

REFLECTANCE SPECTRA OF LOW-TEMPERATURE CHLORIDE AND PERCHLORATE HYDRATES AND THEIR RELEVANCE TO THE MARTIAN SURFACE. J. Hanley, V. F. Chevrier, B. L. Davis, T. S. Altheide, A. Francis, W. M. Keck Laboratory for Space Simulation, Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, USA, 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 have been suggested to be the major constituents of some spectrally distinct units in Mars Odyssey THEMIS mid-infrared observations, and along with other geomorphologic arguments for their existence in the martian regolith [2], the recent discovery of chlorides and perchlorates in the north subpolar latitudes by NASA's Phoenix Lander [3] reinforced the potential for the global distribution of chlorides on Mars.

Neither chlorides nor perchlorates have ever been observed by near infrared spectrometers such as Mars Express OMEGA or MRO CRISM. This is because chlorides present in databases lack spectral features (absorption bands) in the near-infrared [4] and most spectral libraries contain only high temperature "Earth-relevant" chlorides, such as NaCl or KCl. Similarly, not much is really known about perchlorate spectral features. However, at typical Martian relevant temperatures, hydrates are more stable [1]. Our study will serve to alleviate the lack of data in the current spectral libraries for hydrates that exist on Mars.

Methods: The following salts and their low-temperature hydrates were synthesized and their near-infrared reflectance spectra were measured: KCl, NaCl, CaCl₂, MgCl₂, FeCl₂, FeCl₃, NH₄Cl, NaClO₂, NaClO₃, Mg(ClO₃)₂, NaClO₄, KClO₄, and Mg(ClO₄)₂. We also measured eutectic mixtures of ice and salt. Reflectance spectra were taken using a Nicolet 6700

FTIR Spectrometer equipped with fiber optics to allow analysis in the range 1.0-2.5 μm. For comparison reasons, chlorides and perchlorates stable at ambient temperature were also measured. In the case of eutectic mixtures, we corrected for ice content using KCl + ice as a control sample since it does not form any hydrate. Anhydrous spectra were collected on a hot plate set to 120°C, under nitrogen flow for two hours.

Results: *Chlorides.* KCl does not exhibit any significant features, nor does anhydrous NaCl (Fig. 1). However, other anhydrous chlorides (e.g. CaCl₂), as well as their hydrated forms, clearly show evidence of additional absorption bands. The most significant bands are located at 1.19, 1.44 and 1.97 μm, the latter two due to hydration. Also, notice that the absorption band depth increases with increasing hydration state.

Oxychlorine compounds. Spectra were measured for sodium chlorate (NaClO₃) and chlorite (NaClO₂, Fig. 2), as well as magnesium chlorate (Fig. 4). Sodium chlorate does not form any hydrates [5], which explains its lack of water bands. NaClO₂, which only has one hydrate (3H₂O), shows absorption in the 1.9 μm "water" range, but only weakly at 1.4 μm. However, they both show a similar band at 2.2 μm. This band is also shared by Mg(ClO₃)₂, indicating that it is not due to the cation-anion interaction, but likely a Cl-O mode.

Perchlorates. Perchlorate spectra show numerous absorption bands (Figs. 3 and 4). Even anhydrous perchlorates have significant spectral features, as shown by KClO₄, which shows major absorption bands at 1.23, 1.55, 2.01 and 2.13 μm (Fig. 3A). NaClO₄·H₂O

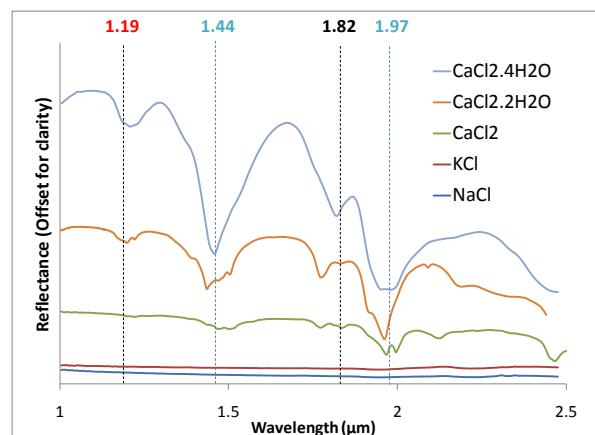


Figure 1. Diffuse reflectance spectra of various Mars-relevant chlorides. Note the presence of spectral features in all hydrated forms, as well as in anhydrous CaCl₂.

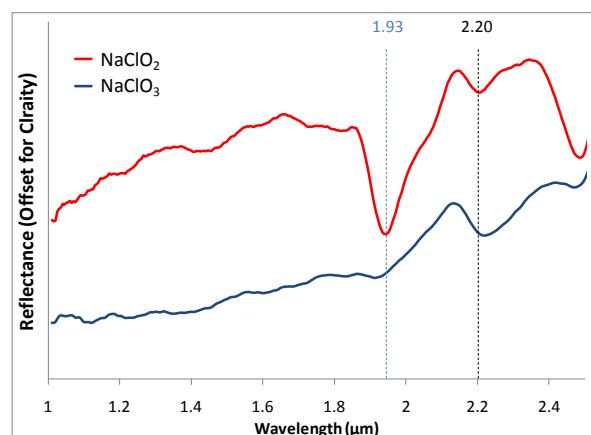


Figure 2. Near-infrared reflectance spectra of NaClO₂ (red) and NaClO₃ (blue). NaClO₃ does not form hydrates, thus lacks any bands associated with water. NaClO₂ and NaClO₃ share a common band at 2.20 μm.

