

STABILITY DIAGRAM OF AQUEOUS CHLORATE SOLUTIONS UNDER MARTIAN RELEVANT TEMPERATURES AND RELATIVE HUMIDITIES.

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Introduction: Oxy-chlorine salts, mainly chlorates and perchlorates, are proposed to constitute an important fraction of the Martian regolith [1, 2]. Their highly hygroscopic nature [3-5] and the ability to depress the freezing point of water [2, 6] make oxy-chlorine salts a possible repository for liquid brines to be sporadically stable at the Martian surface despite the prevailing cold and dry conditions. Evidence proving the flowing brines across the Martian surface includes the seasonal recurring slope lineae (RSL) [7] and the spheroids on the leg of Phoenix lander [8]. The Curiosity Rover also measured that the changes in the hydration state of perchlorate salts within the subsurface are consistent with an active atmosphere-soil water exchange [9]. To better understand the water cycle on Mars, it is important to figure out the stability field of aqueous oxy-chlorine salt brines against temperature (T) and relative humidity (RH). The stability of aqueous solution is mainly controlled by its water activity (a_w), which is defined as the partial vapor pressure of water in a solution relative to the standard state partial vapor pressure of pure water. The water activity of a saturated salt solution is equal to the deliquescence relative humidity (DRH) of the dry salt [4, 5]. A plenty of experimental and modeling studies have investigated the deliquescence of perchlorate under Martian relevant conditions [3-5]. However, little work has been done on chlorates, especially at subzero temperature. Therefore, in our study, we constructed the T-RH phase diagram of $\text{NaClO}_3/\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_3)_2/\text{H}_2\text{O}$ binary system at supercooling temperature range based on their water activity (a_w), while their a_w data were derived from the measured heat capacity data of solutions at varying molalities and temperatures.

Methods:

Sample preparation. Aqueous solutions at various molalities (from ~1m to saturated) were prepared by dissolving NaClO_3 or $\text{Mg}(\text{ClO}_3)_2$ salt into deionized water, respectively. While solid NaClO_3 salt was directly purchased from Sigma-Aldrich[®], solid $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ was synthesized by slowly mixing aqueous $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and MgSO_4 solution under constant stirring. After centrifuging the mixture to get rid of the BaSO_4 precipitation, we evaporated the remaining supernatant under vacuum at room

temperature for ~3 days to grow the crystalline $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Measurement of Heat Capacity. The specific heat capacity C_{sp} ($\text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$) of chlorate solution was quantitatively measured by a differential scanning calorimeter, Netzsch DSC 200 F3 Mafia[®]. The DSC basically tracks the heat flux (HF) across the sample against that of a reference during a dynamic thermal cycle, while the heat flux is proportional to C_{sp} . Liquid sample at each molality was sealed in an aluminum crucible, and cooled from 298.15K to 173.15K at a constant cooling rate of $10\text{K} \cdot \text{min}^{-1}$ using a liquid nitrogen cooling system. Then a standard run using Al_2O_3 powder with known C_{sp} were conducted under the same thermal cycle to calculate the unknown C_{sp} of samples at various molalities and temperature.

Calculation of water activity. From the measured C_{sp} data, we derived the a_w of each chlorate solution sample as a function of temperature and molality according to the thermodynamic relations given by Toner and Catling (2015) [10] as followed:

$$R \ln a_w = R \ln a_{w,298.15K} + \bar{L}_{1,298.15K} \left(\frac{1}{T} - \frac{1}{298.15} \right) - \int_{298.15}^T \left(\frac{1}{T^2} \int_{298.15}^T (\bar{C}_{p,1} - C_{p,1}^0) dT \right) dT$$

While $\bar{C}_{p,1}$ is derived from our measurements, all the other quantities were taken from the published results [5, 11-13].

