CONTROL OF THE WATER CYCLE BY THE REGOLITH AT THE PHOENIX LANDING SITE.

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Introduction: Although there has been no direct evidence for liquid water on the surface of Mars, indirect evidence from recent gully formation suggests the presence of liquid water processes near the surface [1,2]. However, pure water is unstable in its liquid form due to the low pressures and temperatures associated with the Martian surface [3,4]. Water is likely to be kept frozen and sublimating, or evaporating/boiling, if liquid [3]. Brines or salt-rich solutions have been suggested since they are known to lower evaporation rates and the freezing point [5]. The behavior of brines is nevertheless dependent not only on the temperature but also on the atmospheric humidity which is directly related to the thermodynamic activity of water in the brine solution [6].

Looking at models that predict the RH, local GCM models slightly overestimate the relative humidity during daylight hours while under approximating it during night [6]. Moreover, some GCM models contain constants that are fitted to data such as MGS-TES [7]. While being accurate at predicting atmospheric conditions, these constants do not explain the physics behind. These observations suggest a local control by atmosphere-regolith humidity exchange processes such as adsorption onto regolith grains [8,9] and/or hydration changes of salts [10].

NASA's Phoenix mission provided a unique opportunity to study both the regolith and atmospheric conditions in the north polar regions of Mars [11]. Phoenix measured relative humidity (RH) and temperatures [12], as well as regolith compositions. Such local scale experiments allow for the validation of various hypotheses concerning the interactions between the regolith and the atmosphere, particularly concerning the water cycle.

One particularly interesting ion identified by Phoenix in the soil is perchlorate ClO_4^-, essentially because it forms compounds extremely soluble and apt at maintaining water liquid to extremely low temperatures (206 K for $Mg(ClO_4)_2$, e.g. [6,13]). Moreover, perchlorate compounds often exhibit several hydration states (for example $Mg(ClO_4)_2$ has the 0, 2, 4 and 6 hydration states).

Recent studies have shown that slow adsorption kinetics can strongly affect the diffusion of water vapor through the regolith [9]. Moreover, adsorption onto regolith grains may well explain the cohesiveness of the regolith at the Phoenix site [12].

The major question we are trying to answer in this study is what are exactly the nature and importance of the interactions between the regolith and the atmosphere. In other terms, does the atmosphere control the hydration state of the regolith or does the regolith control the atmospheric water cycle? Such interactions depend not only on the thermodynamic properties of the regolith but also on the kinetics of the exchanges. For example it has been demonstrated that at long timescales, adsorption could be neglected or rather timely averaged [14,15]. However, the validity of this hypothesis for short timescale processes has not bbeen established. This is often due to the lack of kineti parameters to use in the models.

Here we present some experimental and modeling results on the thermodynamics and kinetics of water vapor transfer in the regolith. We have investigated two aspects that potentially control the water cycle through regolith-atmosphere coupling: salt hydrates and adsorption/desorption.

The salts hydrates were studied using evaporation experiments of liquid brines, which, while being directly relevant to the stability of liquid water on Mars (evaporation of paleolakes [16]), allow us also to determine the thermodynamic parameters required in the model of water vapor transfer. Of the intermediate oxidation species of chlorine between chloride Cl^- and perchlorate ClO_4^-, chlorate ClO_3^- is the most stable [17,18] and is therefore expected to be present in the regolith. Therefore, in a first step we focused on sodium and magnesium perchlorate and chlorates as the most relevant to the Phoenix chemistry [6,13]. The ultimate aim is to develop a thermodynamic model of brine behavior at low temperatures, including evaporation and freezing [13,19,20], both being necessary for the dynamic model. The link between both models is the activity of water in the liquid which controls the freezing (frost point depression) and the evaporation rate (saturation vapor).

In parallel to these experiments, we developed a model of sublimation / evaporation of solid / liquid water including the effect of freezing / thawing and in terms of diffusion / adsorption through a potential regolith. This model includes also the effect of hydration changes of salts. To fully describe these regolith processes, we must first observe the average local water density. Then the experiments can be used first to obtain the required parameters, in particular the kinetic

constants for the various processes (diffusion coefficients, adsorption kinetic constants, chemical reaction constants for hydration, dehydration etc.) but also to validate the results of the model before application to the martian surface.

Evaporation Rates. Experiments were performed in a Mars simulation chamber. A sample of solution was lowered into a chilled CO_2 environment, which was then pumped down to 7 mbar, while still maintaining less than 1% relative humidity. Mass loss (in grams) was measured, and from this, the evaporation rate E (in mm h^{-1}) was determined (Fig. 1). The evaporation rates typically show a strong dependency on the temperature which controls the water vapor gradient between the surface of the sample and the atmosphere. The evaporation rate also decreases with increasing concentration due to the dependency of the activity of water on the concentration of salt. Therefore, from evaporation rates we are able to extract the activity of water [3].

