



Experimental investigation of the stability and evaporation of sulfate and chloride brines on Mars

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ABSTRACT

We have investigated the evaporation of concentrated magnesium and ferrous sulfate, and magnesium and ferric chloride brines as possible sources for liquid water on the surface of Mars, with special emphasis on the effect of freezing and crystallization of solutions. Experimental evaporation rates range from 0.04 mm h⁻¹ for 25 wt.% MgSO₄ at 271.9 K, to 0.19 mm h⁻¹ for 18 wt.% FeSO₄ at 270.5 K. For chloride solutions, evaporation rates range from 0.09 mm h⁻¹ for 40 wt.% FeCl₃ at 261.34 K, to 0.43 mm h⁻¹ for 20 wt.% MgCl₂ at 267.2 K. These evaporation rates are significantly lower than for pure water, i.e. 1.35 mm h⁻¹ at 273 K. Using the Pitzer ion interaction model, we show that the decrease in evaporation rate is due to lower water activity in concentrated solutions, down to 0.91 for saturated MgSO₄ and 0.97 for saturated FeSO₄, at their eutectic temperatures. For saturated MgCl₂ and FeCl₃, the calculated water activities are 0.57 and 0.60 at their respective eutectic temperatures. In addition, we show that the water activity drops significantly when salts are crystallizing, down to 0.17 and 0.21 for MgSO₄ and FeSO₄, respectively. Our experiments and calculations show that the water activity and evaporation rate are dependent on the hydration state of the precipitating salt, which is in turn controlled by the temperature and the relative humidity. Low-hydration state salts precipitate at lower humidity, with lower evaporation rates. Our study suggests that martian brines could remain stable for longer periods of time, at low temperatures and low humidity, than previously thought. Brines formed from these salts would be a more stable source of water on Mars, thus beneficial for any putative martian life, past and/or present.

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1. Introduction

Liquid water is known to be unstable on the surface of Mars, although gullies found in valleys and on crater slopes suggest recent liquid activity (Mellon and Phillips, 2001; Heldmann et al., 2005; Malin et al., 2006). The present-day surface conditions on Mars are very close to the triple point of water, and under some conditions liquid water could form and remain (presumably metastable) for a certain period of time (Hecht, 2002; Richardson and Mischna, 2005; Moore and Sears, 2006). In addition, lander and orbital observations have detected numerous water-related minerals and features indicating warmer and wetter past conditions (Chevrier and Mathe, 2006). Dissolved salts can stabilize liquid water because of lower freezing temperatures (Brass, 1980; Kargel, 1991; Knauth and Burt, 2002; Chevrier and Altheide, 2008) and lower evaporation rates (Sears and Chittenden, 2005; Chevrier and Altheide, 2008).

Recent exploration of the surface of Mars has revealed abundant magnesium sulfate (MgSO₄) salts (Bibring et al., 2005; Clark et al., 2005;

Gendrin et al., 2005; Mangold et al., 2008), while ferrous sulfate (FeSO₄) may be present in the regolith (Lane et al., 2004) and is an important part of the geochemistry of Meridiani Planum (Tosca et al., 2008b). This suggests that past and/or present martian brines might contain high sulfate concentrations. Moreover, Mg-sulfates have been shown to possibly account for part of the water present in the regolith (Feldman et al., 2004; Vaniman et al., 2004), highlighting the importance of studying the interaction between Mg,Fe-sulfates and water in and out-of-equilibrium, for example during evaporation processes.

Chloride-bearing materials have been identified by the Mars Odyssey THEMIS instrument in Noachian-aged highlands in the southern hemisphere (Osterloo et al., 2008), and preliminary data from Phoenix have suggested that the soil in the northern polar region may contain high concentrations of chlorides (http://www.nasa.gov/mission_pages/phoenix/images/press/WCL_delivery_2.html). These findings highlight the potential importance of chloride salts in stabilizing water in alkaline, icy environments, possibly participating in maintaining the water cycle on Mars for the past 3.5 billion yr.

