

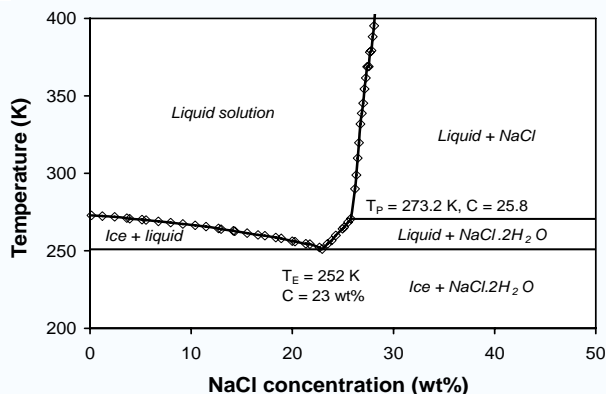
**REFLECTANCE SPECTRA OF LOW-TEMPERATURE CHLORIDE AND PERCHLORATE HYDRATES AND THEIR RELEVANCE TO THE MARTIAN SURFACE.** B.L. Davis<sup>1</sup>, V.F. Chevrier<sup>1</sup>, T.S. Altheide<sup>1</sup>, C. Swaffar<sup>1</sup>, <sup>1</sup>W.M. Keck Laboratory for Space Simulation, Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, USA, [bld002@uark.edu](mailto:bld002@uark.edu).

**Introduction:** Chlorides may be present on Mars [1], favoring potential low-temperature aqueous solutions because of low temperature eutectics [2] and related lower evaporation rates [3]. More recently, chlorides have been suggested to be the major constituents of some spectrally distinct units in Mars Odyssey THEMIS mid-infrared observations, along with other geomorphologic arguments for their existence in the martian regolith [4].

The recent discovery of chlorides and perchlorates ( $\text{ClO}_4^-$  ion) on Mars by NASA's Phoenix Lander [5] reinforced the potential for chlorides on Mars. Perchlorates are very rare on Earth and found naturally in extremely arid environments such as the Atacama Desert in Chile [6], where they are supposed to result from photochemical oxidation of chlorides [7].

Neither chlorides nor perchlorates have ever been observed by near infrared spectrometers such as Mars Express OMEGA or MRO CRISM. This is due to their lack of spectral features (absorption bands), even in the mid infrared. Most spectral library contain only high temperature "Earth-relevant" chlorides, such as NaCl or KCl. However, at typical martian relevant temperatures, hydrates are more stable (Fig. 1 and 2). Similarly, not much is really known about perchlorate spectral features.

Sulfate hydrates present more significant features than anhydrous phases. Using this hypothesis, we propose to study reflectance properties of hydrated chlorides and perchlorates, which could have significant features, and thus eventually be present on the surface of Mars.

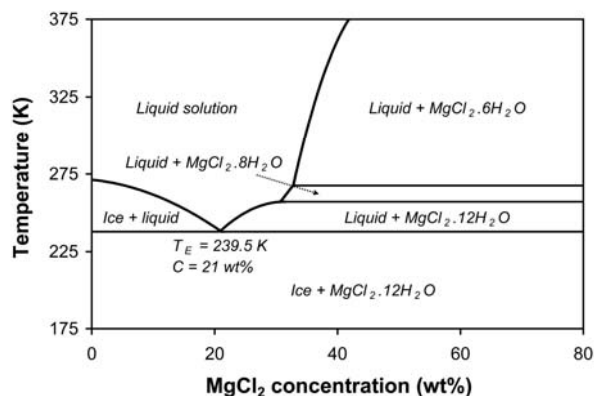


**Figure 1.** Calculated phase diagram of monovalent cation chloride: NaCl. At martian relevant temperature, the stable phase is  $\text{NaCl}\cdot 2\text{H}_2\text{O}$ .

**Experimental protocol:** This project is separated in two parts. In the first part stability diagrams were

generated for various chlorides and perchlorates relevant to Mars. Various diagrams are available from the literature, or can be calculated by knowing the thermodynamic parameters for the various hydrates involved. We present in an associated abstract the thermodynamic diagram for two perchlorates potentially present on Mars:  $\text{NaClO}_4$  and  $\text{Mg}(\text{ClO}_4)_2$  [8].