We are currently building an extensive database of thermodynamic properties at low temperature, to be used in the Geochemical workbench software, to calculate the thermodynamic behavior of solutions during freezing or evaporation, which is necessary for the dynamic model described in the next section. However, there is a clear lack of thermodynamic data for the various species of oxidized chlorine. From the literature and our own data, we have constructed stability diagrams for $NaClO_4$, $NaClO_3$ $Mg(ClO_4)_2$ and $Mg(ClO_3)_2$ (Fig. 2). While normally we can use theoretical calculations from the Pitzer parameters [8] to calculate the equilibrium lines between ice and liquid or between the various hydrates and the solution, these have never been calculated for Mg^{2+} and ClO_3^-. Two approaches can therefore be used to determine these Pitzer parameters: either using the "ice line" i.e. the equilibrium line between the ice and the solution, or using evaporation rates. In both cases the activity of water can be determined and from the activity, the Pitzer parameters.

Then, using these parameters, combined with the temperature and water vapor pressures measured by the Phoenix lander, we were able to calculate the evaporation rates of eutectic concentration solutions the two main perchlorates suggested to be present in Phoenix: magnesium $Mg(ClO_4)_2 \cdot nH_2O$ ($0 \leq n \leq 6$) and sodium $NaClO_4 \cdot nH_2O$ ($0 \leq n \leq 2$) [6]. Potassium perchlorate has a very low solubility and does not form any hydrate and is therefore highly unlikely to participate in the humidity cycle.. The major conclusion of these calculations (for simple salt solutions) was that most of the time the liquid brines were either frozen (temperature below the eutectic of the salt solution, Fig. 3A) of evaporation (saturation pressure higher than the water vapor pressure in the atmosphere and

therefore, temperature "too high", Fig. 3B). However, there is a short window were the temperature is in the right range and the solution is thermodynamically stable in the conditions of the Phoenix surface (green lines in Fig 3C).
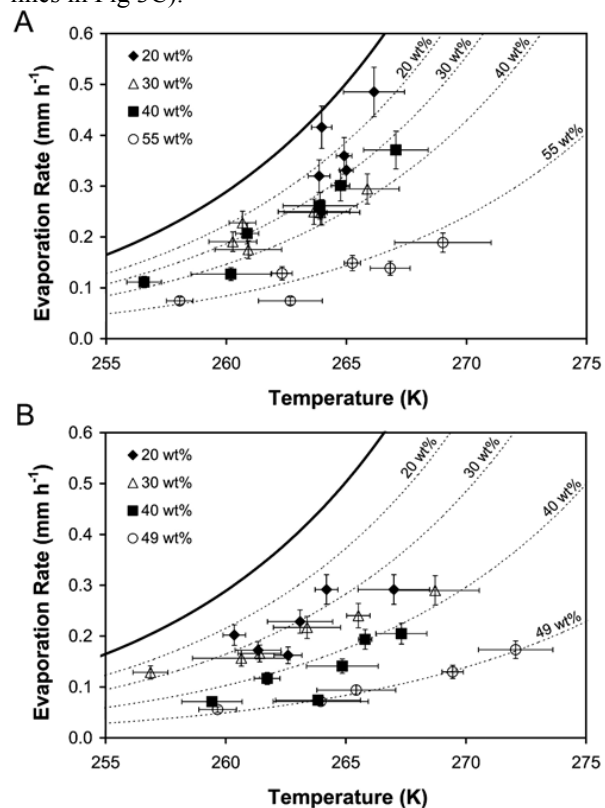

Figure 1. Evaporation rates of A) $NaClO_4$ and B) $Mg(ClO_4)_2$ as a function of sample temperature and concentration. Dashed lines are theoretical evaporation rates for each concentration, calculated from a modified Ingersoll [7] equation and Pitzer model [8]. The solid line is for pure supercooled liquid water.
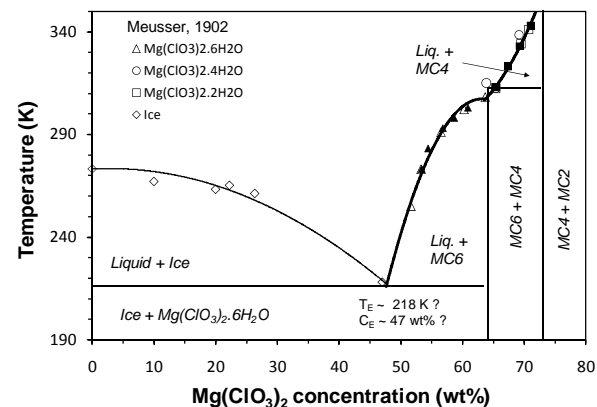

