Spectroscopic Investigations of Gypsum-Salt Interactions Across Mars Relevant Temperatures: Implications for Modern Mars Geochemistry

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Calcium sulphate hydrates, including gypsum ($CaSO_4 \cdot 2H_2O$) and bassanite ($CaSO_4 \cdot 0.5H_2O$), as well as their dehydrated form, anhydrite ($CaSO_4$), are commonly found together in many terrestrial settings, especially in marine evaporative deposits of the Earth. These Ca-sulphate minerals have also been detected at several locations on Mars, including gypsum dunes in the North Poles of Mars by OMEGA/Mars Express in Olympia Undae(Langevin, Poulet et al. 2005), gypsum-bassanite-anhydrite assemblages in the Gale Crater by the Chemistry and Mineralogy Instrument (CheMin) X-Ray Diffraction (XRD) instrument(Vaniman, Martínez et al. 2018), as well as bassanite detected in the Mawrth Vallis(Bishop, Lane et al. 2014). The dehydration of gypsum into its dehydrated phases of bassanite and anhydrite is highly responsive to environmental factors such as changes in relative humidity, temperature, and pH. For instance, gypsum can lose its structural water (i) when heated above ~95–100 °C or (i) mixed with salts at ~83 °C, which both enable the transformation of gypsum to bassanite and then to anhydrite(Bishop, Lane et al. 2014). Formation pathways between these Ca-sulphate phases are still complicated, and there are very few studies focused on the gypsum-Cl salt interactions at relevant Mars temperatures. Additionally, the CheMin instrument on the Curiosity rover faced challenges in distinguishing gypsum, bassanite, and anhydrite depending on the instrument's resolution limit because the crystal structure of bassanite and soluble anhydrite exhibits strong similarities. A study from (Vaniman, Martínez et al. 2018) suggested that bassanite and the other dehydrated Ca- sulphate mixtures' detection may depend on the dehydration of gypsum in the warm sample chamber of CheMin during the XRD measurements over Martian soils.

In this study, we address the need for more laboratory experiments to evaluate spectral datasets collected from orbit. This study focuses on the gypsum and Cl-salt interactions across an extended temperature range (-90 to 400 °C) using various spectral techniques (VNIR, mid-IR, Raman, XRD) and thermal analyses (e.g., Temperature Programmed Desorption (TPD)-FTIR, Thermal Gravimetric Analyses (TGA)). Our results reveal that water/rock ratio, applied heating/cooling rates, and temperature influence the formation of different calcium sulphate phases, and the detection of these phases depends on the technique used. As a noteworthy change, our XRD analyses revealed the formation of gypsum-bassanite from gypsum/$CaCl_2$ mixtures at elevated temperatures, which was not observed from pure gypsum or gypsum/NaCl mixtures. While the transition temperature in our experiments was too high to compare gypsum transformation to bassanite with the CheMin instrument, a slower heating rate and higher salt concentrations may facilitate this transformation at lower temperatures(Bishop, Yeşilbaş et al. 2021). VNIR reflectance spectra of gypsum measured under Mars-like conditions revealed sharpened structural H_2O bands at nearly the same wavelengths as room-temperature spectra(Yeşilbaş, Vu et al. 2022). This confirms the orbital detection of gypsum on Mars. Accurate characterization of gypsum and the formation pathways of its dehydrated phases will help to constrain the aqueous and geochemical history of Mars and assess potential water resources for future human missions to Mars.

References

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