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Freezing of perchlorate and chloride brines under Mars-relevant conditions

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Abstract

Perchlorate and chloride salts on Mars could readily absorb water vapor and deliquesce into aqueous solutions. The deliquescence relative humidity (RH) as well as the efflorescence (recrystallization) RH of several Mars-relevant salts are now well known; however, the conditions that could cause a brine to freeze are not well established. It is often assumed that ice formation will occur whenever the saturation with respect to ice, S_{ice}, of the system is greater than or equal to unity; however, ice nucleation is often hindered due to a kinetic barrier. For ice to form, a critical cluster of the ice crystal must first be achieved, often requiring $S_{ice} > 1$. Here we use a Raman microscope and an environmental cell to examine the RH and temperature conditions required for $Mg(ClO_4)_2$ and $MgCl_2$ brines to freeze into ice. By examining the salt phase present both optically and spectrally under different low temperature conditions, it is found that both salts exhibit S_{ice} values much greater than unity, meaning that supersaturation readily occurs and brines can persist under conditions previously thought to lead to freezing. The RH range of ice formation for $Mg(ClO_4)_2$ from 218 to 245 K is 83–95%, respectively, corresponding to $S_{ice} = 1.30–1.54$. The RH of ice formation for $MgCl_2$ ranges from 80 to 100% for temperatures between 221 and 252 K, corresponding to $S_{ice} = 1.30–1.35$. In addition to ice nucleation, the deliquescence and efflorescence relative humidity values for $MgCl_2$ were determined. Two hydrates for $MgCl_2$ were observed, and exhibited different deliquescence relative humidity (DRH) values. The DRH for $MgCl_2{\cdot}4H_2O$ was found to be $12.8 \pm 0.3\%$ at 243 K with slightly increasing DRH as temperature decreased. The DRH for $MgCl_2{\cdot}6H_2O$ was found to be $31.3 \pm 0.6\%$ at 242 K with little temperature dependence. The DRH of $MgCl_2{\cdot}6H_2O$ was measured below the previously reported eutectic, 240 K, suggesting that the eutectic might be incorrect or that there is a different relevant hydration state. The aqueous solutions of $MgCl_2$ recrystallized to the tetrahydrate at low RH in the range of 3–9% RH at temperatures 265–235 K. Together, the ice nucleation, DRH, and efflorescence relative humidity (ERH) results show that $Mg(ClO_4)_2$ and $MgCl_2$ brines on present day Mars may have the ability to exist for up to 2 h longer than previously predicted.

Keywords: Perchlorate; Freezing brines; Chloride; Deliquescence

1. INTRODUCTION

Possible evidence of liquid water on Mars today includes recurring slope lineae (RSL) (Chevrier and Rivera-Valentin, 2012; McEwen et al., 2013; Ojha et al., 2015; Chojnacki et al., 2016), potential smaller scale brines

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(Martín-Torres et al., 2015), and globules on the landing leg (Rennó et al., 2009). Both the melting of ice and the deliquescence of salts have been proposed as sources of a liquid water phase on current Mars. Deliquescence is the process of absorption of water vapor by salts, leading to the formation of a saturated aqueous solution. Previous studies have suggested that Mars-relevant salts, primarily perchlorates and chlorides, may deliquesce into a liquid brine phase at certain times of the day or year (Gough et al., 2011; Nuding et al., 2014; Chojnacki et al., 2016; Gough et al., 2016). To accurately understand the duration of potential salty solutions on Mars, the freezing of brines into ice, as well as their recrystallization into solid salt, must be studied. There is strong evidence for water ice on Mars, (Kieffer, 1979; Bell et al., 2008) but understanding the conditions needed for the transition from brine to ice, and how these conditions differ from equilibrium predictions, will provide insight to the stability and metastability of aqueous solutions on Mars.

Perchlorate salts have been detected in the shallow subsurface of Mars by instruments onboard the Viking Lander (Navarro-González et al., 2010), Phoenix lander, (Hecht et al., 2009) and the Curiosity rover (Glavin et al., 2013) and may exist globally due to a potential atmospheric formation mechanism (Catling et al., 2010). Perchlorates are of interest to the Mars science community for several reasons, one of which is their ability to deliquesce into aqueous solutions at low to moderate relative humidities ($RH < 50\%$) even at low temperatures (Zorzano et al., 2009; Gough et al., 2011; Nuding et al., 2014; Nikolakakos and Whiteway, 2015). Further, perchlorate salts have been shown to exhibit a strong hysteresis effect; the observed efflorescence relative humidity (ERH) is significantly lower than the observed deliquescence relative humidity (DRH) (Gough et al., 2011), although under thermodynamic equilibrium conditions, efflorescence should occur at the same RH as deliquescence. Some supersaturated perchlorate solutions could persist down to $RH < 20\%$.

