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Comment

Deliquescence and efflorescence of calcium perchlorate: An investigation of stable aqueous solutions relevant to Mars

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ABSTRACT

Calcium perchlorate ($Ca(ClO_4)_2$) is a highly deliquescent salt that may exist on the surface of present-day Mars; however, its water uptake properties have not been well characterized at temperatures and relative humidity conditions relevant to Mars. Here, we quantify the deliquescent relative humidity (DRH) and efflorescent relative humidity (ERH) of $Ca(ClO_4)_2$ as a function of temperature (223–273 K) to elucidate its behavior on the surface of Mars. A Raman microscope equipped with an environmental cell was used to simulate Mars relevant temperature and relative humidity conditions and monitor deliquescence (solid to aqueous) and efflorescence (aqueous to solid) phase transitions of $Ca(ClO_4)_2$. Deliquescence and efflorescence were monitored visually using optical images and spectroscopically using Raman microscopy. We find that there is a wide range of deliquescence RH values between 5% and 55% RH. This range is due to the formation of hydrates in different temperatures regimes, with the higher DRH values occurring at the lowest temperatures. Experimental deliquescence results were compared to a thermodynamic model for three hydration states of $Ca(ClO_4)_2$. The model predicts that the higher hydration states deliquesce at a higher RH than the lower hydration states. Calcium perchlorate was found to supersaturate, with lower ERH values than DRH values. The ERH results were less dependent on temperature with an average 15 ± 4%, but values as low as 3 ± 2% were measured at 273 K. Levitation experiments were performed on single particles of $Ca(ClO_4)_2$ and $Mg(ClO_4)_2$ at 298 K. While efflorescence was observed around 15% RH for $Mg(ClO_4)_2$, the efflorescence of $Ca(ClO_4)_2$ was not observed, even when exposed to 1% RH at 298 K. Additionally, a 17-h experiment was conducted to simulate a martian subsurface diurnal cycle. This demonstrated $Ca(ClO_4)_2$ aqueous solutions can persist without efflorescing for the majority of a martian sol, up to 17 h under Mars temperature heating rates and RH conditions. We find that $Ca(ClO_4)_2$ aqueous solutions could persist for most of the martian sol under present-day conditions. The aqueous phase stability and metastability quantified for $Ca(ClO_4)_2$ under Mars relevant temperature and relative humidity conditions has important implications for the water cycle and the stability of liquid water on present day Mars.

1. Introduction

One of the most unexpected discoveries made by the Phoenix Lander in the martian arctic plains was the presence of 0.5% by weight perchlorate (ClO_4^-) with the Wet Chemistry Laboratory (WCL) (Hecht et al., 2009; Cull et al., 2010). Perchlorate was also confirmed with the Thermal and Evolved Gas Analyzer (TEGA), which heated martian soil samples and detected evolved oxygen gas (O_2) at the thermal decomposition temperatures expected for alkali or alkaline Earth perchlorates (Hecht et al., 2009). Reanalysis of the Viking gas chromatography-mass spectrometry results also suggest perchlorates were present in the soil (Navarro-González et al., 2010). Additionally, the Mars Science Laboratory (MSL) rover has potentially found perchlorate at Gale Crater (Glavin et al., 2013; Leshin et al., 2013; Ming et al., 2014).

The presence of perchlorate is important because of its impact on the soil's ability to retain water, thus influencing the water cycle and potential habitability of Mars. Perchlorate salts are known to readily absorb water vapor from the atmosphere and deliquesce (crystalline solid to aqueous solution) into aqueous solutions (Chevrier et al., 2009; Zorzano et al., 2009; Gough et al., 2011). Perchlorates, like most salts, also tend to remain in a supersaturated aqueous phase instead of efflorescing (aqueous solution to crystalline solid) back into a solid crystal (Wills et al., 2009; Gough et al., 2011). When the solutions persist below the RH where deliquescence is observed, a metastable state is achieved. A metastable state is one that is not an energetic minimum, but can persist for some time due to kinetic limitations. This hysteresis behavior allows liquid brine solutions to exist at low relative humidity (RH) values, relevant to the martian day. Understanding the deliquescent and efflorescent properties of perchlorates under martian temperature and RH conditions can give insights into present-day water activity on Mars.

