Deliquescence of Calcium Perchlorate: An Investigation of Stable Aqueous Solutions Relevant to Mars

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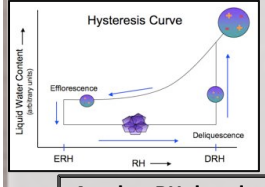
Introduction

• Previous work has shown that perchlorate salts may be responsible for the formation of aqueous solutions at low relative humidity values[1,2]. Right: Phoenix Lander's Snow White trench marks first discovery of perchlorate on Mars and dissolved salt concentrations were quantified.

•Salt mixtures can deliquesce (DQ) and efflorescence (EF) as the atmospheric relative humidity changes.

• Salt solutions spontaneously crystallize at the efflorescence relative humidity (ERH), releasing all water into the gas phase.

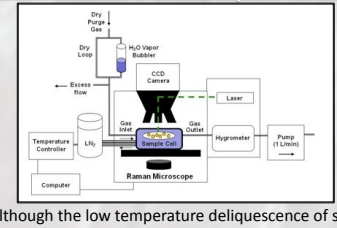


• Solid salt crystals spontaneously absorb gas-phase H_2O to form a saturated aqueous solution at the deliquescence relative humidity (DRH).

•Perchlorate deliquescence has been demonstrated at relative humidity (RH) values as low as 40%, supporting the idea that aqueous perchlorate solutions can exist in the present Martian environment[2].

At what RH do salts in the Martian regolith deliquesce and effloresce?

Experimental Setup



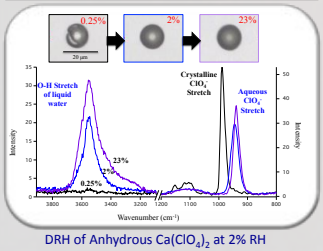
• Although the low temperature deliquescence of several perchlorate salts is now well characterized, instruments onboard Phoenix and MSL have identified calcium perchlorate, ($Ca(ClO_4)_2$) as the likely parent salt.

•$Ca(ClO_4)_2$ solution was nebulized to generate 1-40 µm particles and deposited onto a hydrophobic quartz disc. The sample was then cooled to the desired temperature where relative humidity can be controlled and monitored with a chilled-mirror hygrometer.

• The Raman spectrometer is equipped with a 532 nm laser used to collect spectral information and an optical microscope was used to directly observe phase transitions to quantify DRH/ERH.

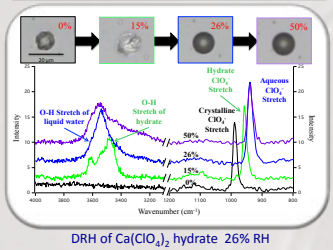
Results

DRH of Anhydrous $Ca(ClO_4)_2$ at 0° C



DRH of Anhydrous $Ca(ClO_4)_2$ at 2% RH

DRH of Hydrated $Ca(ClO_4)_2$ at -20° C

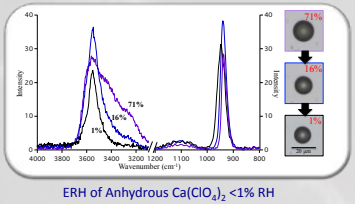


DRH of $Ca(ClO_4)_2$ hydrate 26% RH

Spectral and optical changes upon deliquescence:

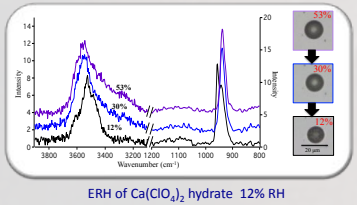
- Anhydrous (left): O-H stretch of liquid water (~3550 cm^{-1}); Cl-O stretch shifts from 998 to 938 cm^{-1} when perchlorate anion is solvated by 2% RH. Visually, particle becomes spherical, darker, larger, and smoother in appearance.
- Hydrate (right): O-H stretch grows in by 15% (green), but with unique peaks different from what we see with a liquid water O-H stretch. The perchlorate peak shifts to 958 cm^{-1} and the particle visually brightens. At 26% RH (blue), optical images suggest deliquescence to an aqueous solution supported by the Raman O-H stretch broadening and the ClO_4^- stretch shifts to 938 cm^{-1}.

