

**EFFECTS OF FREEZING POINT DEPRESSION ON MARITIAN PALEOLAKE STABILITY.** E. G. Rivera-Valentin<sup>1</sup>, V. F. Chevrier<sup>1</sup>, R. Ulrich<sup>2</sup>, L. Roe<sup>1,3</sup>, <sup>1</sup>Arkansas Center for Space and Planetary Sciences (eriverav@uark.edu), <sup>2</sup>Dept. of Chemical Engineering, University of Arkansas, <sup>3</sup>Dept. of Mechanical Engineering, University of Arkansas.

**Introduction:** Studies have found positive identification of martian paleolakes via observations of strandlines [1], crater floor polygons too large to be formed by only thermal processes [2], and polyhydrated sulfate and salt signatures on the floor and inner walls of craters, specifically Columbus crater (29.8°S, 166.1°W) [3]. We have previously modeled surface and subsurface martian temperatures along with simulating sublimation processes and have validated our model results against lander and experimental data [4, 5]. Here we study the freezing process on a martian paleolake, specifically observing the freezing point depression caused by increasing lake salinity as water is removed from the system. We are particularly interested in the scenario where the solution freezing point is much lower than the average surface temperature at which point a residue brine may be formed. This remaining saline lake is of astrobiological interest and may help to explain observations of features that may have been produced by evaporative processes.

**Methods:** We modeled a 1 m<sup>2</sup> column in the lake that is not in direct contact with any of the crater walls; thus, we can assume an adiabatic boundary between the column and identical columns around it. For simplicity, we assume the lake is vertically well mixed. It has been suggested that if the initial temperature of the emplaced fluid is warm enough, ice-cap synthesis can be avoided for ~3-8 years [6]. However, we begin our analysis once the ice cap has reached a thickness that is beyond the skin depth such that the local temperature is the average surface temperature with minor fluctuations. This assumption allows for a semi-analytical interpretation of the freezing process.

**Freezing Model:** The freezing process is modeled as an energy conservation process whereby geothermal heat and heat of fusion is lost via conduction through the ice such that:

$$k \frac{dT}{dz} = q + \rho \Delta H_{fus} \frac{dz}{dt} \quad (1)$$

where  $k$  and  $\rho$  are the thermal conductivity and density of ice,  $T$  is temperature,  $z$  is the instantaneous ice thickness,  $\Delta H_{fus}$  is the enthalpy of fusion, and  $q$  is geothermal heat flux (30 mW/m<sup>2</sup> [7]). Since we assume ice cap thickness beyond the skin depth, the temperature gradient can be considered between the liquid

freezing point temperature ( $T_f$ ) and the average surface temperature, considered here to be 220 K. Solving for ice thickness ( $z$ ) we attain a function that can be solved via recursive means:

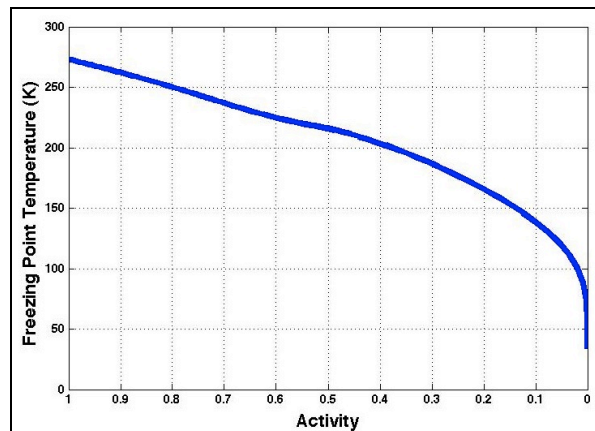
$$z_{i+1} = z_i + \left[ \frac{\Delta t}{\varepsilon} \left( \frac{k \Delta T}{z_i} - q \right) \right] - s \quad (2)$$

where  $\Delta t$  is taken as a small time step,  $\varepsilon$  is the volumetric heat of fusion ( $\rho \Delta H_{fus}$ ) and  $s$  is the amount of ice sublimated from the top [5].

**Freezing Point Depression:** As the system freezes, water mass is taken from the solution such that over time the salinity increases thus changing the activity of water ( $a_{H_2O}$ ) and freezing point temperature. By the Pitzer model, the activity of water can be determined as a function of concentration. In turn, freezing point temperature can be provided as a function of activity. We use the equation set by Chevrier and Altheide [8] to describe freezing point depression with increasing salinity:

$$T_f = \left( \frac{1}{T_0} - \frac{R \ln a_{H_2O}}{\Delta H_{fus}} \right)^{-1} \quad (3)$$

