

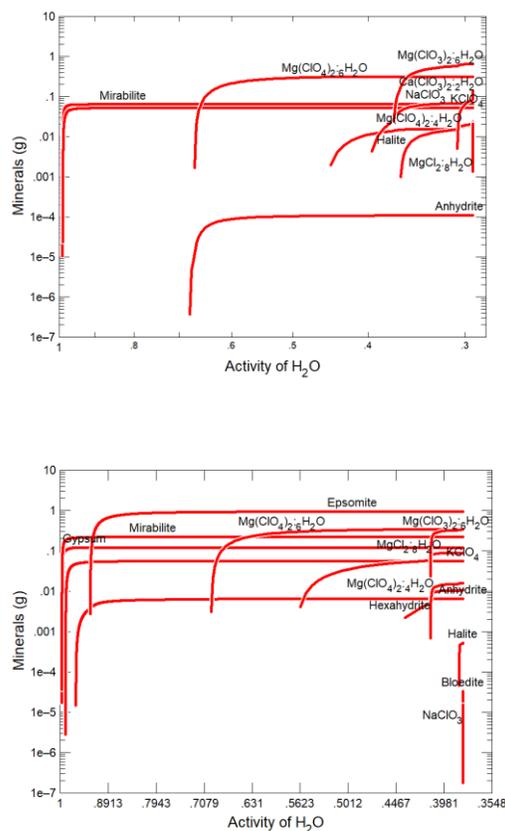
## MODELING THE DELIQUESCENT OF COMPLEX SALT MIXTURES AND APPLICATION TO THE HABITABILITY OF THE MARTIAN SURFACE. V. F. Chevrier<sup>1</sup>, A. Fitting<sup>1</sup>, E.G. Rivera-Valentín<sup>2</sup>, A. Soto<sup>3</sup>.

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**Introduction:** The habitability of the surface of Mars depends on multiple factors, including, but not limited to, temperature, relative humidity, UV, and nutrients [1]. Of these parameters, temperature and relative humidity control the presence of liquid water, which is of primary astrobiological importance and has driven the exploration of Mars for the past two decades. Pure water is generally unstable on the surface of Mars, being subjected to freezing, evaporation and boiling, but these processes are highly variable depending on the location and intrinsic properties of the liquid [2]. Indeed, the presence of abundant hydrated salts on the surface of Mars suggests the possible presence of brines [3,4], which present the advantage of stabilizing liquid water at lower temperatures [2,5]. Previous work on mapping the stability of brines on the surface and subsurface of Mars have focused on single brines, such as, for example, calcium or magnesium perchlorates [6]. However, it is widely known that mixtures of salts can significantly reduce the freezing or deliquescence points for brines [7,8]. However, no comprehensive model has been undertaken to simulate the behavior of complex brines at the surface of Mars. Therefore, in this abstract we present the first results on deliquescence of mixtures of salts, using the composition determined by the Phoenix lander [9,10].

**Methods:** The objective of this work is first to determine the deliquescence relative humidity at the Phoenix landing site as a function of temperature, for a realistic ionic composition as measured by the Wet Chemistry Laboratory (WCL) onboard the Phoenix lander. In a second step we will apply these results through a diurnal and seasonal model of relative humidity and temperature at the surface of Mars to determine the locations and times of the day where deliquescence occurs on the surface (and in the shallow subsurface). This abstract focuses on the first part of this process. Unfortunately, of the widely used thermodynamic codes for thermodynamic simulations, such as FREZCHEM or Geochemist's Workbench, none of them directly simulates water activity (or deliquescence) as a function of temperature. Therefore, we used an indirect method [8], in which we modelled the evaporation of individual brine solutions at fixed temperatures (Fig. 1). We then noted the water activity at each salt precipitating until the code stopped or evaporation was complete (Fig. 2). Because in thermodynamic modeling, deliquescence and efflorescence occur at the same point, measuring the evaporation di-

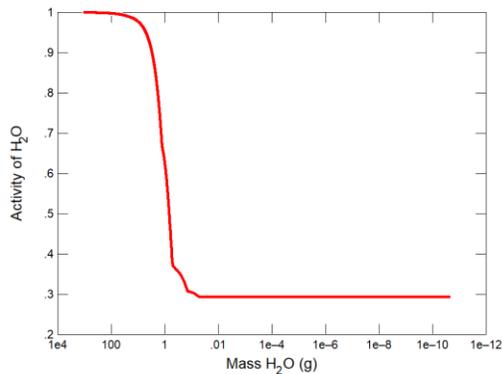
rectly gave us the deliquescence water activity values for each temperature and salt composition. The first salt to precipitate is equivalent to the point of complete deliquescence and the last salt to precipitate gives the deliquescence relative humidity (or eutonic point). We ran the simulations in 5 K increments between 198 and 293 K.



**Figure 1:** Evaporation of brines A - model 1 (chlorate-rich) and B - model 3 (sulfate-rich) at 273 K. The process was repeated at each temperature between 193 K and 298 K by 5 K increments.

We used three different models depending on assumption on the initial ionic composition measured by the WCL [9] with various methods to balance the ionic charge. Model 1 is rich in chlorate ion, model 2 is balanced between chlorate and sulfate, and model 3 is rich in sulfate and magnesium (see [8] for detailed discussion on model description). Each composition measured by the WCL was evaporated starting from 1000 g of liquid brine. And the activity of water was recorded

at each precipitating salt. This water activity corresponds to the deliquescence relative humidity for the salt mixture.