Previously, we performed laboratory studies to investigate the deliquescence and efflorescence of two perchlorate salts at low temperatures. These studies showed that sodium perchlorate ($NaClO_4$) and magnesium perchlorate ($Mg(ClO_4)_2$) are highly deliquescent, forming aqueous solutions at humidity values as low as

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40% RH at temperatures as low as 223 K (Gough et al., 2011), which were conditions observed at the Phoenix landing site (Zent et al., 2010). A significant hysteresis was observed during efflorescence of these salt solutions, as expected, due to the kinetic inhibition of crystal nucleation. The efflorescence RH values of sodium and magnesium perchlorate solutions were found to be 13% RH and 19% RH, respectively, indicating that perchlorate salts could exist as stable or metastable aqueous solutions over a wide range of martian RH and temperature conditions (Gough et al., 2011).

Although the low temperature deliquescence and efflorescence of sodium and magnesium perchlorate salts has been characterized, instruments onboard Phoenix and MSL have identified calcium perchlorate ($Ca(ClO_4)_2$) as the likely parent salt (Cull et al., 2010; Glavin et al., 2013; Kounaves et al., 2014). Calcium and magnesium chlorate may also be present at the MSL landing site (Glavin et al., 2013; Leshin et al., 2013; Ming et al., 2014), but the highly deliquescent properties and low eutectic point of $Ca(ClO_4)_2$ (Pestova et al., 2005) motivated the investigation of $Ca(ClO_4)_2$. The deliquescence and efflorescence behavior of $Ca(ClO_4)_2$ have not yet been quantified as a function of temperature. Here, we report experimentally determined deliquescence and efflorescence relative humidity values of $Ca(ClO_4)_2$ as a function of temperature utilizing Raman microscopy. Results are also presented for efflorescence of levitated $Ca(ClO_4)_2$ and $Mg(ClO_4)_2$ particles at room temperature. The experimental DRH and ERH results are then plotted on a theoretical $Ca(ClO_4)_2$ thermodynamic stability diagram to demonstrate where stable and metastable aqueous solutions persist. Results are compared to modeled surface and subsurface temperature and RH environments at the Viking and Phoenix landing sites, respectively, to assess martian conditions where an aqueous $Ca(ClO_4)_2$ solution could persist. Finally, a diurnal cycle experiment was performed to simulate the martian subsurface temperature and RH environment to further investigate the phase state of $Ca(ClO_4)_2$ in Mars relevant conditions.

2. Experimental setup

2.1. Raman and optical methods, materials

To characterize the deliquescence and efflorescence of $Ca(ClO_4)_2$, changes in salt phase and hydration state were studied using a combination of Raman and optical microscopy. The instrument setup used in this study is described in detail in Baustian et al. (2010), Gough et al. (2011) and shown in Fig. 1. A Raman microscope equipped with an environmental cell was used to determine the deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) as a function of temperature (223–273 K). Specifically, a Nicolet Almega XR Dispersive Raman spectrometer was outfitted with a Linkam THMS600 environmental cell, a Linkam automated temperature controller, and a Buck Research chilled-mirror hygrometer.

$Ca(ClO_4)_2 \cdot 4H_2O$ was purchased from Sigma Aldrich (99% purity). A calcium perchlorate solution (1% by weight) was nebulized using high purity nitrogen and droplets were deposited onto a hydrophobic quartz disk that was placed directly on a silver block in the environmental cell. The temperature of the silver block was controlled by a combination of cooling using a continuous flow of liquid nitrogen and resistive heating. Particle size diameters ranged from 1–40 μm.

Initially, high purity dry N_2 (99.9% purity) continuously flowed through the cell to ensure a dry environment with RH <1%. The RH in the cell was controlled by combining a separate stream of N_2 passed through a H_2O vapor bubbler before connecting to the dry flow. After passing through the cell, the flow was directed to a frost point hygrometer for measurement of water vapor. Frost point measurements, specifically dewpoint, from the hygrometer and sample temperature measurements from the platinum resistance sensor allow determination of RH with respect to the sample. A diaphragm pump pulling at a rate of 1 L/min was attached to the outlet of the hygrometer to ensure a constant airflow through the cell regardless of any variability in flow rate through the H_2O vapor bubbler. For experiments above 253 K, H_2O vapor was increased or decreased stepwise (at intervals less than or equal to 1% RH) while temperature was held constant. For experiments below 253 K, temperature was varied while holding H_2O partial pressure constant. This process allowed for fine tuned RH control at lower temperatures. RH was varied slowly ($\leqslant$1% RH/min) and then held at each value for several minutes until the vapor flow through the cell was constant (for step-wise experiments) and the Raman spectra of the individual particles did not change. The estimated uncertainty in the DRH and ERH values due to the accuracy of the instrumental apparatus is ±1% RH. Uncertainty in the experimental data due to reproducibility of results is larger (±1–5% RH). Error is reported as the standard deviation of multiple measurements with at least three experiments per data point.

