

DISTRIBUTION, DETECTION, AND IMPLICATIONS OF CHLORINE SALTS ON MARS. J. Hanley^{1,2}, V. F. Chevrier², M. Mellon¹, ¹Southwest Research Institute, 1050 Walnut Street #300, Boulder, CO, ²Arkansas Center for Space and Planetary Sciences, MUSE 202, University of Arkansas, Fayetteville, AR 72701; jhanley@uark.edu.

Introduction: Chlorine has been ubiquitously detected on Mars, making its salts more important in understanding both the past and present stability of water. Chlorides (Cl⁻) have been found at every landing site [1-5], and perchlorates (ClO₄⁻) have been detected by Phoenix in the north polar plains [2], and potentially by MSL at Gale Crater [6]. Reanalysis of Viking data suggests perchlorates could have been present there as well [7]. Chlorates (ClO₃⁻), which are almost as stable as perchlorates [8], are found on Earth everywhere that perchlorates exist [9], making them likely to be present on Mars too [10]. Other oxidized chlorine salts, such as hypochlorites (ClO⁻) and chlorites (ClO₂⁻), may be present in limited quantities as precursors to the formation of perchlorate [8, 11].

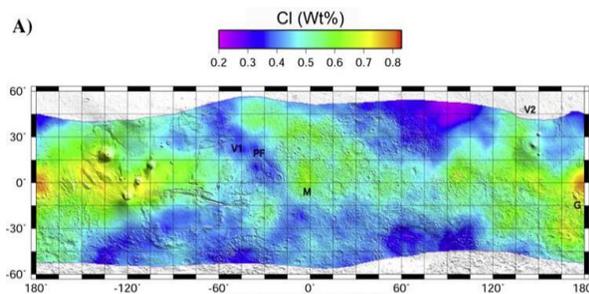


Figure 1. Distribution of equatorial and mid-latitude chlorine on Mars as detected by the Mars Odyssey GRS [12].

Distribution: Chlorine is distributed globally on Mars (Fig. 1), as detected by the Mars Odyssey Gamma Ray Spectrometer (GRS) [12]. It is important to note, however, that this distribution is heterogeneous. From this it is unclear in what form the chlorine is present, but upper limits place the concentration at 1 wt% of the regolith. This is similar to values measured by various missions (Tab. 1). It is unknown what the vertical distribution is throughout the regolith, which is important in understanding the subsurface stability of water.

Table 1. Average measured concentrations (wt%) of chlorine at landing sites [1-5]. Note Phoenix was the only lander to directly measure chloride and perchlorate concentrations.

	Chlorine	Chloride	Perchlorate
Phoenix	-	0.04	0.6
Spirit	0.2-1.94	-	-
Opportunity	0.33-0.68	-	-
Pathfinder	0.37-0.57	-	-
Viking 1	0.8 ± 0.3	-	-
Viking 2	0.6 ± 0.3	-	-

Detection: Anhydrous chloride salts are notoriously difficult to detect through remote sensing due to their lack of spectral features in the near-infrared (NIR). Deposits of chlorides have been seen in Terra Sirenum [13, 14], found *because of* their lack of spectral features. It is important to note, though, that there exist many stable hydrates of chlorine salts that could be detected by their hydration features, just as sulfates have been found. In fact, the dominant feature of all hydrated minerals in the NIR is that of water; therefore, many hydrated salts may be difficult to distinguish from one another in mixed terrain (Fig. 2). We have collected spectra for many of the chlorine salts that are likely to be on Mars [15]; however, many hydrates are difficult to synthesize and much work is needed to complete the spectral library.