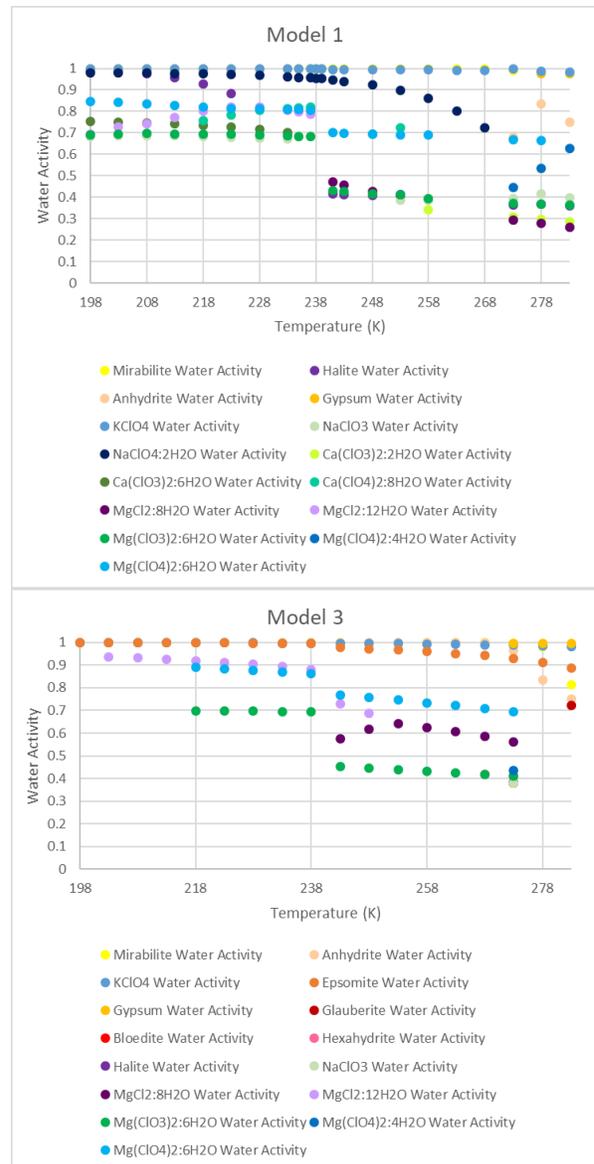


**Figure 2:** Activity of water as a function of residual mass of liquid water during the evaporation of model 1 brine (chlorate-rich) at 273 K.

### Results and discussion:

Several interesting observations can be made in the deliquescence diagrams of the multi-salt assemblages. First the deliquescence water humidity (DRH) always increases with decreasing temperature. This is mostly because of the higher hydrates forming at lower temperatures. Secondly, we observe roughly two regions, apparent in all models. At high temperatures (above 238-240 K), deliquescence occurs at relative humidity around 0.3-0.4. At lower temperatures, deliquescence occurs around 0.7. The sudden transition around 240 K is still unclear and could possibly correspond to the formation of a high hydrate (for example  $\text{MgCl}_2$  has a twelve hydrate at this temperature). Three, in all models, the first salt to deliquesce is  $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ , so surprisingly not a perchlorate but a chlorate. Calcium perchlorate is present in model 1 and deliquesces slightly after  $\text{Mg}$  chlorate (Fig. 3A). In model 1,  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  controls the DRH only at high temperatures above 273 K. In all models, sulfates deliquesce at much high relative humidity and therefore do not really contribute to the DRH of the mixture.

**Conclusions:** In all simulated brines of Phoenix-type composition, we observed that the deliquescence relative humidity is essentially controlled by chlorine bearing salts (chlorides, chlorates or perchlorates) and sometimes even by a single species. Deliquescence occurs at DRH as low as 0.3 at temperatures around 273 K so lower than for single salts (0.52 for Calcium perchlorate but at much lower temperature, 198 K). Despite, this slightly increased stability field for multi-brines, it is unlikely this will provide and much more habitable environment at the surface of Mars.



**Figure 3:** Water activity or deliquescence relative humidity as a function of temperature for models 1 and 3.

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**References:** [1] Rummel J. D. et al. (2014) *Astrobiology* 14 (11), 887-968. [2] Chevrier V., T. S. Altheide (2008) *Geophysical Research Letters* 35 (L22101). [3] Chevrier V. F., E. G. Rivera-Valentin (2012) *Geophysical Research Letters* 39 (L21202). [4] Gough R. et al. (2019) *Icarus* 321, 1-13. [5] Chevrier V. et al. (2009) *Geophysical Research Letters* 36 (L10202). [6] Chevrier V. F. et al. (2019) *Lunar and Planetary Science Conference L* (2019). [7] Gough R. V. et al. (2012) *Lunar and Planetary Science Conference XLIII* (1706). [8] Elsenousy A., V. F. Chevrier, paper presented at the 45th Lunar and Planetary Science Conference, The Woodlands, Texas, March 17-21, 2014. [9] Hecht M. H. et al. (2009) *Science* 325, 64-67. [10] Kounaves S. P. et al. (2010) *Geophysical Research Letters* 37 (9), L09201.