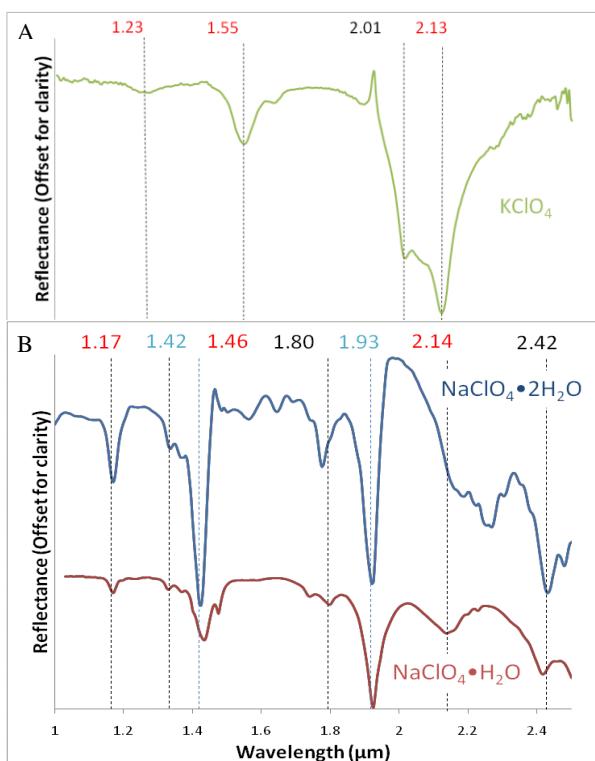


Figure 3. Diffuse reflectance spectra of (A) KClO_4 and (B) NaClO_4 hydrates.

shows even more absorption bands (Fig. 3B), although at different positions. One band that appears in both spectra is at $\sim 2.14 \mu\text{m}$ (possibly due to the Cl-O bond in the perchlorate ion). Other major bands of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ 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. We do not observe any significant spectral difference between $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ except an increase in band depth due to the higher water content and a possible shift of the 2.14 μm feature to $\sim 2.25 \mu\text{m}$.

Discussion: Results from the literature suggest that vibrational modes for perchlorates and chlorates would appear in the mid- to far-infrared, generally around 10 μm [6]. However, given the similarities between magnesium chloride, perchlorate and chlorate (Fig. 4), it is possible that features we are seeing are interactions of the Mg-Cl bond, particularly at 1.16 μm . An even stronger argument can be made for it being Mg-O at ~ 2.20 and $\sim 2.40 \mu\text{m}$, due to the strength and similarity of bands between the chlorate and perchlorate spectra. These may be shifted slightly between species, but given their prominence in the spectra, it is an important relationship.

Similarly, there are strong parallels between NaCl , NaClO_2 and NaClO_3 , particularly the lack of features not associated with water. NaClO_4 demonstrates more

bands, but also has multiple hydration states unlike the other sodium species.

Future work will include spectra of other calcium and potassium compounds, as well as obtaining spectra of the remaining hydrates for each of the studied compounds.

Conclusions: Chlorides and perchlorates show significant spectral features that should allow for their identification on the surface of Mars. Common across almost all spectra are that hydrates show bands characteristic of hydrated phases (1.4 and 1.9 μm), and hydration band depth increases with increasing hydration state. The cation is important, as its features tend to carry over from chloride to chlorate to perchlorate (e.g. magnesium bands at $\sim 1.16 \mu\text{m}$). Similarly, the anion is equally important in determining spectral features. Chloride on its own does not have any intrinsic bands. Chlorate bands are present at $\sim 2.2 \mu\text{m}$, and perchlorate bands are present at ~ 1.2 , ~ 1.5 , & 2.11-2.14 μm .

Therefore, some unidentified hydrates could be chlorides, chlorates or perchlorates. Although it is unknown what hydration state chlorides or perchlorates would be found in, our database aims to include all known hydration states for each compound, potentially allowing for not just identification of the compound, but even its hydration state.

References: [1] Chevrier, V. F. et al. (2009) *GRL*, L10202, doi:10.1029/2009GL037497. [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] Hanley, J. et al (2010) LPSC This conference [6] Nakamoto, K. **Infrared Spectra of Inorganic and Coordination Compounds**. New York: Wiley-Interscience, 1970.

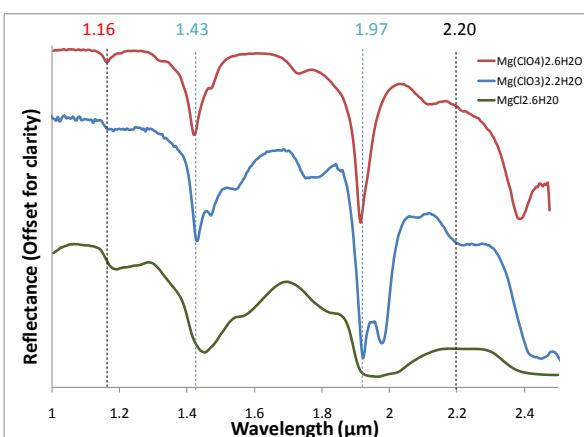


Figure 4. Comparison of various magnesium compounds. Red: $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, Blue: $\text{Mg}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$, Green: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. All show strong absorption features at 1.4 and 1.9 μm , indicating water/hydration, as well as a band around 1.16 μm , which could be due to Mg-Cl. The $\text{Mg}(\text{ClO}_3)_2$ and $\text{Mg}(\text{ClO}_4)_2$ show similar, though shifted, bands at 2.2 μm and 2.4 μm , possibly due to an Mg-O mode.