MODELING AQUEOUS PERCHLORATE CHEMISTRIES WITH APPLICATIONS TO MARS.

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Introduction: Among the most interesting findings of the Phoenix Mission to Mars was the presence of a perchlorate salt, probably magnesium, in the North Polar region [1-4]. Naturally occurring perchlorate salts are rare on Earth; so rare that no perchlorate salt has yet been given an official "mineral" name [5] despite its known occurrence as a salt in the Atacama Desert in Chile [5-6]. The high solubility of most perchlorates would lead to significantly low eutectic temperatures {e.g., -68.6°C [$Mg(ClO_4)_2 \bullet 8H_2O$] and -74.6°C [$Ca(ClO_4)_2 \bullet 6H_2O$]} [7] that may play an important role in cold geochemical processes on Mars. The objectives of this paper were to (1) describe integrating perchlorate chemistries into the FREZCHEM model, and (2) discuss the significance of these salts to Martian biogeochemistry.

FREZCHEM Model: FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions (to ionic strengths > 20 molality) using the Pitzer approach [8-9] for the temperature range from <–70 to 25°C and the pressure range from 1 to 1000 bars [10]. The current version of the model is parameterized for the Na-K-Mg-Ca-Fe(II)-Fe(III)-Al-H-Cl-Br-SO_4-NO_3-OH-HCO_3-CO_3-CO_2-O_2-CH_4-Si-H_2O system and includes 95 solid phases including ice, chloride minerals, sulfate minerals, carbonate minerals, solid-phase acids, nitrate minerals, acid-salts, iron oxides and hydroxides, aluminum hydroxides, silicon minerals, gas hydrates, and bromide sinks. What is currently lacking in this model for Mars applications are perchlorate salts.

Perchlorate Chemistry: Pitzer parameters and solubility products for $NaClO_4 \bullet H_2O$, $KClO_4$, $HClO_4$, $Ca(ClO_4)_2 \bullet 6H_2O$ (Fig. 1), and $Mg(ClO_4)_2 \bullet 6H_2O$ and $\bullet 8H_2O$ (Fig. 2) were integrated into the FREZCHEM model from 25°C to their respective eutectic temperatures, which for the above salts are -32°C, -0.18°C, -60°C, -74.6°C(Fig.1), and -68.6°C(Fig. 2), respectively. $KClO_4$ is an anomaly for perchlorate salts because of its low solubility, and as a consequence, high eutectic temperature (-0.18°C).

The degree of hydration for $Mg(ClO_4)_2 \bullet nH_2O$ is an important question for Mars because it would tie up water to different degrees in the soil. The "old data" for salts in Fig. 2 [11,12] designated the hydration number as 6, while the "new data" from Pestova et al. [7] designated the hydration number as 8. If we treat these two datasets as independent and estimate and integrate solubility products for both $Mg(ClO_4)_2 \bullet 6H_2O$ and $Mg(ClO_4)_2 \bullet 8H_2O$ into the FREZCHEM model, then the model calculated peritectic (transition between $\bullet 8H_2O$ and $\bullet 6H_2O$) occurs at 33°C, which is in excellent agreement with an earlier estimate of 32°C [13]. It appears that $\bullet 8H_2O$ is likely to be the dominant $Mg(ClO_4)_2$ hydrate for cold aqueous processes on Mars.

Mars Applications: The newly perchlorate-parameterized FREZCHEM model will allow us to simulate natural environments on Mars where perchlorate salts are forming along with associated alkaline carbonates. But these simulations will ultimately require detailed analysis of released Phoenix Mission reduced datasets that are still in process. But meanwhile, we can still address broad questions related to perchlorate salts on Mars.

What are the forms of the perchlorate salts that are forming on Mars? Most indirect evidence to date suggest $Mg(ClO_4)_2$ because of substantial amounts of magnesium and perchlorate found by the Phoenix Mission [1,3-4]. These soils also have pH values in the 8-9 pH range suggesting $CaCO_3$ precipitates [2-3]. Because of the relative insolubility of $CaCO_3$ and $CaSO_4$ minerals that are likely present at the Phoenix Mission site, it seems unlikely that perchlorates have precipitated as the highly soluble $Ca(ClO_4)_2$ salt. However, on Earth, it is precisely in cold polar regions that the similar $CaCl_2 \bullet 6H_2O$ (antarcticite) mineral naturally forms [14-16]. Therefore, $Ca(ClO_4)_2 \bullet 6H_2O$ could possibly form on a cold planet such as Mars. On the other hand, the insolubility of $KClO_4$ argues in favor of this salt as a possible sink for perchlorate in solutions that dry out. In support of this argument are the observations that perchlorates are often found associated with K-rich materials such as potash (K_2CO_3), playa crusts, and plant materials [5-6].