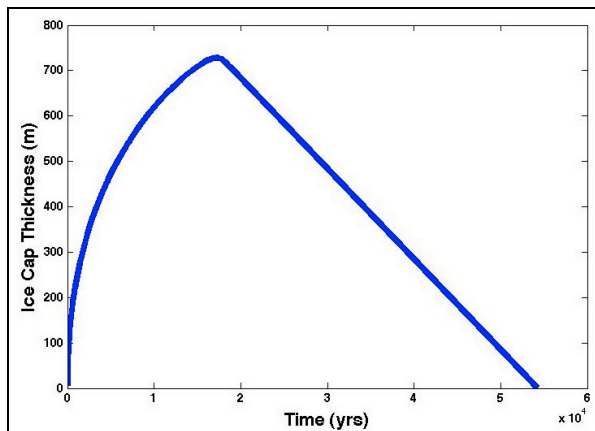
where  $T_0$  is the freezing temperature of pure water, and  $R$  is the ideal gas constant. In this case, the enthalpy of fusion is temperature dependent and the activity of water is concentration dependent. This model has been validated by experiments for ferric sulfate [8], (Fig 1).



**Fig. 1:** Freezing point temperature as a function of solution activity for ferric sulfate as predicted by [8].

**Results:** Figure 1 demonstrates the expected decrease in the freezing point temperature as the activity of the solution decreases with increasing salt concentration content. In the case of ferric sulfate, at a concentration of  $\sim 0.33$ , the water has an activity of  $\sim 0.55$ , and the solution's freezing point has been depressed to  $\sim 220$  K. At this point, the solid-liquid temperature gradient is essentially zero and thus the freezing process halts.

Figure 2 demonstrates our modeled ice cap growth results. For the following result, we assume an initial molar salt concentration of 0.01 and a sublimation rate of 0.02 m/martian year, as was found in our earlier results concerning water-ice sublimation at the Columbus crater site [5]. There exists two processes that govern ice cap growth: freezing and sublimation. Although the sublimation rate is of minor consequence when the freezing point is much higher than the local temperature, it becomes the active process when freezing is hindered due to the decrease in the activity of the solution.



**Fig. 2:** Ice cap thickness over time as simulated by our equation set, which incorporates freezing point depression as water is removed from the system.

**Discussion:** Our preliminary results concerning a martian paleolake whose initial salt concentration (ferric sulfate) is 0.01 show that at about  $\sim 700$  m of ice cap growth the salt concentration has increased sufficiently so as to depress freezing and allow sublimation to be the primary process. Thus, if a lake were initially deeper than  $\sim 700$  m, there would indeed exist a brine residue. This may help in explaining some formations most probably produced by an evaporative process. As has been shown by [2], there is evidence for crater floor polygons too large to be formed by only thermal processes. If, however, a liquid was present and evaporating, formation of these features would be facilitated.

Model results suggest that if a paleolake existed whose liquid content indeed had an initial salinity, a briny solution could remain for several years while sublimation of the ice cap occurs. Afterwards, the remaining solution would evaporate at a slower rate than pure water, prolonging the existence of liquid water on the martian surface [9, 10]. For our specific study, the brine residue would avoid evaporation for  $\sim 3.6$  ka. The availability of a liquid for such a long time, and its activity, has significant biological implications.

**Conclusions:** By observing the freezing point temperature depression associated with the expected increase in solution salinity as a paleolake freezes, we have found that a brine residue will exist if the initial lake depth is  $> \sim 700$  m and the initial molar salt concentration is at least 0.01. Higher initial salt concentrations would only serve to hasten the production of the brine residue, thereby decrease the amount of ice formed and increase its longevity.

We have made several simplifications in our current model. For example, we assumed an ice cap had already formed whose thickness was greater than the skin depth such that temperature fluctuations would be minimal. Once ice cap thickness has decreased beyond this point due to sublimation, surface temperatures variations become relevant. Future analysis will incorporate the complete processes in order to study how long the brine residue may be present at any given location, and we also will expand this study to examine the effects of various salts.

**References:** [1] Di Achille, G. *et al.* (2009) *GRL*, 36, L14201. [2] El Maarry, M. R. *et al.* (2009) *Workshop on Modeling Martian Hydrous Environments*, Abstract #4021. [3] Wray, J. J. *et al.* (2010) *JGR*, in press. [4] Rivera-Valentin, E. G. *et al.* (2009) *Workshop on Modeling Martian Hydrous Environments*, Abstract #1482. [5] Rivera-Valentin, E. G. *et al.* (2010) *LPS XLI*, Abstract #1446. [6] Kreslavasky, M. A. and J. W. Head (2002) *JGR*, 107. [7] Urquhart, M. (2005) *LPS XXXVI*, Abstract # 2337. [8] Chevrier, V. F. and T. S. Altheide (2008) *GRL*, 35, L22101. [9] Chevrier, V. F. *et al.* (2009) *GRL*, 36, L10202. [10] Hanely, J. *et al.* (2010) *LPS XLI*, Abstract #1971.