Figure 2. Stability diagram of magnesium chlorate solutions versus temperature. Therefore the lines are simply polynomial fits which include an extrapolated eutectic temperature of 218 K.
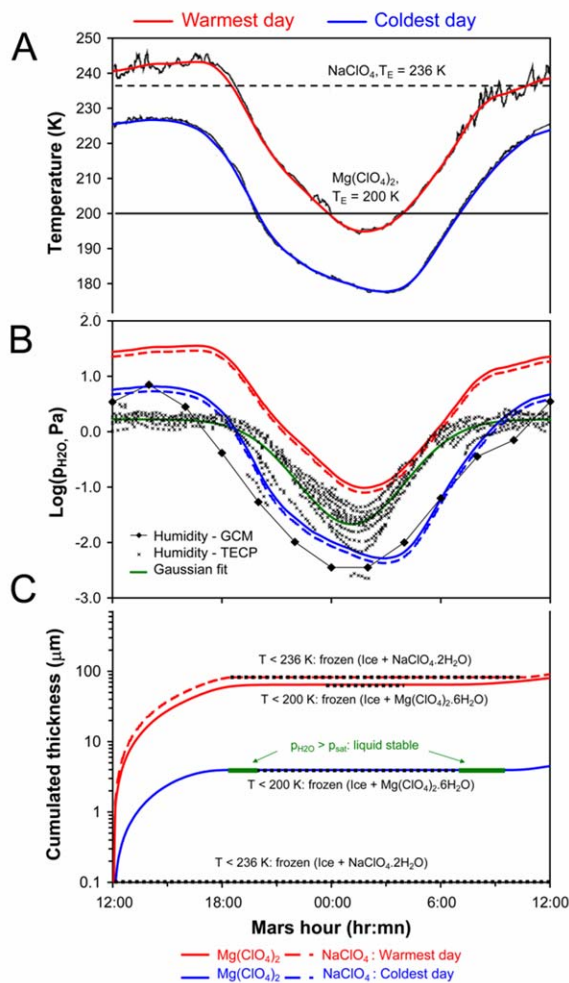
Figure 3. Application of results to Phoenix conditions. (A) Temperatures of the coldest and warmest days as a function of time as measured by the Phoenix lander (black curves). The superimposed red (warmest day) and blue (coldest day) curves are smoothed curves of the data, used for the calculations of evaporation rates. The two horizontal lines represent the eutectic temperatures for Na (dashed) and Mg (solid) perchlorates. (B) Comparison of Phoenix humidity data measured in the soil by the TECP (black circles) and the predicted variation by the GCM (black line). The solid green line is a Gaussian fit to the data points. The blue and red lines are the equilibrium vapor pressures above the solutions calculated using the equation for supercooled water and the activity of water. (C) Cumulative thickness of evaporated solution for each salt. Superimposed thick dotted black lines indicate the periods where the temperature is under the eutectic, and thus where liquid is frozen. The thick superimposed green lines indicate that liquid is thermodynamically stable.

Control of humidity by perchlorate hydrates. Figure 4A shows the thermodynamic diagram for $Mg(ClO_4)_2$, which exhibits a eutectic at 206 K, while $NaClO_4$ has a eutectic of 236 K [6]. Such diagrams represent equilibriums with the liquid phase (represented in shaded grey

for reference). However, when equilibriums with the gas phase are also present it is more useful to represent these diagrams as a function of the water activity (in solution), which is equivalent to the relative humidity in the gas phase. From previous experimental data [21], we observe an additional hydrate, which does not equilibrate with the liquid, only with the vapor phase. Various thermodynamic arguments suggest that this is a pentahydrate $Mg(ClO_4)_2.5H_2O$, mostly stable at low temperature (< 300K) and low relative humidity ($R_H <$ 0.1-0.01).
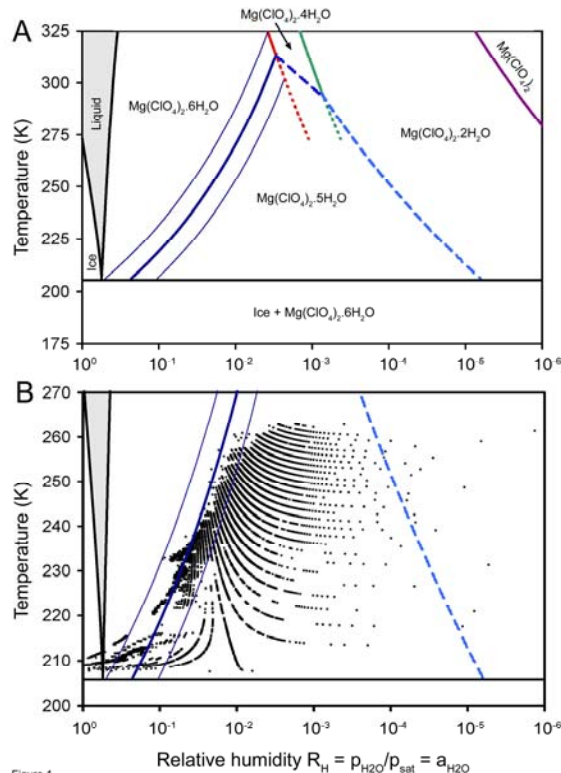