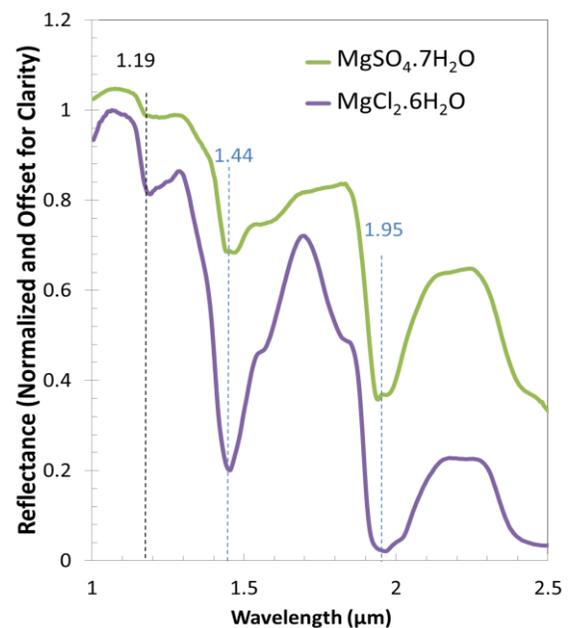


Figure 2. Comparison of epsomite (MgSO₄·7H₂O) and bischofite (MgCl₂·6H₂O) [15].

Stability of Water: Past Stability of Water. It appears that chlorine salts are globally distributed, yet with distinct heterogeneous structures. There are two separate questions that need to be answered: **1)** The formation of the chloride salts. These could be from volcanic, aeolian, aqueous or hydrothermal processes. **2)** The formation of the oxidized chlorine species. These could form through atmospheric oxidation processes [11], which could then support a global distribution of perchlorates and chlorates, or they can

be formed by photochemical reactions of aqueous chloride solutions under UV radiation [8]. In either case, determining the global distribution of the various chlorine salts would provide a greater understanding of their formation processes, which in turn will shed some light on the past conditions of Mars.

Current Stability of Water and Habitability: Perchlorate and chlorate salts can suppress the freezing temperature of water down to 204 K [10, 16]. In order to form gullies or lakes at present day Mars temperatures, much more salt is needed than is reported from remote observations or bulk analysis on the ground (generally around 1 wt%). Given the amount of chlorine salts detected, there would only be small amounts of actual liquid formation at the eutectic temperature. For example, for an eutectic $\text{Mg}(\text{ClO}_4)_2$ solution, 44 wt% is needed (Fig. 3A): from a 1 kg sample at the Phoenix landing site, and 0.6 wt% perchlorate [2], we can assume a maximum of 3 g $\text{Mg}(\text{ClO}_4)_2$, meaning only ~ 7 g liquid solution over 1 kg regolith. This is not enough for running water, but it may be enough to alter the landscape and geochemical makeup of the regolith through freeze-thaw cycles.

Another important consideration is that humidity plays a significant role in the stability of these salts, in both their liquid and solid phases (Fig. 3B). Humidity is directly related to the activity of water ($a_{\text{H}_2\text{O}}$) of these solutions. In order to achieve freezing temperatures down to ~ 204 K, the water must be at $a_{\text{H}_2\text{O}} = 0.5$ (e.g. Fig. 3B). Even chlorine salts in mixtures will lower the activity of water enough to achieve liquid at present day conditions, and almost certainly in the past, as evidenced by possible paleolakes [17]. Unfortunately, life as we know it does not thrive at low water activity. There are certain organisms that can survive down to $a_{\text{H}_2\text{O}} = 0.61$ [18], and other halophiles that tolerate saline conditions [19], but they are limited by conditions such as radiation and temperature.

Implications for Soil Mechanics: Chlorine salts may also play a role in the mechanical properties of the regolith, as well as the stability of subsurface water. High soil cohesion was encountered at the Phoenix landing site making sample analysis challenging; these soils were also reported to contain perchlorates [2]. Such cohesion may result from hydrated salts and eutectic brines bonding grains together at their contacts by wetting, or from dehydrated salts crystallizing at grain contacts. Changes in hydration state with time (such as diurnally or seasonally) may then result in correlated changes in cohesive properties with time.

