features [5,6]. Water (including that of hydration) is particularly sensitive. Reference spectra of surface materials at relevant temperatures are critical to derive abundance estimates through spectral modeling. We measured the spectra of each hydrate at both room temperature (RT) and at 80K. Our study will alleviate the lack of data in current spectral libraries for hydrates that exist on Mars and other planetary surfaces.

Methods: The following salts and their hydrates were synthesized and their reflectance spectra were measured: KCl, NaCl, CaCl₂, MgCl₂, FeCl₂, FeCl₃, NH₄Cl, NaClO₂, NaClO₃, Mg(ClO₃)₂, NaClO₄, KClO₄, and Mg(ClO₄)₂. Reflectance spectra were taken using a Nicolet 6700 FTIR Spectrometer equipped with fiber optics to allow analysis in the range 1.0-25 μm and an ASD FieldSpec Pro in the range 0.3-2.5 μm for the low temperature measurements. Spectra were measured at two temperatures: 296K (RT) and 80K. Anhydrous compounds were heated to 120°C for two days to drive off excess water. Lower hydrates were synthesized by heating the RT stable compounds in a programmable tube furnace. Salts could also be dehydrated in a dessicator under low humidity controlled by saturated salt solutions. Spectral measurements were repeated at both temperatures to ensure no changes had taken place.

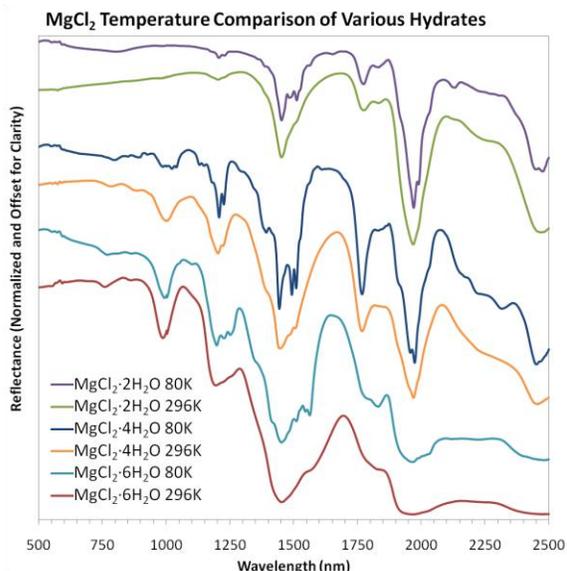


Figure 1. Diffuse NIR reflectance spectra of various hydrates of MgCl₂ at 296K and 80K. Note how spectral features become more enhanced at very low temperature.

Results: Chlorides. KCl does not exhibit any significant NIR features, nor does anhydrous NaCl. However, hydrated MgCl₂ salts demonstrate a myriad of spectral features in the 2, 4 and 6H₂O forms (Fig. 1). These features are affected by two conditions. First, the level of hydration controls the depth, breadth and number of absorption bands, which increase with water content. Second, as predicted, changes in temperature produce a number of effects. For example, the band for MgCl₂·6H₂O at ~1.2 μm splits into a triplet at the lower temperature. In addition, bands tend to become narrower and shift toward longer wavelengths. These effects are seen in almost all absorption bands (Figs. 1 and 2).

Perchlorates. Perchlorate spectra show numerous absorption bands (Figs. 2 and 3). Even anhydrous perchlorates such as KClO₄ have significant spectral features [7]. However, the spectrum of anhydrous NaClO₄ does not exhibit any NIR features, except for some adsorbed water at 1.9 μm (Fig. 2). NaClO₄·H₂O (Fig. 2) and Mg(ClO₄)₂·6H₂O (Fig. 3) show mostly features that are due to water. A band appears at ~2.14 μm (possibly due to the Cl-O bond in the perchlorate ion) in both spectra. Other major bands of NaClO₄·H₂O are located at 1.17, 1.42, 1.46 and 1.93 μm, the latter three corresponding to the usual hydration bands observed in all the hydrated phases.

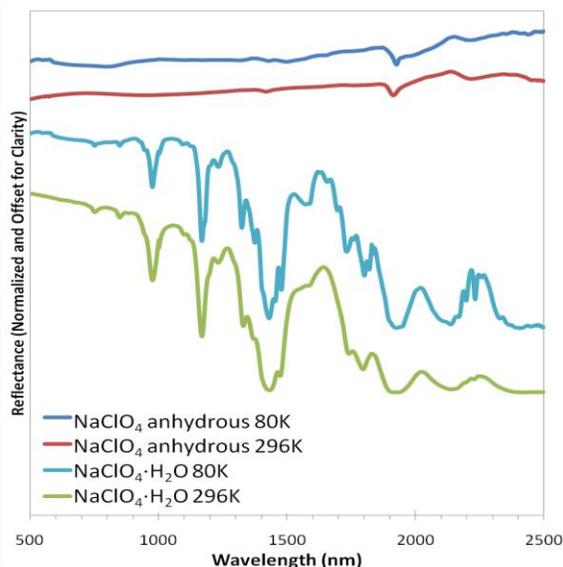


Figure 2. NIR reflectance spectra of NaClO_4 anhydrous and monohydrate at 296K and 80K. Note the lack of spectral features in the anhydrous form at both 296K and 80K.

