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Brine formation via deliquescence by salts found near Don Juan Pond, Antarctica: Laboratory experiments and field observational results

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ABSTRACT

The observed darkening of water tracks near Don Juan Pond (DJP) as well as the formation of wet patches elsewhere in the McMurdo Dry Valleys is attributed at least partially to deliquescence, a process by which salts absorb atmospheric water vapor and form brine, coupled with liquid-phase growth when the atmospheric relative humidity exceeds the water activity. Here we perform laboratory experiments to investigate the temperature and relative humidity conditions necessary for deliquescence to occur in calcium chloride-rich sediments collected from the DJP watershed. We use a Raman microscope equipped with an environmental cell to study both deliquescence and efflorescence (recrystallization) of the soluble salt component of DJP soils between −30 and +15 °C. In this temperature range, we find that the soluble salt component of the DJP sediments begins to deliquesce between 19 and 46% RH, slightly higher than the deliquescence relative humidity of the primary pure component, calcium chloride. We find a limited hysteresis between deliquescence and efflorescence, but much greater supersaturation of the salt brine can occur at temperatures above 0 °C. The relative humidity conditions were varied either slowly (over ∼8 h) to observe near-equilibrium phases or rapidly (over <1 h) to better mimic Antarctic conditions and no differences in deliquescence relative humidity or efflorescence relative humidity were noted. The results of this work can help predict when deliquescence could be actively occurring in the soils near Don Juan Pond and explain darkening of the salt pan after a high humidity period. In tandem with field data, our experimental results suggest that brines can be generated near Don Juan Pond via deliquescence frequently during the southern summer and autumn. Additionally, the soluble salts may persist in the aqueous phase continuously for several months during the southern summer. This work also suggests that salt deliquescence could be impacting the year-round hydrological cycle of the DJP watershed. Steep-sloped water tracks found near DJP have been suggested as a terrestrial analog for recurring slope lineae on Mars, for which salt deliquescence is a proposed formation mechanism. Therefore, understanding the formation of deliquescent brines in a hyper-arid region on Earth may have relevance to Mars.

1. Introduction

The McMurdo Dry Valleys in Antarctica are a cold, dry desert (Doran et al., 2002; Marchant and Head, 2007; Fountain et al., 2009; Marchant et al., 2013; Head and Marchant, 2014). Limited precipitation in the region has led to the accumulation of high levels of soluble salts (chlorides, nitrates, sulfates) in the soils (Meyer et al., 1962; Claridge and Campbell, 1977; Wilson, 1979; Keys and Williams, 1981; Toner and Sletten, 2013; Bisson et al., 2015), as well as the existence of shallow, hyper-saline lakes such as Don Juan Pond (DJP) in the South Fork of the Upper Wright Valley. Despite the arid conditions, shallow groundwater is present in seasonally thawed active soil layers, expressed at the surface as wet patches and water tracks (Head et al., 2007; Levy et al., 2011, 2012) and potentially deeper within permafrost-affected soils (Dickinson and Rosen, 2003; Mikucki et al., 2015). These hydrological features are believed to form, at least partially, due to the deliquescence of the abundant salts in the shallow subsurface (Wilson, 1979; Levy et al., 2012, 2015; Dickson et al., 2013).

Water tracks near Don Juan Pond have been suggested as a possible terrestrial analog for recurring slope lineae (RSL) on Mars (Levy, 2012; Dickson et al., 2013; McEwen, 2014). RSL are widespread, narrow, low-albedo features that appear, grow and fade seasonally on steep slopes on Mars (McEwen et al., 2011; Ojha et al., 2014, 2015, Stillman et al., 2014, 2017). While the seasonality is consistent with RSL being triggered by an H_2O phase change and the RSL growth patterns are compatible with downslope flow of a liquid through a soil matrix (Levy, 2012),

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the source and composition of the material moving downslope is unknown and actively debated (Dundas et al., 2016). Because deliquescence is a proposed mechanism for the formation of liquid in RSL (McEwen et al., 2011; Ojha et al., 2014, 2015; McEwen, 2014), it is important to understand the conditions under which deliquescent brines play a role in terrestrial hyper-arid regions that lack pluvial (rainfall) activity.

Deliquescence, the phase transition from a crystalline solid to an aqueous solution, occurs when the relative humidity (RH) is equal to or greater than the deliquescence relative humidity (DRH) of a salt (Martin, 2000; Davila et al., 2010). At equilibrium, the brine formed has a water activity equal to the relative humidity (%) divided by 100. For each salt or salt mixture, the DRH varies as a function of temperature (Seinfeld and Pandis, 1998), with deliquescence occurring at temperatures as low as the eutectic temperature of the salt. Calcium chloride ($CaCl_2$) is a highly soluble and deliquescent salt that is abundant in the MDV, having been found in shallow groundwater (Wilson, 1979) and lakes and ponds (Meyer et al., 1962; Torrii and Ossaka, 1965; Siegel et al., 1979). Calcium chloride has a DRH that can be as low as 12% RH but as high as 80% RH depending on the hydration state of the crystalline salt and on the temperature (Gough et al., 2016).