Conclusions: Chlorine salts (chlorides, perchlorates and chlorates) are an important aspect of understanding the stability of water on Mars, as well as the potential habitability. Locating and identifying the types of chlorine salts present would help pin down

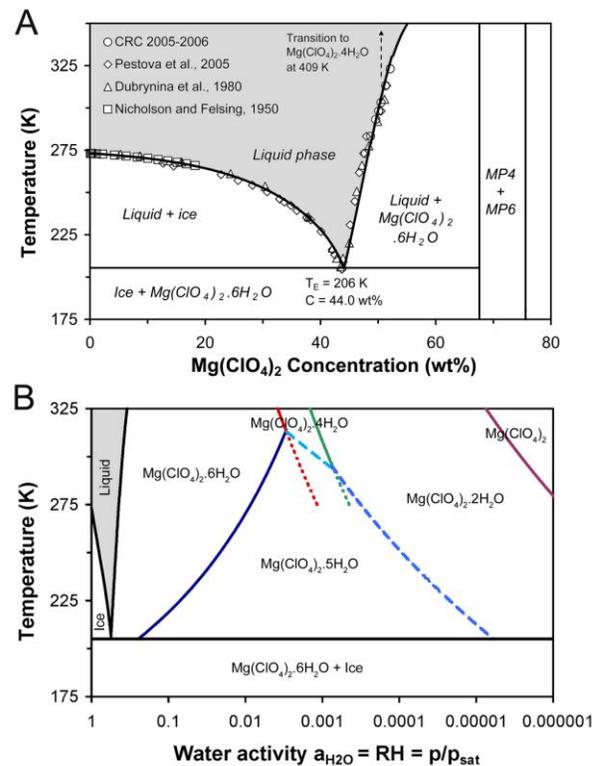


Figure 3. Stability diagram for $\text{Mg}(\text{ClO}_4)_2$ and water as a function of A) $\text{Mg}(\text{ClO}_4)_2$ wt% and B) activity of water [16].

both the current and past conditions; however, distinguishing hydrated chlorine salts from other hydrated minerals through remote sensing, especially when in a mixture, may prove difficult. The amount of chlorine salt we have detected so far does not support large amounts of liquid water. Salt mixtures, though, can lower the freezing temperature enough to support even lakes [17]. Life does not need much to survive, as we know, perhaps existing on just a few salty droplets every so often.

References: [1] Clark B. C. et al. (1976) *Science*, 194, 1283-1288. [2] Hecht M. H. et al. (2009) *Science*, 325, 64-67. [3] Schmidt M. E. et al. (2008) *JGR*, 113. [4] Wänke H. et al. (2001) *Space Science Reviews*, 96, 317-330. [5] Rieder R. et al. (2004) *Science*, 306, 1746-1749. [6] Blake D. F. et al. (2012) *2012 Fall Meeting, AGU, San Francisco, Calif., 3-7 Dec., #U13A-03*. [7] Navarro-González R. et al. (2010) *JGR*, 115, E12010. [8] Kang N. et al. (2006) *ACA*, 567, 48-56. [9] Rao B. et al. (2010) *Environ. Sci. Tech.*, 44, 8429-8434. [10] Hanley J. et al. (2012) *GRL*, 39, L08201. [11] Catling D. C. et al. (2010) *JGR*, 115, E00E11. [12] Keller J. M. et al. (2006) *JGR*, 111, E03S08. [13] Glotch T. D. et al. (2010) *GRL*, 37, L16202. [14] Osterloo M. M. et al. (2008) *Science*, 319, 1651-1654. [15] Hanley J. et al. (2013) *in prep.* [16] Chevrier V. F. et al. (2009) *GRL*, 36, L10202. [17] Rivera-Valentin E. G. et al. (2013) *JGR*, under review. [18] Grant W. D. (2004) *Phil. Trans. Roy. Soc. London*, 359, 1249-1267. [19] Davila A. F. et al. (2008) *JGR*, 113, G01028.