WHAT LURKS IN THE MARTIAN ROCKS AND SOIL? INVESTIGATIONS OF SULFATES, PHOSPHATES, AND PERCHLORATES Spectral and thermal properties of perchlorate salts and implications for Mars

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ABSTRACT

 K^+ , Na⁺, Ca²⁺, Mg²⁺, Fe²⁺, Fe³⁺, and Al³⁺ perchlorate salts were studied to provide spectral and thermal data for detecting and characterizing their possible presence on Mars. Spectral and thermal analyses are coordinated with structural analyses to understand how different cations and different hydration levels affect the mineral system. Near-infrared (NIR) spectral features for perchlorates are dominated by H₂O bands that occur at 0.978–1.01, 1.17–1.19, 1.42–1.48, 1.93–1.99, and 2.40–2.45 µm. Mid-IR spectral features are observed for vibrations of the tetrahedral ClO_4^- ion and occur as reflectance peaks at $1105-1130 \text{ cm}^{-1}$ (~8.6–9 µm), 760–825 cm⁻¹ (~12–13 µm), 630 cm⁻¹ (~15.9 µm), 460–495 (~20–22) μ m), and 130–215 (~50–75 μ m). The spectral bands in both regions are sensitive to the type of cation present because the polarizing power is related to the band center for many of the spectral features. Band assignments were confirmed for many of the spectral features due to opposing trends in vibrational energies for the ClO₄ and H₂O groups connected to different octahedral cations. Differential scanning calorimetry (DSC) data show variable patterns of water loss and thermal decomposition temperatures for perchlorates with different cations, consistent with changes in spectral features measured under varying hydration conditions. Results of the DSC analyses indicate that the bond energies of H₂O in perchlorates are different for each cation and hydration state. Structural parameters are available for Mg perchlorates (Robertson and Bish 2010) and the changes in structure due to hydration state are consistent with DSC parameters and spectral features. Analyses of changes in the Mg perchlorate structures with H₂O content inform our understanding of the effects of hydration on other perchlorates, for which the specific structures are less well defined. Spectra of the hydrated Fe^{2+} and Fe^{3+} perchlorates changed significantly upon heating to 100 °C or measurement under low-moisture conditions indicating that they are less stable than other perchlorates under dehydrated conditions. The perchlorate abundances observed by Phoenix and MSL are likely too low to be identified from orbit by CRISM, but may be sufficient to be identifiable by a VNIR imager on a future rover.

Keywords: Perchlorate, Mars, reflectance spectroscopy, differential scanning calorimetry, hydrated salts