

SEASONAL BRINE FORMATION IN SHALLOW SUBSURFACE ON MARS. *M. A Kreslavsky*¹, ¹Earth and Planetary Sciences, University of California – Santa Cruz, Santa Cruz, CA, 95064, USA, mkreslav@ucsc.edu.

Introduction: “Shallow subsurface” refers here to martian regolith layers below the diurnal thermal skin, which is a few centimeters thick, down to several meters, including the seasonal thermal skin, which is on an order of a meter thick. In the shallow subsurface, temperature never exceeds 273 K, and the only thermodynamically allowed state of pure H₂O is ice. It has been understood long ago [1] that the actual presence of ground ice in the shallow subsurface is controlled by H₂O vapor exchange with the atmosphere. Ice stability against vapor exchange is defined by two climate factors: the temperature regime in the shallow subsurface and the ambient air humidity regime. Calculations [e.g., 2, 3] has shown that shallow subsurface ice is stable below some level at high latitudes, and not stable at any depth at low latitudes, and observations [e.g., 4, 5] has confirmed this prediction.

Dissolved salts decrease the freezing point of water. Concentrated aqueous solutions (“brines”) are thermodynamically allowed under much wide range of conditions than pure water. Perchlorate salts discovered to be abundant on Mars [e.g., 6, 7] effectively depress brine freezing point. The potential roles of brines on Mars have been discussed in numerous publications.

In a number of recent papers [e.g., 8, 9] it was shown that the instant temperature and air humidity in some places on Mars in the evening may result in deliquescence (= formation of brines from crystalline salts and H₂O vapor) of perchlorates or chlorides. This would occur at the surface, where salt grains are in immediate contact with atmosphere. Such deliquescence can only produce tiny amounts of brines limited by availability of water vapor in the atmospheric boundary layer.

Here I theoretically explore different phenomena, deliquescence and efflorescence (process opposite to deliquescence) in the shallow subsurface, where the presence of brines is controlled by diffusive vapor exchange with the atmosphere. This theoretical treatment is analogous to the theory of ground ice stability [1-3, 10]. In contrast to ice, brines can only exist, when the temperature T exceeds the eutectic temperature (that depends on salt composition), which, in a sense, makes the range of brine stability narrower in comparison to ice. On the other hand, saturated vapor pressure of brine $P_{sat,brine}(T)$ is lower than that of ice $P_{sat,ice}(T)$ at the same temperature; this potentially enables brine stability in places, where ice is not stable.

Calcium perchlorate $\text{Ca}(\text{ClO}_4)_2$ has the lowest eutectic temperature of 199 K among all salts that would be reasonably expected on Mars. I performed all calculations for this salt.

Methods: I retrieved the saturated vapor pressure $P_{sat,brine}(T)$ as a function of temperature T for the saturated $\text{Ca}(\text{ClO}_4)_2$ brine using FREZCHEM code [11].

I used Mars Climate Database (MCD) (version 5.3, <http://www-mars.lmd.jussieu.fr>) [12] as a source of information on martian climate system. I used the “Climatology” dust scenario as the best proxy for typical conditions. I extracted pressure and H₂O vapor mixing ratio near the surface and thus obtained partial pressure of H₂O vapor P_v ; I also extracted surface temperature T_s . The MCD data result from climate modeling, however, the model parameters were specially tuned to best fit all available observational data, and MCD is the best currently available climatic data source in the absence of direct observational data. I adopted day-average T_s as a proxy of seasonal temperature just below the diurnal thermal skin and calculated the temperature field $T(z, t)$ as a function of depth z and a periodic function of time (season) t by solving linear heat diffusion equation semi-analytically. For linear heat diffusion, the thermophysical properties of material affect only the vertical scale of temperature field, therefore my results are independent on the material; z is normalized by seasonal thermal skin depth (on the order of a meter).

