STRATEGIES FOR DETECTING CHLORINE SALTS IN VISIBLE/NEAR-INFRARED SPECTRA AT MARS.
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Introduction: The oxychlorine salt perchlorate has been directly identified on Mars in situ by lander observations [1-2] and inferred based on orbital spectra [3]. The presence of oxychlorine salts on Mars could have major implications for the stability of water, such as lowering the freezing temperature and suppressing the evaporation rate [4-5]. Thus, the presence oxychlorine salts would extend the lifetime of liquid water at or near the surface. Oxychlorine salts can also help us understand the history of evaporation and chemical content of lakes and playas on Mars [5]. Hanley *et al* [4] measured lab spectra of oxychlorine salts from 1 to 25 µm at differing levels of hydration. These spectra are now available to aid in identification of oxychlorine salts using orbital visible/near-infrared (VNIR) spectra. However, oxychlorine salts are hard to detect using VNIR spectra due the fact that their spectral features are similar to other common Martian minerals. In particular, oxychlorine salts and sulfates share spectral features, so previous identification of sulfates, particularly hydrated sulfates, could actually be oxychlorine salts such as perchlorates [4]. This possible misidentification could change our perspective on potential Martian habitability, since perchlorates indicate much lower water activity brines, which are less favorable for habitability than sulfates [4]. To overcome this problem, previous orbital detections of perchlorates relied on a unique absorption at 2.14 microns [3], but recent studies have shown that this spectral feature may instead be due to incomplete atmospheric correction [6]. In this study, we create and evaluate a new method for detection of oxychlorine salts using combinations of spectral parameters.

Method: To ease 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 [7] were compared to spectra collected by [4] of oxychlorine salts to determine the best combination of spectral parameters to most uniquely 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 [7] 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 & SINDEX2) as well as the two newly created parameters in order to see which of the old parameters highlighted (passed a threshold value of >.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 [7] capable of separating out oxychlorine salts.

Results: BD2130 is designed to detect the ~2.14 µm absorption in anhydrous perchlorates (with an exception of $Mg(ClO_3)_2.6H_2O$), as the average between band depths calculated at 2.12 and 2.14 µm. Iron oxides and primary mafic silicates all showed up with a value greater than zero for the parameter, but only orthopyroxene was above the threshold. Other potentially troublesome minerals include alunite and gypsum from the sulfates, and kaolinite and margarite from the phyllosilicates. However, this absorption is potentially negatively affected by poor atmospheric corrections [6], and so should only be used in tandem with other parameters.

BD2220 is designed to detect the ~2.2 µm absorption that is common in various oxychlorine salts. This is similar to BD2230 from [7], but changing the calculations to be centered around 2.22 µm significantly increased the parameter value for anhydrous salts while lowering the parameter values in the hydrated salts, with few exceptions. For the common minerals, only 3 of the phyllosilicates had values above the threshold for the parameter. All other minerals were below the threshold.

Name	Parameter	Formulation	Kernel Width	Rationale	Caveats
BD2130	2.14 µm ClO_4-H_2O 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	Anhydrous 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. [7]. 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.*

None of the sulfates were highlighted, so the parameter might be useful in distinguishing between sulfates and oxychlorine salts.

The new parameters can be used together to detect anhydrous perchlorates. When BD2220 is highlighted, and BD2130 is not, the most probable mineral detections will be an anhydrous perchlorate, nontronite, talc, or zeolite. Then through visually inspecting the mineral it can be determined to be an anhydrous perchlorate or a more common mineral. One key difference is the shoulder on the absorption feature past 2.22 µm that exists in the phyllosilicates and zeolite but not in anhydrous perchlorates.

Several parameters created by [7] are important for oxychlorine salt identification. SINDEX2 highlights almost all the oxychlorine salts. BD1435 is above the threshold for every hydrated chlorine salt (except $FeCl_2.4H_2O$), and even $NaClO_2$ and $KClO_4$. BD1400 is primarily positive for the hydrated perchlorates, but rarely for any of the other hydrated salts. BD1900_2 is not useful in differentiating minerals, as it showed up positive for almost every mineral including several of the anhydrous salts. The exception was anhydrous chlorates, which are the only salt not highlighted by BD1900_2. BD2100_2 highlights alunite and kieserite, but not chlorine salts -- only one salt ($NaClO_4.2H_2O$) showed a positive value.