Then, using these thermodynamic diagrams, the relevant hydrates were synthesized in the lab. Eutectic solutions were made of the following salts: KCl (20 wt%), NaCl (23 wt%, Fig. 1),  $\text{CaCl}_2$  and  $\text{MgCl}_2$  (magnesium chloride 21 wt%, Fig. 2B), all of which were then frozen at or below their respective eutectic temperatures. Such mixtures consist of ice + salt at the eutectic. Also synthesized were salt hydrates at temperatures and concentrations higher than the eutectic to avoid the presence of ice.

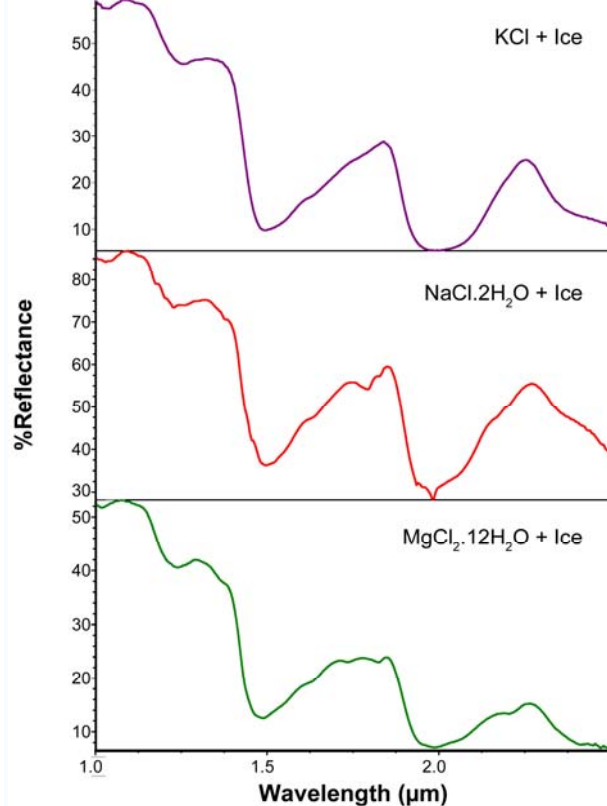


**Figure 2.** Calculated phase diagram of  $\text{MgCl}_2$  [9] showing the stability of higher hydrates at lower temperatures.

Reflectance spectra were taken using a Nicolet 6700 FTIR Spectrometer, using the following configuration: white light, quartz beamsplitter and InGa detector, to allow analysis in the range 1.0-2.5  $\mu\text{m}$  (usual range for OMEGA / CRISM observations). A fiber optic probe attachment was used in conjunction with the spectrometer to take the readings with the samples placed in a styrofoam container filled with dry ice and/or liquid nitrogen to keep the samples frozen. For each sample, 300 spectrum were averaged at a resolution of 4  $\text{cm}^{-1}$ . For comparison reasons, chlorides and perchlorates stable at ambient temperature were also measured.

**Results: Chlorides.** Chloride eutectic solids are composed of a mixture of salt (hydrate) and ice. We use KCl as a control sample. Indeed, contrary to NaCl, KCl does not form any hydrate. As expected the spectra are quite dominated by water ice, with the three