Magnesium and ferrous chloride brines possess eutectic temperatures lower than sulfates, i.e. 252 K and 236.5 K, respectively, versus 269.6 K and 267.2 K for MgSO₄ and FeSO₄, respectively (Brass, 1980;

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Marion et al., 2003; Sears and Chittenden, 2005). Alternatively, ferric chloride (FeCl_3) has a higher eutectic temperature than its sulfate equivalent ($\text{Fe}_2(\text{SO}_4)_3$), i.e. 238 K (Marion et al., 2008) versus 205 K (Chevrier and Altheide, 2008). Experimental studies have shown that calcium and sodium chloride significantly stabilize liquid water through freezing point depression and lower evaporation rates (Sears and Chittenden, 2005). Further study on ferric sulfate showed that water activity plays a significant role in stabilizing the liquid phase (Chevrier and Altheide, 2008). Therefore, we have investigated the behavior of liquid magnesium and ferrous sulfate, and magnesium and ferric chloride brines between 258 K and 278 K, under 7 mbar of CO_2 . In this study, we especially focused on the effect of water activity (related to ion concentration) and for the first time on the effect of sulfate hydrate crystallization on the evaporation rates of the brines.

2. Methods

For the present study, the brine samples were prepared at 25 °C from quad-filtered DI water containing 5 to 25 wt.% MgSO_4 (Mallinckrodt #6070-12), 11 to 18 wt.% FeSO_4 (corrected from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, J.T. Baker #2074-01), 20 to 40 wt.% FeCl_3 (corrected from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; Alfa Aesar #10025-77-1), and 15 to 30 wt.% MgCl_2 (corrected from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; BDH #0244). Mass loss measurements revealed that the initial water content of the original samples varied slightly from calculated values (Table S1), generally less than 5%. The density of each solution was measured at approximately 10 °C (Table S2), and further used to calculate the evaporation rates of the brines (see Section 3). The previous concentrations were chosen to investigate undersaturated, saturated, and supersaturated solutions with respect to the eutectic values of each salt (Table 1).

The experimental setup and the environmental chamber used for studying the evaporation of liquid water and brines (Fig. 1) have been described in our previous works (Chevrier and Altheide, 2008; Sears and Chittenden, 2005; Sears and Moore, 2005). The atmosphere was first evacuated from the chamber by lowering the pressure to less than 0.09 mbar. The chamber was then filled with pure CO_2 to atmospheric pressure and cooled below 0 °C. Once filled, the chamber was opened and the sample quickly placed on a loading analytical balance. The platform supporting the balance set-up was then lowered into the chamber, the lid sealed, and the pressure pumped down to 7 mbar. Once the pressure reached 7 mbar, we waited 20 min to accommodate the instruments, especially the balance, to the new conditions (temperature and pressure). Then we started recording mass, temperature of the chamber and the sample, pressure, and relative humidity (Table S2). The pressure was maintained at 7 ± 0.03 mbar during the whole experiment.

Table 1

Summary of Pitzer parameters (C_{NX} and the parameters used in Eq. (11) to calculate B_{NX}) used in calculations of water activity (see Sections 4.2 and 4.3), and the resulting water activities for eutectic conditions and highest concentrations tested.

	MgSO_4	FeSO_4	MgCl_2	FeCl_3
<i>Pitzer Parameters</i>				
α_1 ($\text{kg}^{1/2} \text{mol}^{-1/2}$)	1.4	1.4	2.0	2.0
α_2 ($\text{kg}^{1/2} \text{mol}^{-1/2}$)	12.0	12.0	0	0
$\beta^{(0)}$ ($\text{kg}^{1/2} \text{mol}^{-1/2}$)	0.221	0.2568	0.3523	0.3419
$\beta^{(1)}$ ($\text{kg}^{1/2} \text{mol}^{-1/2}$)	3.343	3.063	1.681	1.535
$\beta^{(2)}$ ($\text{kg}^{1/2} \text{mol}^{-1/2}$)	−37.43	−42.0	0	0
C_{NX} ($\text{kg}^{1/2} \text{mol}^{-1/2}$)	0.025	0.0209	0.00979	−0.01417
<i>Eutectic values</i>				
Temperature (K)	268.6	267.2	252.0	238.4
Concentration (wt.%)	18.0	13.7	21.0	28.8
Water activity	0.95	0.99	0.78	0.79
<i>Maximum concentration</i>				
Concentration (wt.%)	25	18	30	40
Water activity	0.91	0.97	0.50	0.60

Values are from (Pitzer, 1991; Mellon and Phillips, 2001; Marion et al., 2008).

