MODELING THE DELIQUESCENCE OF COMPLEX SALT MIXTURES AT THE PHOENIX LANDING

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Introduction: Several factors influence the habitability of the Martian surface. Among these are temperature, relative humidity, UV radiation, and nutrients [1]. Liquid water has key astrobiological importance for Mars, the stability of which is controlled by relative humidity and temperature. On the Martian surface, pure water is subjected to evaporation, boiling, and freezing, causing it to be generally unstable, although these processes are quite variable depending on location as well as the intrinsic properties of the liquid [2]. The possible presence of brines on the surface of Mars may be suggested by the abundant presence of hydrated salts [3,4]. Brines are significant because they hold the ability to stabilize liquid water at lower temperatures [2,5]. Previous works that have dealt with mapping the surface and subsurface stability of brines have focused on single brines, such as magnesium or calcium perchlorates [6]. However, given the complex nature of the Martian regolith, mixtures of salts are more realistic and are known, at least for binary solutions, to change the stability of brines [7]. Here, we present the first results on the deliquescence of salt mixtures, constrained by the regolith composition as determined by the Phoenix lander [8.9].

Methods: The objective of this work is first to determine the deliquescence relative humidity (DRH) of the salt mixtures 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 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 [10], in which we modelled the evaporation of individual brine solutions at fixed temperatures (Fig. 1). We then determined the water activity at each salt that precipitated, until evaporation was complete. For each evaporation run, we also graphed water activity as a function of water mass (Fig. 2). Because in thermodynamic modeling, deliquescence and efflorescence occur at the same point, measuring the evaporation directly 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 minimum deliquescence relative humidity (or eutonic point). We ran the simulations in 5 K increments between 198 K and 283 K.

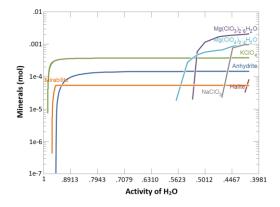


Figure 1: Evaporation of brines using model 1 (chloraterich) at 273 K. The processus was repeated at each temperature between 198 K and 283 K by 5 K increments.

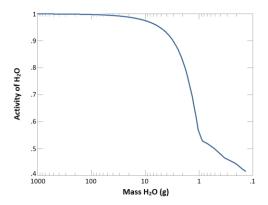


Figure 2: Activity of water as a function of residual mass of liquid water during the evaporation of model 1 brine (chlorate-rich) at 273 K.

We used three different models depending on assumption on the initial ionic composition measured by the WCL [8] with various methods to balance the ionic charge [10]. 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 [10] for detailed discussion on the model descriptions). This abstract

focuses on model 1, which has the highest chlorate composition (and thus lowest sulfate). 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.

Results and Discussion: An interesting observation relating to the deliquescence diagrams of the multi-salt assemblages is that the DRH always increases with decreasing temperature. This is mostly because of the higher hydrates forming at lower temperatures. We created a combined graph from our data showing the water activity of each precipitating mineral as a function of temperature (Fig. 3). Across all temperatures, sulfates tended to have high water activity values. At higher temperatures (>258 K), chlorides exhibit the lowest water activity values, whereas between 208 K and 253 K, chlorates were lowest. At the lowest temperatures (<208 K), chlorides once again showed the lowest water activity values, with chlorates close behind. Combining the lowest water activity values at each temperature for model 1, creating a solidus line, with an ice stability line, we can see a zone (below the ice line and above the solidus line) where liquid may be stable. We added data from the Phoenix lander to test for potential brine formation (Fig. 4). Data points from PHX that are associated with potential evidence for liquid brines, through melting or adsorption as inferred from the regolith's dielectric signatures [11], have been highlighted in red, blue, and green. Most of these colored points do not land in the liquid stability zone, but some do, indicating that there may be a possibility of liquid brine formation.

Conclusions: In all simulated brines of Phoenixtype 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 0.37 at temperatures around 273 K, so lower than for single salts (0.52 for Caperchlorate but at much lower temperature, 198 K). Despite this slightly increased stability field for multibrines, it is unlikely this will provide improved habitable environment at the surface of Mars. In addition, while the water activity of the solidus line does drop close to 0.4, this is at higher temperatures. In the temperature range where Phoenix data points fall in the liquid stability zone, the water activity is not lower than about 0.5, showing again that it is unlikely that the multibrines will increase the likelihood of stable liquids at the surface of Mars.

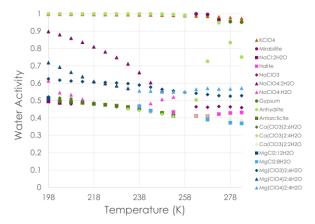


Figure 3: Water activity or deliquescence relative humidity as a function of temperature for model 1.

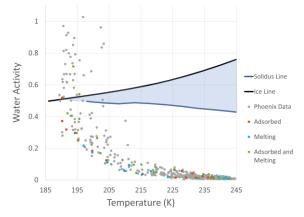


Figure 4: Lowest water activity or deliquescence relative humidity as a function of temperature for model 1, with an ice stability line and data from the Phoenix lander.

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