ERH of Anhydrous $Ca(ClO_4)_2$ at 0° C



ERH of Anhydrous $Ca(ClO_4)_2$ <1% RH

ERH of $Ca(ClO_4)_2$ into Hydrate at -20° C

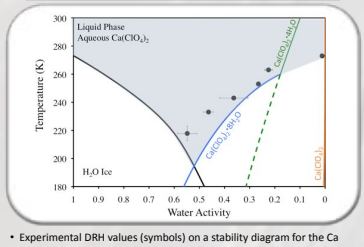


ERH of $Ca(ClO_4)_2$ hydrate 12% RH

Spectral and optical changes upon efflorescence:

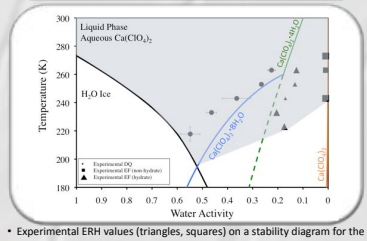
- Anhydrous (left): As RH is decreased, the particle optically decreases in volume but recrystallization is not observed. At 1% RH, the ClO_4^- stretch is consistent with aqueous $Ca(ClO_4)_2$ particles. The O-H stretch remains at 3550 cm^{-1} throughout the entirety of the experiment. Experimental efflorescence was not observed.
- Hydrate (right): As RH is decreased, the particle decreases in volume and by 12% RH the particle effloresces into a hydrated crystal. The ClO_4^- stretch shifts from 938 cm^{-1} to 958 cm^{-1} with the sharp features returning in O-H stretch region. The Cl-O stretch shifts from 988 to 1015 cm^{-1} when perchlorate starts to precipitate.

DRH results of $Ca(ClO_4)_2$



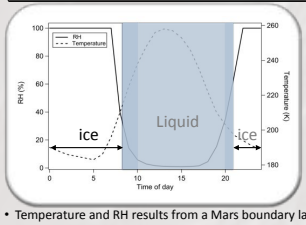
• Experimental DRH values (symbols) on a stability diagram for the Ca $(ClO_4)_2$ + H_2O system. Thermodynamically predicted phase transitions are represented by lines. The light blue shaded region represents the upper limit of stable aqueous $Ca(ClO_4)_2$ solutions.

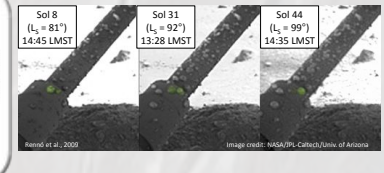
ERH results of $Ca(ClO_4)_2$



• Experimental ERH values (triangles, squares) on a stability diagram for the $Ca(ClO_4)_2$ + H_2O system. Triangles represent hydrate formation when RH was decreased whereas squares indicate EF occurred below 1% RH. The light blue shaded region represents the upper limit of metastable aqueous $Ca(ClO_4)_2$ solutions.

Martian Implications





Change in particles over time observed on Phoenix Lander[4]. All images were taken when RH was less than 10%, but salt mixtures may allow for liquid water stability at times of higher RH.

• Temperature and RH results from a Mars boundary layer model based on Viking data[5]. The solid line represents RH and the dashed line represents temperature. The eutectic point of calcium perchlorate is represented by the black ice line and the expected liquid stable-metastable region is shown by the blue shaded region. Given the extremely low eutectic point of calcium perchlorate, temperature and relative humidity conditions allow for deliquescence as early as 07:00. Previous perchlorates studied typically crystallize by 10:00[2], but the unique characteristic of calcium perchlorate allows the liquid phase to potentially persist from 10:00-17:00 due to a temp above 240 K where EF less than 1% occurs. By 21:00, the relative humidity and temperature conditions favor ice formation. By applying our experimental results to modeled Martian conditions, we see that Calcium perchlorate allows for stable and metastable aqueous solutions to persist throughout a large portion of the Martian sol.

References: 1) Chevrier et al. (2009) GRL, 36, L10202. 2) Gough et al. (2011) *EPSL, 312, 371-377. 3)* Baustian et al. (2009) *ACP, 10, 2307-2317. 4)*Renno et al. (2009) *JGR-Planets, 114, E00E03. 5)* McEwen et al. (2011) *Science, 333, 740-743. 6) Hecht et al. (2009) Science, 325, 64-67.* 5) Savijarvi, et al. (1995) *Icarus, 117 (1), 120–127.*

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