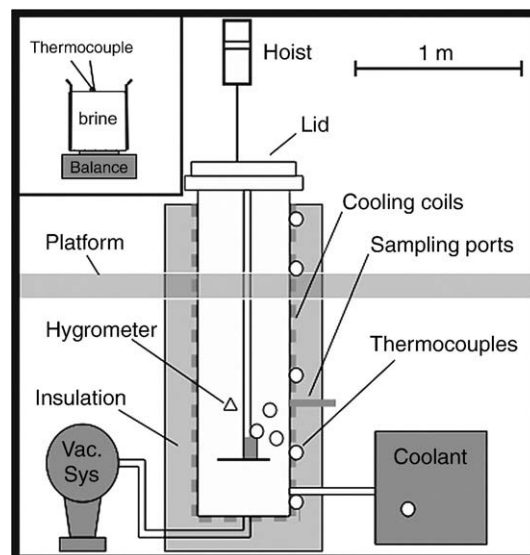


Fig. 1. Schematic of the Andromeda simulation chamber used for the brine evaporation experiments described in this study.

Finally, the atmosphere was continuously exchanged to maintain relative humidity below 1%.

Fourier Transform Infrared (FT-IR) spectra of crystallized MgSO_4 samples were measured using a Nicolet 6700 Smart Diffuse spectrometer with N_2 purge gas. Spectra were recorded in reflectance mode in the range of 1.0–2.6 μm with a resolution of 4 cm^{-1} . Our configuration consisted of a quartz-halogen source, a CaF_2 beam splitter, and a DTGS detector. Background spectra using a Spectralon white standard were taken before each sample spectra. Spectra of magnesium sulfate hydrates were acquired from the following: epsomite MS7 (Sigma-Aldrich product #230391), hexahydrate MS6 (Fluka product #00627), and kieserite MS1 (Sigma-Aldrich product #434183), where MS = magnesium sulfate and the number beside is the hydration state (thus MS7 = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Sanderite MS2 was synthesized by heating MS7 at 100 °C for 2 h (Robson, 1927). Finally, considering its relevance at low temperature, we synthesized meridianiite MS11 by freezing a 20 wt.% solution of MgSO_4 at −30 °C. The resulting mixture contains nevertheless a substantial amount of water ice (~47 wt.%).

3. Results

3.1. Magnesium and ferrous sulfates

Mass loss curves show a remarkable linearity with $R^2 = 0.98$ or above (Fig. 2A), implicating steady state mass transfer between the liquid phase and the atmosphere. Evaporation rates for both sulfates (in mm h^{-1}) were calculated by normalizing the mass loss rate data (in g min^{-1}) to the surface area of the sample and the density of the brine. The error on the evaporation rate was determined from the error on the regression line, the uncertainty on the mass measurement (0.01 g) and the error on the density of the brine. We estimate that this error is on average 10% of the evaporation rate value, a value also observed in our former works (Chevrier and Altheide, 2008).

Overall, the experimental evaporation rates demonstrated by the Mg^{2+} and Fe^{2+} sulfate brines are significantly lower than the evaporation/sublimation of pure water (Fig. 3). The evaporation rates of 10 and 15 wt.% MgSO_4 are fairly dependent on the temperature of the brine solution (Fig. 3A), as previously shown for other sulfate brines (Chevrier and Altheide, 2008). For example, at 262.2 K the 15 wt.% solution evaporated at 0.49 mm h^{-1} , while at 269.16 K the rate increased to 0.676 mm h^{-1} . This relationship is not obvious for 20 and 25 wt.% MgSO_4 , but alternate processes dominate in these brines

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