Deliquescence may play a role in the hydrological cycle of Don Juan Pond and the Dry Valleys in general, and possibly regional geochemistry as well. Wilson et al. (1979) first proposed that deliquescence of soluble salts could be responsible for the fractionation of different salt species on the surface and in lakes of the Dry Valleys. Dickson et al. (2013) observed that water tracks near Don Juan Pond rapidly responded to high humidity air by absorbing atmospheric water vapor and darkening. They suggested that the source of the salts in the pond and perhaps the source of some of the water in the pond is saline groundwater flowing above the permafrost. Some of this brine is formed from salt deliquescence during periods of high humidity (Levy et al., 2015). $CaCl_2$-rich solutions formed via salt deliquescence in the water tracks and flushed by streamwater and snowmelt could then percolate through the soil matrix or along the top of the permafrost table, subsequently flowing into Don Juan Pond, impacting its geochemistry and area/volume. Shallow groundwater (water track) discharge from the eastern margin of Don Juan Pond, is consistent with this process (Kounaves et al., 2010; Dickson et al., 2013). However, brines formed this way are susceptible to efflorescence, the recrystallization of salt solution into a crystalline phase. Efflorescence typically requires drier conditions than deliquescence for a given salt at constant temperature but has not been studied in detail for MDV soils. The efflorescence relative humidity (ERH) is lower than the DRH for most inorganic salts (Tang, 1997; Martin, 2000) because crystallization is kinetically hindered. Supersaturated salt solutions are metastable and can exist for at least several hours at RH < DRH (Gough et al., 2011; Nuding et al., 2014; Davis et al., 2015; Martin, 2000). Laboratory experiments are needed to determine the extent and duration of this hysteresis because it cannot easily be calculated thermodynamically.

Levy et al. (2015) performed laboratory studies to test the hypothesis that atmospheric water vapor can be concentrated in high salinity soils via deliquescence and subsequent solution growth. Indeed, the water content of salt-rich MDV soils from Taylor Valley was found to be as high as 7% by mass after dry soils were exposed to 75% RH in the laboratory and as high as 16% by mass after dry soils were exposed to 100% RH. In certain cases, the sediment visibly darkened, became clumpy, and the presence of standing water was even observed as solution volume grew to exceed the pore space. This study was performed at room temperature; however, lower temperatures could impact the deliquescence of salts in the sediments by changing the DRH of the salts, as well as impacting the kinetics of water uptake. Accordingly, the investigation of deliquescence of MDV salts under lower temperatures relevant to Antarctica is warranted, and essential for any potential application to Mars.

Here we report the results of laboratory studies of the deliquescence and efflorescence of salts in soil collected from the salt pan around Don Juan Pond. Most of the dissolved salt is $CaCl_2$ (Torrii and Ossaka, 1965; Harris et al., 1979; Levy et al., 2011; Toner and Sletten, 2013) but sodium, magnesium and sulfate are also present (Torrii and Ossaka, 1965). We focus on the deliquescence behavior of the soluble salt component of the DJP sediments. Once the environmental conditions needed for the deliquescence and efflorescence phase transitions are understood, estimates can be made regarding when and where deliquescence of $CaCl_2$-rich salts near DJP can occur and how long surface or shallow subsurface brines may persist until efflorescence occurs.

2. Materials and methods

2.1. Sample preparation

The sample used for this work was a green-brown, fine-grained silt collected from the salt pan around Don Juan Pond (77.564015° S, 161.189716° E) during 2012. Although a few experiments were performed on the entire sediment sample, for most experiments we focused on the soluble portion. These salts are likely controlling deliquescence. To extract the soluble portion of the sediment, 10.0 mL of high-purity water was added to 5.00 g of soil. After mixing well, the mixture sat for 24 h at room temperature. The slurry was then filtered through a 0.2 μm filter, which yielded a colorless solution. The mixture of soluble salts that resulted from this aqueous extraction will be called "DJP extract" in this paper. The DJP extract was analyzed via ion chromatography and inductively coupled plasma mass spectrometry to quantify the concentration of dissolved anions and cations, respectively.

To prepare a sample of DJP extract for a deliquescence experiment, the aqueous solution was nebulized onto a hydrophobic quartz disk. The DJP extract particles generated were crystalline and ranged from 5 to 30 μm in diameter. For the deliquescence experiments performed on the entire sediment sample, (not just the soluble extract), a thin layer was deposited onto the disk with no prior physical or chemical treatments.

2.2. Environmental cell and Raman microscope

A brief summary of the experimental setup and protocol is given here, with more details in the supplemental material. The Raman microscopy system (Fig. S1) has been previously described in detail (Baustian et al., 2010; Gough et al., 2011). Briefly, a Nicolet Almega XR Dispersive Raman spectrometer was outfitted with a Linkam environmental cell, Linkam automated temperature controller, and Buck Research chilled-mirror hygrometer. In this work, temperatures in the environmental cell were varied from −30 to 25 °C, and RH ranged from <1 to 100%. Changes in phase (solid vs. aqueous) or hydration state of individual salt particles were monitored visually with the optical microscope (Olympus BX51 with ×10, ×20, and ×50 magnification capabilities) or spectrally using Raman spectroscopy. A 532 nm laser was used to collect spectra between 400 and 4000 cm^{-1} with 2 cm^{-1} resolution. Spectra were always collected in the center of a particle. The Raman spectra obtained allow for molecular identification of individual particles as small as 1 μm. Raman spectroscopy is sensitive to the phase of water; water in the liquid, ice, and hydrated, crystalline phases exhibit different spectra, particularly in the O–H stretching region (∼3400 cm^{-1}).

We performed experiments on two different timescales. Longer experiments (6–10 h) were used to probe equilibrium or near-