Figure 4. Phase diagrams for $Mg(ClO_4)_2$. A. Temperature versus activity of water. Solid lines are calculated from the experimental data of [21]. The equilibrium between the penta- (MP5) and the hexahydrate (MP6) has been extrapolated to low temperatures. Dashed lines are theoretical lines supposing a pentahydrate. Dotted lines are the extension of the data from [21] in the stability field of the pentahydrate. the thin lines being the equilibrium between the penta- and hexahydrate including the error on the determination of the thermodynamic parameters [21]. B. Comparison of the temperature versus relative humidity (T-R_H) stability diagrams with the Phoenix humidity data for A. Magnesium perchlorate and B. Sodium perchlorate. Lines in Fig. A are identical to Fig. 2B with the solid line being the MP5-MP6 equilibrium and the dashed line the MP5-MP4 theoretical equilibrium.

When looking at the activity of water versus temperature as measured by Phoenix (Fig. 4B), we notice that the high humidity values are limited by two equilibriums in the $Mg(ClO_4)_2$ stability field: first the MP5-

MP6 curve at high temperatures (220 < T < 260 K) and by the eutectic limit at T < 220K (Fig. 3A). Almost all the data lie in the stability field of $Mg(ClO_4)_2.5H_2O$, with only the data at low-T high RH being in the stability field of the hexahydrate. We also notice that the data largely extend beyond the T-R_H limit for liquid (i.e. some data lay in the grey area and in the ice + liquid area at very high humidity). This suggests that liquids should form by possible melting of $MgClO_4.6H_2O$ (Fig. 3C).

Modeling of water vapor transfer.

Heat and Mass Transfer Model: An indirect method of measuring annual average humidity is by observing ice table depths. The regolith and atmosphere exchange H_2O due to concentration gradients, which vary across the year. Subsurface ice stability will then occur when its water vapor density averaged across the year is equivalent to the average local atmospheric water density.

We use a finite element procedure to solve the heat transfer equations in a regolith column [22] whose thermal properties are derived from Phoenix data [12]. Our upper boundary heat flux condition includes atmospheric perturbations to direct sunlight as shown in [16,23]. Knowing the temperature with depth profile we can then apply the theoretical construct provided by McKay [24] in order to estimate local average relative humidity. For every simulated sol, we use our temperature profile to calculate the saturation vapor pressure of water (P_{sat}) with depth, which at the end of a martian year is averaged in order to create an averaged saturation vapor density ($\overline{P_{sat}}$) with depth profile. By McKay, the average water vapor density ($\overline{P_{H_2O}}$) at any given point is then given by:

$$\overline{P_{H_2O}} = RH \int P_{sat}(T)dt = RH\left(\overline{P_{sat}}\right)$$

where *RH* is relative humidity. The frost point temperature (T_f) is then the temperature that satisfies the following condition:

$$0 = \overline{P_{H_2O}} - P_{sat}(T_f)$$

By varying the value of RH, we can produce frost point temperature with depth profiles for various plausible scenarios (Fig. 5). The intersection between the average surface temperature at the Phoenix landing site and the frost point temperature is then the ice table depth. We can see that for an average yearly temperature of 180 K and an observed depth of the ice table of ~8 cm, the average humidity has to be between 0.5 and 1%. Such humidity values are too low to be due to perchlorates alone. Perchlorates may nevertheless con-

trol humidity when values become relatively high or the temperature low enough (Fig. 4). Another process which is still being investigated is adsorption. Indeed, preliminary calculations suggest that a monolayer adsorbed on the regolith would equilibrate around 0.5 to 1% RH, which corresponds to the ice depth layer.
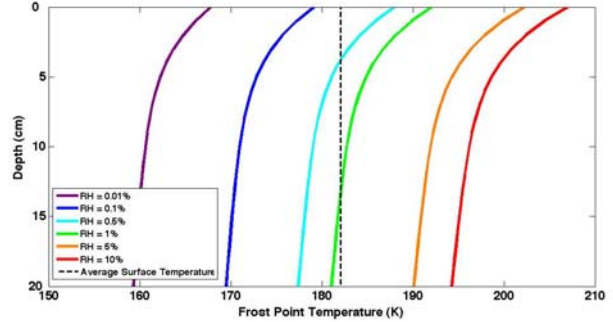

Figure 5. Frost point temperature with depth profile for varying average local relative humidity (solid colored lines). The dotted line represents the expected average surface temperature at the Phoenix landing site.

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