In addition to perchlorates, chloride salts have been observed on Mars and exhibit similar phase transitions. Chloride salts were found by the Phoenix Wet Chemistry Lab (Hecht et al., 2009) and were also found to be globally distributed Mars using the Thermal Emission Imaging System (THEMIS) onboard Mars Odyssey (Osterloo et al., 2010). The DRH and ERH of the chloride salts, KCl and NaCl, have been studied for Earth-like conditions (Martin, 2000; Wise et al., 2012) and a few studies of $MgCl_2$ and $CaCl_2$ have been studied under a small range of Mars-like temperatures (Greenspan, 1977; Gough et al., 2014; Gough et al., 2016). However, the DRH and ERH values of $MgCl_2$ have only been reported at room temperature and two lower temperatures (Greenspan, 1977; Gough et al., 2014; Schindelholz et al., 2014; Gupta et al., 2015) and the reported eutectic temperature is quite high, 237 K (Marion and Grant, 1994). Several other studies have reported similar eutectic points for the $MgCl_2{\cdot}12H_2O$ which have been between 240 K and 237 K (Brass, 1980; Marion and Grant, 1994; Marion and Farren, 1999; Bakker, 2004), but the dodecahydrate was not observed in our work From these differing eutectic points, it is not clear if aqueous solutions of $MgCl_2$ will form and persist under temperatures as low as those found on Mars. The present work explores perchlorate and chloride brine metastability at low RH in the crystalline hydrate stability regime and at high RH in the ice stability regime.

The predicted ice formation conditions are typically described by the ice saturation ratio, S_{ice}, ($S_{ice} = P_{H_2O}Ps,ice(T)$), where P_{H_2O} is the water vapor pressure and $P_{s,ice}(T)$ is the equilibrium saturation vapor pressure of ice at the temperature of interest. Ice formation involving Martian salts is often assumed to occur at the point where ice is thermodynamically stable, i.e. $S_{ice} = 1$. However, ice nucleation is often hindered by the kinetics of critical cluster formation and thus $S_{ice} > 1$ is observed (Hoose and Möhler, 2012). Because $S_{ice} > 1$ is required for freezing to occur, aqueous perchlorate and chloride salt solutions would persist as supersaturated (with respect to ice) liquid brines prior to ice nucleation. This supersaturation of ice could extend the presence of liquid solutions on Mars' surface further into the morning, than previously assumed. This is because the morning on Mars is when the temperature is low and RH is high, which are the conditions when supersaturation of ice occurs (Gough et al., 2011; Nuding et al., 2014).

Perchlorate models have shown that, in theory, ice can exist whenever $S_{ice} \geq 1$ (Chevrier et al., 2009; Marion et al., 2010). However, other studies have found that perchlorate and chloride brines can exist at temperatures below their eutectic point (Stillman and Grimm, 2011; Toner et al., 2014). This ice formation requires supersaturation with respect to ice (also called supercooling) within the metastable brine. These previous studies did not quantify the supersaturation with respect to ice that was achieved. Knowledge of the extent of supersaturation with respect of ice of a potential brine will enable the prediction of the conditions and thus time periods that permit the brine to exist. Additionally, the surface of Mars is likely to contain small perchlorate grains and small droplets of perchlorate solution rather than bulk solutions. Therefore, studying ice nucleation on small particles, as is done here, is relevant to the brine/ice formation mechanisms present on current Mars.

2. EXPERIMENTAL METHODS

2.1. Sample preparation

Approximately 0.1 wt% solutions of either $Mg(ClO_4)_2$ or $MgCl_2$ in water (HPLC grade, submicron filtered, purchased from Fischer Scientific) were prepared and then nebulized onto a fused silica disc. The particles that were formed by nebulization typically ranged from 1 to 30 μm in diameter. The sample was then placed into the environmental cell at 0% RH and room temperature to allow the particles to dry and lose all liquid phase water. Raman spectroscopy confirmed the lack of liquid water present after drying