Results and conclusion: As mentioned above, the a_w of the saturated solution is equal to the DRH of a salt. Thus, the calculated a_w in this study was applied to build stability diagrams of chlorate salts as a function of temperature and relative humidity (RH) as Fig 1 shows. The red curve indicates the calculated values of DRH of each salt varying with temperatures. When the atmospheric RH > DRH, the crystalline salts start to take up humid and gradually deliquesce into aqueous brines; once RH < DRH, liquid brines recrystallize back to solid phase. For NaClO_3 , the DRH is relatively high, increasing from 73% to 80% with decreasing temperature. In comparison, $\text{Mg}(\text{ClO}_3)_2$ is more deliquescent, with DRH climbing up from 20% at room temperature to 41% at ~200K before hitting the ice line. To trace the deliquescence and

efflorescence behavior of both chlorate salts during a sol on Mars, we overlapped a diurnal cycle of T and RH at a depth of ~3cm below the subsurface of the Phoenix landing site from Nuding et al. (2014) [3] as the green line presents on the diagram. While Na-chlorate never had a chance to deliquesce (Fig 1, upper), Mg-chlorate was found to form a stable aqueous phase early in the morning at 10:00 and persist for a few hours before efflorescence into a crystalline hydrate (Fig 1, lower). Then at 21:00 it deliquesced again and lasted for a few hours until ice was formed. There's a large time window, at least 4 hours, for aqueous phases to exist per day. Given the extreme low eutectic temperature of $Mg(ClO_3)_2$ (at ~204K [2]) and its low DRH values (20% ~ 41% in this study), it serves as a potential candidate to periodically form liquid water on the Martian surface, thus may play an important role in the water cycle on Mars.

428. [4] Gough R. V. et al. (2011) *EPSL* 312, 371-377. [5] Toner J. D. and Catling D. C. (2018) *EPSL* 497, 161-168. [6] Toner J. D. et al. (2015) *GCA* 166, 327-343. [7] Ojha L. et al. (2015) *Nature Geoscience* 8.11, 829-832. [8] Rennó, N. O. et al (2009) *JGR: Planets* 114.E1. [9] Martín-Torres F. J. et al. (2015) *Nature Geoscience* 8.5, 357-361. [10] Toner J. D. and Catling D. C. (2016) *GCA* 181, 164-174. [11] Murphy D. M. and Koop T. (2005) *Q J R Meteorol Soc Q J ROY METEOR SOC* 131.608, 1539-1565. [12] Campbell A. N., and Bhatnagar O. (1971) *Can. J. Chem.* 49.2, 217-224. [13] Simoes M. C. et al. (2017) *J. Chem. Eng. Data J CHEM ENG DATA* 62.7, 2000-2013.

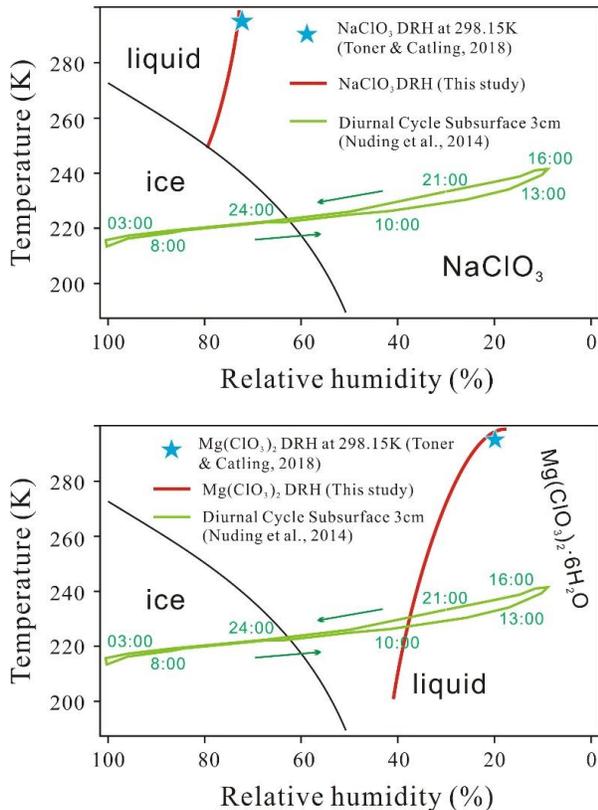


Fig 1. Stability field of $NaClO_3$ (aq) (upper) and $Mg(ClO_3)_2$ (aq) (lower) compared with Martian diurnal cycle of temperature and relative humidity. The Martian diurnal cycle was taken from Nuding et al. (2014)

References: [1] Hecht M. H. et al. (2009) *Science*, 325, 64-67. [2] Hanley J. et al. (2012) *GRL* 39, 8. [3] Nuding D. L. et al. (2014) *Icarus* 243, 420-