THERMODYNAMIC CONSTRAINTS ON LIMITED-WATER INDUCED FRACTIONATION OF MAGNESIUM -PERCHLORATE AND -CHLORIDE: IMPLICATIONS FOR HIGH CLO4-/CL- RATIOS IN MARTIAN POLAR REGIONS.

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Introduction: In the past decade, perchlorate and/or oxychlorine species have been ubiquitously detected in situ on the Martian surface [1-4] and in Martian meteorites [5]. Based on these observations, Phoenix soils at Mars north polar region are unique, with measured ClO_4^-/Cl^- molar ratio of 4.44 in average [1] and the molar proportion of oxychlorine species to total Cl would be even higher (~0.9) if includes ClO_3^- which also possibly presents in these samples [6; Table 3]. In contrast, oxychlorine species detected in other Martian samples in-situ [6; Table 3] or in terrestrial analogue, lunar or meteorite samples [5] are usually low, with approximately less than 20% of total Cl in mole. Experimental simulation studies producing oxychlorine species from chloride also show relatively low $ClOx/Cl^-$ ratios [6-11], suggesting that such high ClO_4^-/Cl^- ratios (>1) as observed in Phoenix soils are not resulting simply by any known production processes. Currently, it is unknown why such high ClO_4^-/Cl^- ratios are present in Martian polar region. Is it a unique signature solely present in polar environments or it may be present somewhere else on Mars? And yet, any proposed concentration processes of ClO_4^- through aqueous-related activities such as evaporation, freeze-thaw cycling, or deliquescence are lack of quantitative constraints.

In this study, we examine $Mg(ClO_4)_2$ + $MgCl_2$ + H_2O system by experimentally measuring solubilities in temperature range 233.15 K to 273.15 K, and conducting comprehensive thermodynamic modeling to construct thermodynamically stable and metastable phase diagrams of the system. By overlapping Phoenix site surface temperature-humidity (*T-RH*%) data obtained by Thermal and Electrical Conductivity Probe (TECP) [12] on the $x(Mg(ClO_4)_2)$-*T-RH*% phase diagrams, we find that eutectic brines can form by deliquescence of mixtures consisted of magnesium -perchlorate (hexahydrate) and -chloride (hexahydrate or octahydrate), or by partially melting of the mixtures if in contact of ice. These eutectic brines contain ClO_4^-/Cl^- ratios varying from 2.5 to 14.4 depending on the hydration states of magnesium chlorides (hexahydrate or octahydrate); but overall, a relative enrichment of perchlorate over chloride signature can be produced.

Solubility Measurements: Solubilities were determined isothermally at 273.15 K, 248.15 K and 233.15 K, respectively. $MgCl_2·6H_2O$ purified by once re-crystallization and $Mg(ClO_4)_2·6H_2O$ without further purification were used. Samples were equilibrated for 5 days at *T* = 273.15 K, while at least 10 days at *T* = 248.15 K and 233.15 K. Compositions of the equilibrium liquids were determined by analyzing the content of Mg^{2+} and Cl^- with gravimetric titrations. Then the concentration of ClO_4^- was determined by subtraction method according to charge balance. The solid phases were determined by the Schreinemakers' wet residues method [13,14].

Thermodynamic Modeling: Modeling was conducted using the CALPHAD type aqueous-mineral equilibrium code ISLEC developed by Li et al. [15,16]. The latest release is Version 4.2, which enables the calculation of high salinity waters by using a Pitzer-Simonson-Clegg (PSC) excess Gibbs energy model. Model parameters for the binary system $MgCl_2$ + H_2O were taken from [17] and these for $Mg(ClO_4)_2$ + H_2O were determined in this study. Mixing parameters in the ternary system were regressed from solubility data [18 and this study] and heat capacity data simultaneously as functions of temperature. The model is valid from 200 K to 363 K and its online version is available at http://www.islec.net/islec-web-mg-cl-clo4/.

Results and Discussion: Our experiments suggest that the thermodynamically stable magnesium chloride hexahydrate is usually kinetically inhibited and replaced by the metastable octahydrate, which therefore important for understanding chloride salt assemblages and their ability to from cryogenic liquid brine. Our model represents the isothermal solubility curves (stable and metastable) reported in published literature [18] and measured in this study at various temperatures well (Fig. 1). Comparing the model simulated crystallization surfaces of the $Mg(ClO_4)_2$ + $MgCl_2$ + H_2O system with surface *T-RH*% conditions at Phoenix site (Fig. 2), we conclude that magnesium perchlorate hexahydrate mixing with either magnesium chloride hexahydrate or octahydrate can form eutectic brines when in contact water-vapor or water-ice under Phoenix site surface *T-RH*% conditions, and the resulting brines can have elevated ClO_4^-/Cl^- molar

ratios to 2.5 and 14.4, respectively. Such values are in good agreement with Phoenix soils that ClO_4^-/Cl^- ratios are of 2.7 to 11.3 [1].
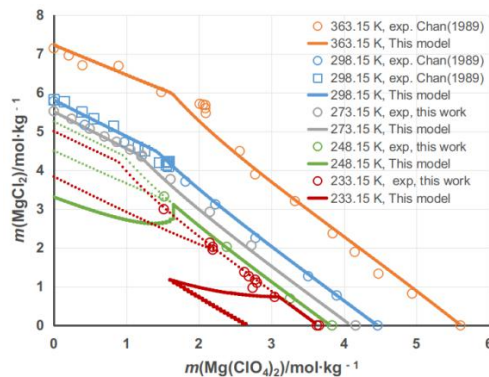

