

STRATEGIES FOR REMOTELY DETECTING CHLORINE SALTS ON MARS. J. Hanley¹, Z. Bandelier², C. Murphy^{3,2}, R. Carmack⁴, B. Horgan⁴. ¹Lowell Observatory, Flagstaff, AZ (jhanley@lowell.edu); ²Northern Arizona University, Flagstaff, AZ; ³Amherst College, Amherst, MA; ⁴Purdue University, West Lafayette, IN.

Introduction: NASA's Phoenix lander provided a unique insight into the regolith of the North Polar Region of Mars through its Wet Chemistry Lab (WCL) analysis. Ions in solution were measured by a sensor array of electrochemically based ion-selective electrodes (ISE). WCL detected a variety of ions, in particular chloride (Cl⁻) and perchlorate (ClO₄⁻) [1-3]. It is also possible that chlorate (ClO₃⁻) was present but masked by the signal of perchlorate [4].

Chlorine salts may also play a role in the mechanical properties of the regolith, as well as the stability of subsurface water. High soil cohesion was encountered at the Phoenix landing site making sample analysis challenging; such cohesion may result from hydrated salts and eutectic brines bonding grains together at their contacts by wetting, or from dehydrated salts crystallizing at grain contacts. Changes in hydration state with time (such as diurnally or seasonally) may then result in correlated changes in cohesive properties with time [5].

The presence of chlorine salts at the Phoenix landing site is important for understanding the geological and chemical history of the North Polar Region, as the presence of chlorine salts can help us infer the chemistry and stability of any water/ice that may be or has been present. This is because chloride, perchlorate, and chlorate salts can all suppress the freezing temperature of water significantly, in some cases with a eutectic temperature down to ~204 K [4, 6, 7]. They also slow down the evaporation rate, extending the lifetime of the liquid water solution. Positively identifying the various chlorine salts, especially their cation-anion pair and hydration state, will allow us to further understand the results from the WCL experiment, and more importantly to assess the stability of water (whether liquid or solid) at the Phoenix landing site. Previous detections of perchlorate and chlorate hydrates in Recurring Slope Lineae (RSL) [8] have been

suggested to be instrument artifacts [9, 10]. Here we present strategies and discuss limitations for detecting chlorine salts through VNIR remote sensing spectroscopy.

Methods: Although we know that chlorine salts exist on the surface at the Phoenix landing site, we do not know what their original hydration state or cation-anion pair was (e.g. Ca(ClO₄)₂·4H₂O vs NaClO₄ anhydrous vs Mg(ClO₃)₂·6H₂O vs NaCl, etc.). The biggest challenge to positively identifying and distinguishing these salts through remote sensing is that many hydrated salts look very similar in the near-infrared, even when comparing to sulfate salts [11]. We have developed routines specifically for identification and mapping of variations in the wavelength locations of absorption band minima in CRISM spectra [12]. We have begun to apply these routines in order to identify chlorine salts in our specified CRISM images [13].

The majority of CRISM analyses use spectral indices, however, these indices are not able to differentiate between spectrally similar minerals. For example, the SINDEXTM measures the convexity at 2.3 μm due to sulfate absorptions at 1.9/2.1 μm (poly/mono-hydrated sulfates) and 2.4 μm. This index, though, will also be positive for any hydrated mineral with a fall off toward 2.5 μm, like kaolinite. Likewise, hydrated minerals are often identified using the CRISM BD1900R parameter, which finds the average depth of absorption between 1.91-1.94 μm relative to ~1.86/2.12 μm; yet, this parameter is non-specific to a particular hydrated mineral.

To aid in identification of oxychlorine salts, we created a rubric of VNIR spectral parameters that can be used to help tell the salts apart from other common Martian minerals. Lab spectra of 33 common Martian minerals [14] were compared to spectra collected by [11] of oxychlorine salts to determine the best combination of spectral parameters to most uniquely

Name	Parameter	Formulation	Kernel Width	Rationale	Caveats
BD2130	2.14 μm ClO ₄ -H ₂ O feature band depth*	$.5 * \left[1 - \frac{R2120}{a * R2030 + b * R2190} \right] +$ $.5 * \left[1 - \frac{R2140}{a * R2030 + b * R2190} \right]$	R2030:5 R2120:3 R2140:3 R2190:5	Hydrous perchlorates	Orthopyroxene Alunite Gypsum Kaolinite Margarite
BD2220	2.2 μm Cl-O combination or overtone feature band depth*	$1 - \frac{R2220}{a * R2140 + b * R2320}$	R2140:5 R2220:3 R2320:5	Oxychlorine salts	Nontronite Talc Zeolite

Table 1. Newly created spectral parameters. Formulation is based off of Viviano-Beck et al. [14]. R#### is the reflectance at given wavelength, kernel width is the number of channels over which the median of the reflectance was taken in order to reduce residual noise when applied to CRISM data.

detect oxychlorine salts. Two new spectral parameters, BD2130 and BD2220, were created to calculate band depths of spectral features specifically found in oxychlorine salts. Band depths were calculated using the process described in [14] and are shown in Table 1.