On Earth in arid environments, perchlorates are often found associated with nitrate salts where these nitrates, such as those in the Atacama, are deposited from atmospheric sources [17]. This analog suggests that perchlorate may be a useful tracer of atmospheric processes. But solution chemistry will be necessary to understand any subsequent aqueous or thermodynamic transformation of the perchlorate. Given that perchlorate is a useful metabolite for certain microbes while it also is a contaminant for drinking water [18], modeling its behavior is important for future Mars missions both to look for life and safely explore Mars with humans.

The bottom line is that the latest version of FREZCHEM, which now contains perchlorate chemistries, provides a means to address these biogeochemical issues..

Acknowledgments: We thank Lisa Wable for help preparing this abstract. Funding was provided by a

NASA DDF project on "Volcanic SO_2, atmospheric photochemistry, and climate on early Mars."

References: [1] Fisher D.A. et al. (2008) *AGU Fall Meet.*, Abstract U11B-0019. [2] Hecht M.H. et al. (2008) *AGU Fall Meet.,* Abstract U14A-04. [3] Smith P.H. et al. (2008) *AGU Fall Meet.*, Abstract P13F-01. [4] Stoker C. et al. (2008) *AGU Fall Meet.* Abstract U11B-0018. [5] Orris G.J. et al. (2003) USGS Open-File Report 03-314. [6] Trumpolt C.W. et al. (2005) *Remediation*, 16, 65-89. [7]Pestova O.N. et al. (2005) *Russ. J. Appl. Chem.* 78, 409-413. [8] Pitzer K.S. (1991) *Activity Coefficients in Electrolyte Solutions,* CRC Press. [9] Pitzer K.S. (1995) *Thermodynamics,* McGraw-Hill. [10] Marion G.M. and Kargel J.S. (2008) *Cold Aqueous Planetary Geochemistry with FREZCHEM*, Springer. [11] Nicholson D.E. and Felsing W.A. (1950) *J. Am. Chem. Soc.* 72, 4469-4471. [12] Linke W.F. (1965) *Inorganic and Metal Organic Compounds, Vol II,* Am. Chem. Soc. [13] Besley L.M. and Bottomley G.A. (1969) *J. Chem. Thermodynamics,* 1, 13-19. [14] Herut B. et al. (1990) *Geochim. Cosmochim. Acta,* 54, 13-21. [15] Marion G.M. (1997) *Antarctic Sci.* 9, 92-99. [16] Starinsky A. and Katz A. (2003) *Geochim. Cosmochim. Acta*, 67, 1475-1484. [17] Michalski G. et al. (2004) *Geochim. Cosmochim. Acta* 68, 4023-4038. [18] Coates J.D. and Achenbach L.A. (2004) *Nature Reviews/Microbiology* 2, 569-580.

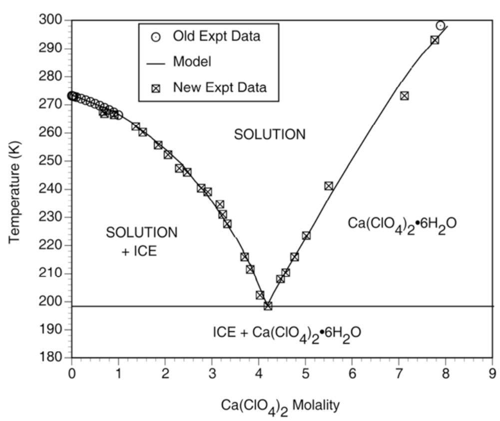

Figure 1. Equilibria for $Ca(ClO_4)_2$ solutions from 25°C to the eutectic. "Old experimental data" are from [11,12], "new experimental data" are from [7].

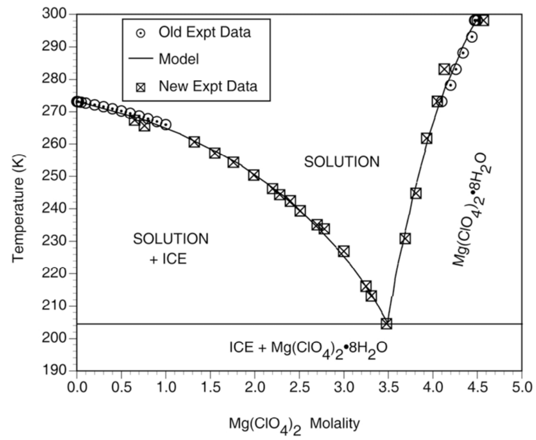

Figure 2. Equilibria for $Mg(ClO_4)_2$ solutions from 25°C to the eutectic. "Old experimental data" are from [11,12], "new experimental data" are from [7].