As shown in [10], ice (or brine) is stable at a depth z against diffusive vapor exchange with the atmosphere, if the year average saturated vapor pressure is less than year-average partial vapor pressure, $\langle P_{sat}(T(z, t)) \rangle_t < \langle P_v \rangle_t$. I use this criterion for perennial stability of ice and brines. I also consider “seasonal stability” against vapor diffusion by comparison seasonal day-average quantities: $P_{sat}(T(z, t)) < P_v$. In addition, I consider diffusive vapor exchange between brines and the perennial ice table at depth z_i with brine stability criterion $P_{sat,brine}(T(z, t)) < P_{sat,ice}(T(z_i, t))$.

Results. A narrow discontinuous zone of perennially stable subsurface brine occurs at ~52°N (Fig. 1), at the southern edge of the ice stability zone (Fig. 2). The stability criteria are only marginally met, and given all uncertainties it remains unknown, whether brine actually stable or not. However, brine is stable seasonally in a wide N high-latitude area, and this prediction is robust. In the S, seasonal stability is patchy, and conditions are closer to the stability margin. Fig. 3 shows brine formation as a function of normalized depth (vertical axis) and season (horizontal axis). In the spring (left part of Fig. 3) subsurface temperature increases above 199 K, however, brine is not stable against vapor diffusion: the atmosphere is too dry. With season progression, the atmospheric humidity increases, becomes sufficiently high, and brine becomes stable (yellow in Fig. 3). Diffusion delivers water vapor from the atmosphere to this zone, and deliquescence occurs. In this way, if calcium perchlorate is actually present in the soil, at least some amount of brine inevitably forms. With further season progression the 199 K isotherm descends deeper, and the

brine stability zone follows it. Its thickness increases, however, its upper boundary also descends, because temperature there becomes too high. By the end of the summer atmospheric humidity drops, and brine becomes unstable again. It does not disappear immediately: the efflorescence occurs gradually; its rate is defined by diffusive vapor transport; some brine still occurs to the right of stability zone in Fig. 3, however, eventually all brine would be converted into salt and vapor, which would be diffusively transported to the atmosphere.

If there is perennially stable ice (Fig. 4), there are depths and seasons, where brines are stable against vapor exchange with the perennial ice (orange in Fig. 4). Fig. 2 (orange shades) maps regions where such brines may occur. There is a thin layer (red in Fig. 4), where brines are stable against vapor exchange with both atmosphere and the ice table. During a few months per year salts at this depth would effectively suck moisture from both the atmosphere and the ground ice. If there is some $\text{Ca}(\text{ClO}_4)_2$ in the ice-filled regolith below the ice table, it would form brines as soon as T exceeds 199 K (pink in Fig. 4).

These thermodynamic calculations only indicate that deliquescence occurs. The amount of actually formed brines is limited by (1) availability of $\text{Ca}(\text{ClO}_4)_2$, (2) rate of diffusive vapor transport in the pore space, and (3) deliquescence kinetics controlled by microphysics, although laboratory experiments [13] shows that deliquescence is fast and the latter factor is not limiting. In and near existing ground ice (red and pink in Fig. 4) diffusion is not limiting H_2O transport, and all available $\text{Ca}(\text{ClO}_4)_2$ goes to brine. The mean Cl abundance in the shallow subsurface is known [14]; if all Cl is in $\text{Ca}(\text{ClO}_4)_2$ and evenly distributed, the amount of brine would be comparable to the regolith pore volume. The former assumption does not seem realistic, however, local concentration of $\text{Ca}(\text{ClO}_4)_2$ is possible, and filling pore space with brine locally is not excluded.

Implications: The seasonal formation of brines has profound implications for a range of processes in the shallow subsurface. Although highly concentrated brines are not as chemically reactive as diluted brines, they still may affect chemistry and certainly affect microphysics of the shallow subsurface layer. The most interesting and rich phenomena would occur if the amount of formed brine is sufficient for brine segregation and percolation. This would concentrate salts at the ice table, which in turn would favor seasonal formation of much liquid locally, with possible further implications for formation of polygonal patterns etc. For example, active polygon-forming processes involving brines might explain extremely young (~ 1 ka) crater retention age of northern polygonal patterns.

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