Discussion: Most hydrated salts exhibit features in the NIR that are due to water. This is confirmed by comparing the hydrates to their anhydrous forms. However, it is very difficult to synthesize some of the anhydrous forms due to the extreme hygroscopic nature of these salts. Even after heating many remain slightly hydrated. This has implications for the amount of water present as hydrated chlorides or perchlorates on the martian surface.

The cations appear to have a strong effect on spectral features. The cation will control the number and quantity of hydration states. For example, potassium salts form no hydrates and sodium salts form only a few (if any) hydration states. Magnesium salts are extremely hygroscopic; under terrestrial conditions of temperature, pressure and humidity their hydration states are likely to be hexahydrate (Fig. 3), but can be hydrated up to $12\text{H}_2\text{O}$. However, the anion seems to have less effect in the NIR region. This is demonstrated in Fig. 3 by the lack of features not associated with water in the spectra of room-temperature MgCl_2 , $\text{Mg}(\text{ClO}_3)_2$ and $\text{Mg}(\text{ClO}_4)_2$.

Future work: Future studies will obtain spectra for the remaining hydrates of each compound shown here, as well as additional calcium and potassium compounds, at various temperatures from 50K to 300K.

Results from the literature suggest that vibrational modes for perchlorates and chlorates would appear in the mid- to far-infrared, generally at or past $10\ \mu\text{m}$ [6]. We have begun investigation into the MIR ($2.5 - 25\ \mu\text{m}$) reflectance features of these salts, and preliminary results support this inference. The next step will be to

examine the effect of temperature on the MIR spectral characteristics for all of these salts.

Conclusions: Chlorides and perchlorates show significant spectral features that should allow for their identification on the surface of Mars. All hydrates exhibit diagnostic bands characteristic of hydrated phases (1.4 and $1.9\ \mu\text{m}$), and hydration band depth increases with increasing hydration state. The cation generates spectral features that tend to carry over from chloride to chlorate to perchlorate (e.g. magnesium bands at $\sim 1.16\ \mu\text{m}$). The anion also controls diagnostic spectral features, especially in the MIR. Determining the structure of each of the salt hydrates would help to understand the spectral characteristics.

Some unidentified hydrates in planetary remote sensing observations could be chlorides, chlorates or perchlorates. Although hydration states of planetary surface compounds are not all known at present, our database aims to include all known hydration states for each compound, enabling not just identification of the compound, but also its abundance and hydration state.

Acknowledgements: This work was carried out at the Arkansas Center for Space and Planetary Science, University of Arkansas; and at the Planetary Ice Characterization Laboratory (PICL), Jet Propulsion Laboratory, California Institute of Technology.

References: [1] Chevrier, V.F. et al (2009) *GRL*, L10202. [2] Osterloo M.M. et al. (2008) *Science* 319, 1651-1654. [3] Hecht M.H. et al. (2009) *Science*, 325, 64-67. [4] Hunt, G.R. et al. (1972) *Mod. Geo.*, 3, 121-132. [5] Dalton, J.B. et al (2005) [6] Hanley, J. and J.B. Dalton (2010) *Bull. Amer. Astr. Soc.* 42, #4, 26.05 [7] Hanley, J. et al (2010) *LPSC XLI* #1953 [8] Hanley, J. et al (2011) *LPSC XLII* [9] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley-Interscience, 1970.

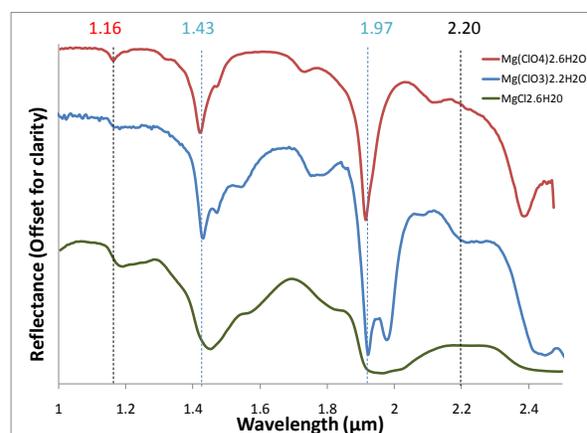


Figure 3. Comparison of various magnesium compounds at 296K. Red: $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, Blue: $\text{Mg}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$, Green: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. All show strong absorption features at 1.4 and $1.9\ \mu\text{m}$, indicating water/hydration, as well as a band around $1.16\ \mu\text{m}$. The $\text{Mg}(\text{ClO}_3)_2$ and $\text{Mg}(\text{ClO}_4)_2$ spectra show similar, though shifted, bands at $2.2\ \mu\text{m}$ and $2.4\ \mu\text{m}$, possibly due to a Mg-O interaction.