2.2. Particle levitation experiments

To probe the phase state and morphology of individual $Ca(ClO_4)_2$ droplets free from any substrate, droplets were levitated in an optical trap recently developed in our laboratory. Fig. 2 shows a schematic of the experimental setup. The concept of optical levitation has been well established since the early 1970s (Ashkin, 1970) and is addressed in detail elsewhere (Dholakia and Zemánek, 2010). In brief, two vertically counter-propagating laser beams generated from the second harmonic output (532 nm) of individual continuous-wave Nd:YAG lasers are focused into the center of a custom made aluminum flow tube (12 mm × 110 mm) to form the trapping site. Droplets are generated from an aqueous solution using a piezo-driven glass capillary device (not shown) with a 15 μm orifice (Microfab, MJ-APB-015) mounted horizontally above the trapping site. Once a droplet enters the trapping site, the radiation pressure from the lasers, as well as an upward-directed humidity controlled nitrogen gas flow, balance the force of gravity acting on the droplet, resulting in levitation. Laser power must be regulated to maintain the proper balance of forces (10–50 mW typical). Using Mie theory, the angular variation in scattered light intensity is used to provide sensitive measurements of the size of levitated calcium perchlorate particles as well as the particle phase and morphology.

2.3. Calcium perchlorate stability diagrams and environmental simulations

A thermodynamic stability diagram for the $Ca(ClO_4)_2 + H_2O$ system was calculated to use as a comparison to the experimental DRH results. The phase transition lines for calcium perchlorate were calculated by first determining the brine-ice equilibrium line using previously published Pitzer parameters (Marion et al., 2010). Although this step is not absolutely necessary, we use this approach to verify that the line (and thus Pitzer parameters) fit previous experimental data. In a temperature verse water activity environment, the ice line is constant and not dependent on the type of salt used. For the ice line we used the data from Pestova

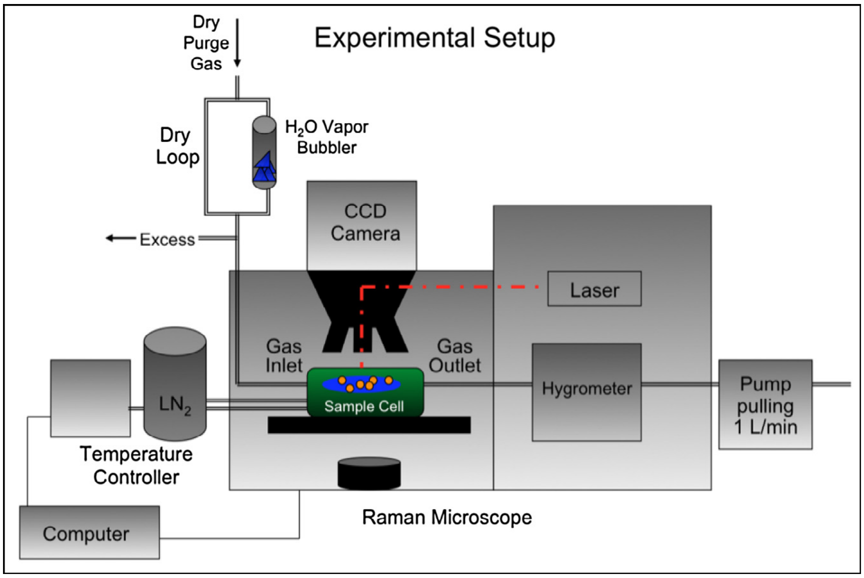

Fig. 1. A schematic of the Raman microscope equipped with an environmental sample cell.