Fig. 1. *Isothermal solubility curves in the system $Mg(ClO_4)_2$ + $MgCl_2$ + H_2O at various temperatures. Open symbols are experimental data, solid lines are model generated thermodynamically stable results, and dash lines show model predicted metastable results.*

Implications for Mars: With cold ($T < 233.15$ K) and transient wet ($RH\% > 50$) conditions like northern polar region of mars, eutectic brines form by deliquescence of perchlorate and chloride salts or congruent melting with water-ice would preferentially enrich of ClO_4^- over Cl^-, resulting ClO_4^-/Cl^- fractionation and elevated ClO_4^- in the brines. Consequent evaporation or freezing of such brines would not fractionate ClO_4^- and Cl^-, so the high ClO_4^-/Cl^- signatures can be preserved in the polar soils. If excess water present, simultaneously leaching of both ClO_4^- and Cl^- are expected, and no ClO_4^-/Cl^- fractionation would occur so the ClO_4^-/Cl^- molar ratio should inherit its production signature. In fact, based on our model, any brine forms with $T > 233.15$ K and $RH\% > 50$ conditions would simultaneously accumulate both ClO_4^- and Cl^-. With warmer and arid conditions ($T > 233.15$ K; $RH\% < 50$) the ClO_4^-/Cl^- molar ratio in the brine cannot exceed 0.5 as well.

Therefore, the high ClO_4^-/Cl^- molar ratios in Phoenix soils are likely a unique signature resulted by limited-water (e.g., water-film) interaction with salts under a cold environment. Dust/soil particles bear perchlorate and chloride salts formed in-situ or elsewhere, but then preferentially leave perchlorate to the ground when limited eutectic brines forms in the polar region. Elevated ClO_4^- signature is likely preserved on the top soil layer which continuously being affected by water vapor in the atmosphere. South polar region of Mars may also have elevated ClO_4^- signature over Cl^-, if similar *T-RH%* conditions are present and eolian processes are dominant and transporting perchlorate and chloride salts in and out of the region.

Calcium and Na -perchlorate and -chlorates might also influence the ClOx/Cl patterns in the polar regions. However, currently, phase diagrams of systems consisted of Ca or Na -oxychlorine and -chloride have not been well constructed down to the eutectic points. Further work is needed to determine the low temperature solubility of perchlorate/chloride and chlorate/chloride systems, in order to evaluate their effects on ClOx/Cl ratios on the Martian surface.
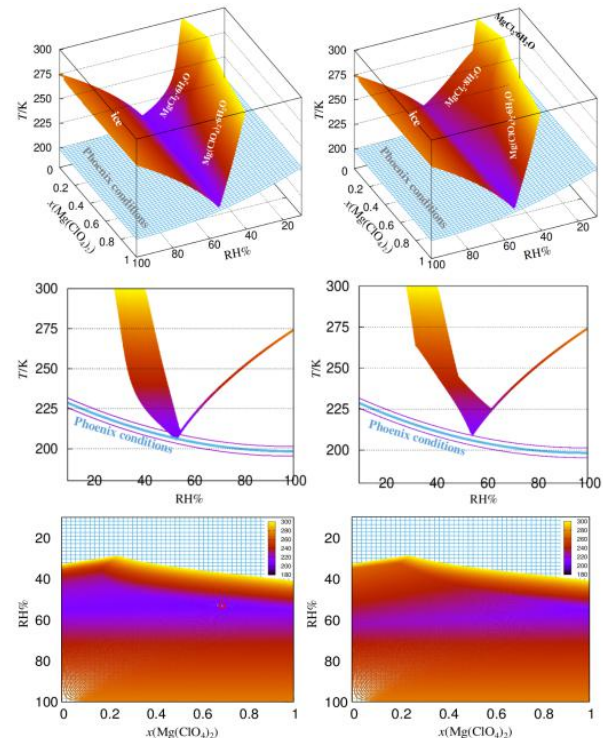

Fig. 2. *Model simulated metastable crystallization surfaces of the $Mg(ClO_4)_2$ + $MgCl_2$ + H_2O system in the temperature range from 200 K to 300 K with the surface T-RH% conditions at Phoenix site overlapped. The left column (three figures) shows the modeling results with solid phases $MgCl_2·12H_2O$ and $MgCl_2·8H_2O$ kinetically inhibited. The right column (three figures) shows the modeling results with solid phase $MgCl_2·12H_2O$ kinetically inhibited.*

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