Implications: Our new parameters aim to improve our ability to identify salts and differentiate between hydrous 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 all previous detections of perchlorates. Since our method of detection does not rely on the 2.1µm 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.

References: [1] Hecht, M. H., et al. (2009) *Science*, *325*, 64–67. [2] Glavin D.P. et al (2013) JGR *118*, 1955–1973. [3] Ojha L. et al (2015) Nat Geosci *8*, 829–832. [4] Hanley J. et al. (2015) *JGR*, *120*, 1415-1426. [5] Hanley J. & Horgan B. (2017) *LPSC*, #2651. [6] Leask E.K. et al (2018) *GRL*, 45, 12180–12189. [7] Viviano-Beck C.E. et al (2014) *JGR*, 119, 2014JE004627.

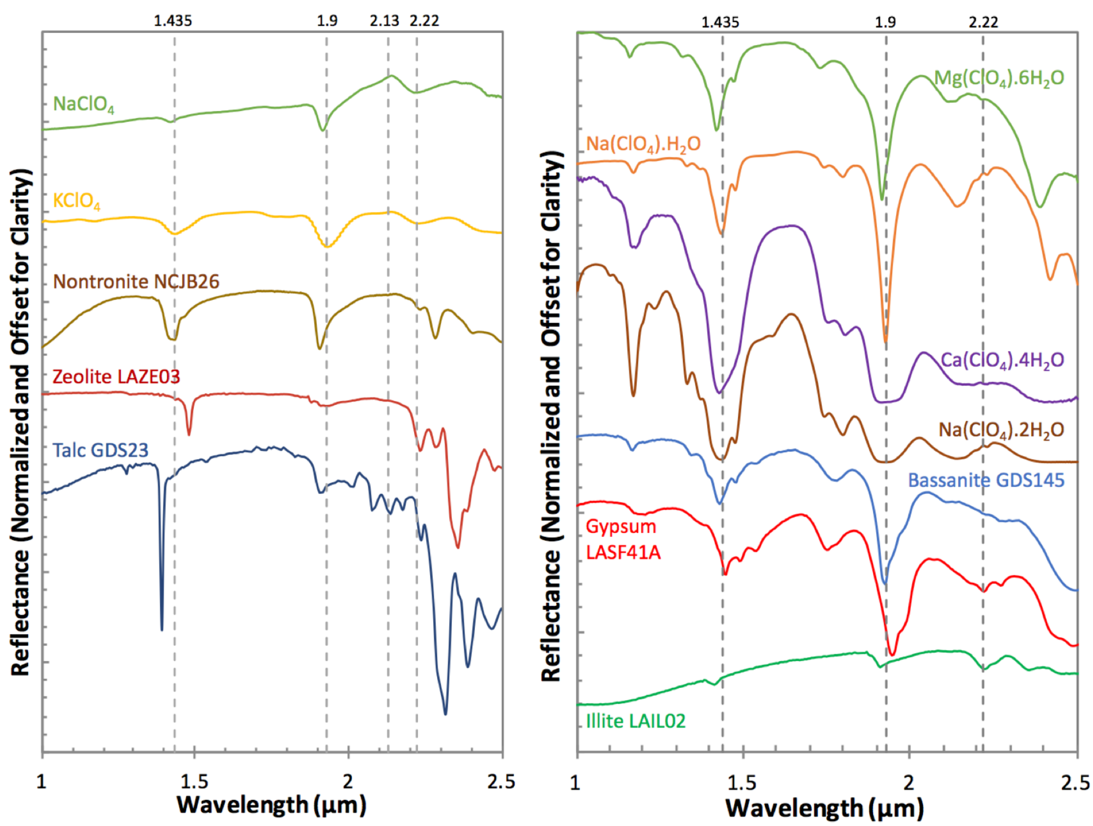

Figure 1. *(left) Spectra of anhydrous perchlorates $NaClO_4$ and $KClO_4$ compared to Nontronite, Zeolite LAZE03 and Talc GDS23. Absorption bands related to relevant parameters are shown with grey dotted lines. (right) Spectra of hydrous perchlorates and Illite LAIL02, Gypsum LASF41A and Bassanite GDS145.*