The common minerals and the oxychlorine salts were run through selected existing parameters (BD1400, BD1435, BD1750_2, BD1900_2, BD1900-R2, BD2100_2, BD2210_2, BD2300, MIN2250 & SINDEXT2) as well as the two newly created parameters in order to see which of the old parameters highlighted (passed a threshold value of > 0.01) the oxychlorine salts and which common minerals were highlighted by the new parameters. With this data we were able to create a rubric for which combination of parameters could be turned into a browse product like those in [14] capable of separating out oxychlorine salts: Hydrated Perchlorate (HPC) and a new Hydrated (HYD2). Our test sites have been Columbus Crater and the Phoenix landing site.

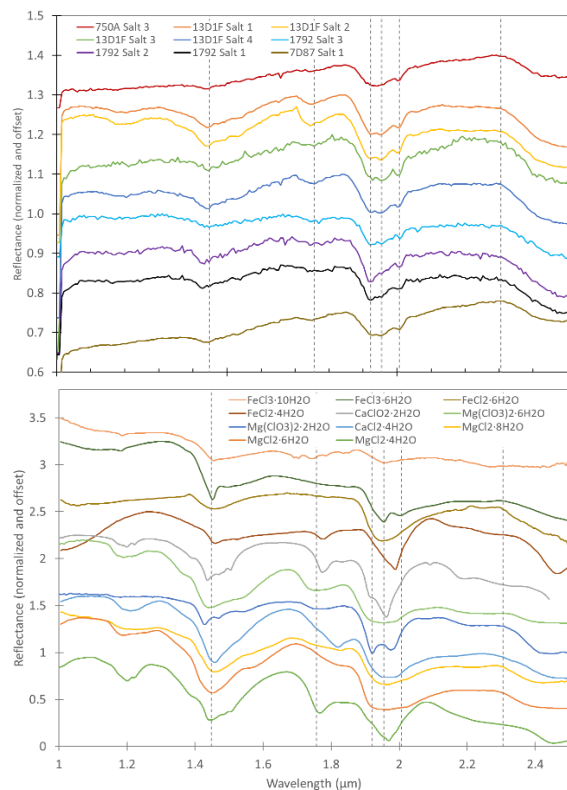


Figure 1. Top: CRISM spectra of potential salts taken from various images in Columbus Crater, Mars. Bottom: Reference laboratory spectra [11] with similar features as potential salts from (top).

Results: The new parameters we used in this study, BD2130 and BD2220 did not detect regions with definite absorptions at the desired wavelengths. Using PHS in ENVI helped by locating phyllosilicates which have similar absorption features to the feature highlighted by BD2220. Areas could be found where

only BD2220 was highlighted in PHS and most parameters in HPC and HYD2. BD2130 did not highlight many areas in many of the CRISM images. There was a large amount of noise in the BD2130 image, which made finding regions that were actually highlighted difficult. BD2130 would often be darkest in the brightest areas of HYD2 and HPC.

Despite their flaws, these parameters did lead to the identification of many spectra that have features suggestive of chlorine salts (Figure 1). Some spectra, including those in FRT_13D1F and HRL_62B6, had absorption features close to 2.22 microns. While it is uncertain whether they are due to chlorine salts, clays, or other minerals, finding this feature is an important step. We will continue to test BD2130 in other locations, as other images in Columbus Crater and beyond could show chlorine salts through the use of this parameter.

Implications: Our new parameters aim to improve our ability to identify chlorine salts and differentiate between hydrated and anhydrous phases. [6] discovered an artifact that appears in CRISM data due to improper atmospheric corrections near 1.9 and 2.1 μm . This artifact could have caused false positives for perchlorate bands, and may be responsible for previous detections of perchlorates. Since our method of detection does not rely on the 2.1 μm band alone, it should be able to compensate for issues with this region of the spectrum. Proper identification of these salts would give insight to the history of brines on Mars. Salts present could lower the freezing point of a liquid they are interacting with such that liquid water could persist under present day Martian conditions. This would increase the possibility for life to persist in near-surface environments on Mars.

If these salts are in the presence of near-surface ice, they will serve to suppress the sublimation rate, as well as encourage liquid formation by lowering the freezing temperature. In the polar summer, the temperatures were such that a eutectic liquid solution of $\text{Mg}(\text{ClO}_4)_2$ could exist for most of the day. This has implications for the long term stability of liquid water and ice in the polar regions of Mars.

Acknowledgements: This work is funded by MDAP #NNX16AJ51G.

References: [1] Hecht, M.H. et al. (2009) *Science*, 325, 64-67. [2] Kounaves, S.P. et al. (2009) *JGR*, 114, E00A19. [3] Kounaves, S.P. et al. (2010) *GRL*, 37, L09201. [4] Hanley, J. et al. (2012) *GRL*, 39, L08201. [5] Hanley, J. et al. (2014) *LPSC*, #2879. [6] Altheide, T. et al. (2009) *EPSL*, 282, 69-78. [7] Chevrier, V.F. et al. (2009) *GRL*, 36, L10202. [8] Ojha, L. et al. (2015) *Nature Geosci*, 8, 829-832. [9] Leask, E.K. et al. (2018) *GRL*, 45, 12,180-12,189. [10] Vincendon, M. et al. (2019) *Icarus*, 325, 115-127. [11] Hanley, J. et al. (2015) *JGR*, 120, 1415-1426. [12] Horgan, B. et al. (2013) *LPSC*, Abstract #3059. [13] Carmack, R. et al. (2019) *LPSC*, Abstract #1701. [14] Viviano-Beck, C.E. et al. (2014) *JGR*, 119, 2014JE004627.