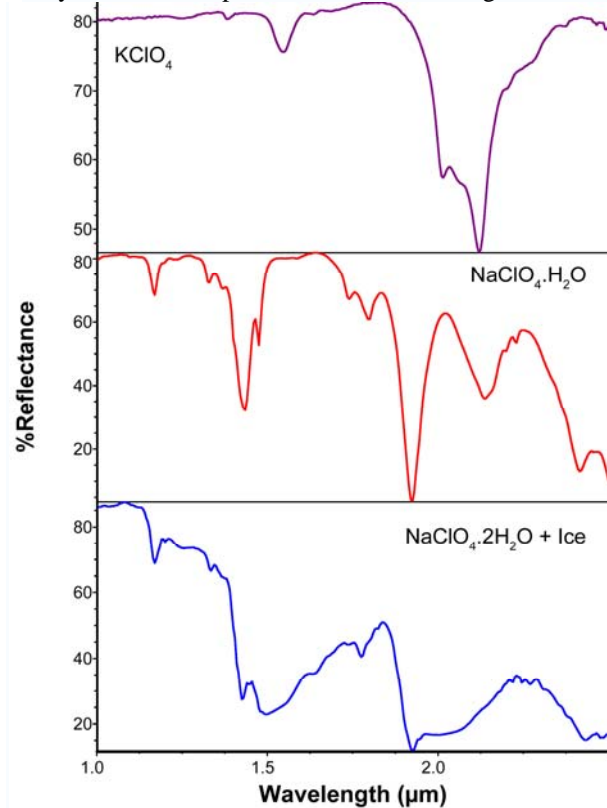
typical broad absorption bands at 1.25, 1.5 and 2.0  $\mu\text{m}$ . KCl does not exhibit any other significant feature (Fig. 3). However, NaCl and  $\text{MgCl}_2$  clearly show evidence of additional absorption bands. The most significant bands are located at 1.79, 1.83, and 1.98  $\mu\text{m}$  for  $\text{NaCl}\cdot 2\text{H}_2\text{O} + \text{Ice}$  and 1.73, 1.82 and 2.21  $\mu\text{m}$  for  $\text{MgCl}_2\cdot 12\text{H}_2\text{O} + \text{Ice}$ . Comparison with the featureless KCl spectrum shows that the features observed are due to chloride hydrates.



**Figure 3.** Diffuse reflectance spectra of various Mars-relevant chlorides at their eutectic conditions.

*Perchlorates.* Perchlorate spectra show numerous absorption bands (Fig. 4). Even anhydrous perchlorates have significant spectral features, as shown by  $\text{KClO}_4$ , which shows major absorption bands at 1.38, 1.55, 2.01 and 2.12  $\mu\text{m}$  (Fig. 4).  $\text{NaClO}_4\cdot\text{H}_2\text{O}$  shows even more absorption bands (Fig. 4), although at different positions, except for the 2.12  $\mu\text{m}$  (possibly due to the Cl-O bond in the perchlorate ion). Other major bands are located at 1.17, 1.43, 1.47 and 1.92  $\mu\text{m}$ , the three last ones corresponding to the usual hydration bands observed in all the hydrated phases. Finally, the spectrum of eutectic  $\text{NaClO}_4$ , composed of the dihydrate and ice (Fig. 4), appears to be a mixture of the monohydrate spectrum and ice, since we observe exactly the same bands between each spectrum. We do not observe any significant spectral difference due to Na-

$\text{ClO}_4\cdot 2\text{H}_2\text{O}$  compared to  $\text{NaClO}_4\cdot\text{H}_2\text{O}$ . Of course this may be due to the presence of water ice large bands.



**Figure 4.** Diffuse reflectance spectra of various Mars-relevant perchlorates at their eutectic conditions.

**Conclusions:** Chloride hydrates and perchlorates (hydrated or anhydrous) show significant spectral features that should allow their identification on the surface of Mars using remote sensing techniques. Several of these hydrates show bands characteristic of hydrated phases. Therefore, all low-temperature phases of such salts should be included in spectral databases.

Future work will focus on separating pure hydrates from ice, using concentrations and temperatures above the eutectic, and characterizing their spectral properties. This will help with comparing different levels of hydration and separating their spectral properties from the ice always present in eutectic compositions.

**References:** [1] Knauth L. P., D. M. Burt (2002) *Icarus* 158, 267-271. [2] Brass G. W. (1980) *Icarus* 42, 20-28. [3] Sears D. W. G., J. D. Chittenden (2005) *Geophys. Res. Lett.* 32. [4] Osterloo M. M. et al. (2008) *Science* 319, 1651-1654. [5] Hecht M. H. et al. (2008) *AGU fall meeting, December 15-19, 2008, San Francisco, USA #U14A-04*. [6] Ericksen G. E. (1981) *Geological Survey Professional Paper #1188*. [7] Kanga N. et al. (2006) *Analytica Chimica Acta* 567, 48-56. [8] Hanley J. et al. (2009) *LPSC* This issue. [9] Bénard J., in *Nouveau Traite de Chimie Minerale, Vol 4, Groupe II: glucinium, magnésium, calcium, strontium, baryum, radium* P. Pascal, Ed. (Masson & Cie, Paris, France, 1958), vol. 4, pp. 173-174.