**MODELING THE STABILITY AND DYNAMICS OF LIQUID BRINES AT THE PHOENIX LANDING SITE THROUGH EVAPORATION, FREEZING AND DELIQUESCENCE USING GEOCHEMIST'S WORKBENCH (GWB) AND FREZCHEM** A. Elsenousy[1], V.F. Chevrier[1]. [1.] Arkansas Center for Space and Planetary Sciences, 346 N Arkansas Av., University of Arkansas, Fayetteville, AR, USA, 72701. amira@uark.edu.

**Introduction:** The NASA Phoenix Lander observed ice in the shallow subsurface of Mars northern polar area and identified the soluble composition of the regolith [1]. These observations imply water transfer dynamics between the ice, regolith and the atmosphere in the present-day cold and dry Martian environment. The Wet Chemistry Lab WCL [2] in the Microscopy, Electrochemistry and Conductivity Analyzer MECA [3] discovered perchlorate ($ClO_4^-$) associated to $Cl^-$, $SO_4^{2-}$, $Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$ in an alkaline (pH~7-8) [3, 4, 5]. Recent studies have modeled the WCL solutions with various thermodynamic codes [6,7] using previously determined thermodynamic properties of perchlorates of $Na^+$, $Mg^{2+}$ and $Ca^{2+}$, and their pitzer parameters [8] to understand the salt assemblages at the Phoenix landing site. However, several intermediate species could interfere between perchlorate $ClO_4^-$ (oxidation state +7) and chloride $Cl^-$ (-1) such as chlorate $ClO_3^-$ (+5), chlorite $ClO_2^-$ (+3) and hypochlorite $ClO^-$ (+1), and thus be present in the solutions analyzed by the WCL but remained undetected. Thus to determine the nature and stability of these salts it requires accurate geochemical modeling including their thermodynamic properties. In addition, the Thermal and Electrical Conductivity Probe (TECP) observed a high humidity variation which could be explained through hydration and dehydration of the associated salts [9, 10, 11]. Therefore, in our study we are using thermodynamic and kinetic modeling to analyze the data received by the Phoenix MECA instrument. We analyzed the dissolved ions measured by the WCL through geochemical modeling using the Geochemist's Workbench (GWB) software and FREZCHEM to infer the original salt composition. We modeled 1- the freezing scenario (T < 0º C using FREZCHEM), 2- the evaporation scenario (T > 0º C using both FREZCHEM and GWB) and finally 3- deliquescence and efflorescence of binary salt mixtures ($ClO_4^-$ and $Cl^-$ using GWB). We also studied the thermodynamic properties of hypochlorite and chlorite salts.

**Experimental Methods**

**1- Freezing and Evaporation modeling:** The evaporation and freezing scenarios of the WCL solutions were modelled with FREZCHEM and was modified to include chlorate salts since chlorate is usually associated to perchlorate in all natural environments [12, 13]. The Geochemist's Workbench® (GWB) software package was also updated to include the Pitzer parameters for chlorate salts as reported in [12]. The initial conditions used as inputs were taken from [3, 14]. All evaporation runs started with 1000 g of water and a water decrement of 0.1 g at constant temperature of 283.15 K. Freezing runs started at 273.15 K down to 173.15 K with a temperature decrement of 1 K. Both evaporation and freezing simulations were established with an initial $CO_2$ pressure of 3 mbar. In the Geochemist's Workbench® (GWB) software, the evaporation took place with initial pH of 7.7 using the composition as defined in [3]. In this case, a fixed calcite concentration of 4.5 wt% [4] was added to the simulation to test for the presence of carbonates.

**2- Deliquescence and efflorescence of perchlorate and chlorides binary salt mixtures:** Deliquescence of individual perchlorate salts has been studied experimentally [15]. However, the effect of other species found in the Martian regolith such as chlorides (Cl-) on deliquescence of perchlorates is not well studied yet. Therefore, we modeled the deliquescence and efflorescence of various binary salt mixtures which is more relevant to the Martian regolith. The mixtures tested in our study are: $KClO_4/KCl$ , $Mg(ClO_4)_2/MgCl_2$ and $Ca(ClO_4)_2/CaCl_2$ at 298, 273, 243 and 253 K. To model the effect of the perchlorate mole ratio $mClO_4^-/(mClO_4^- + mCl^-)$ on the deliquescence relative humidity (DRH) of these mixtures, we used the GWB software package. Neither GWB nor any other designated geochemical model is able to directly calculate the evolution of salt equilibriums by varying the relative humidity. Therefore, we used the inverse approach, and rather than starting from a pure salt and increasing the humidity (to reach the deliquescence point), we started from a liquid solution and decreased the amount of water through evaporation (to reach the efflorescence point). Even though previous experiments showed there is a hysteresis between deliquescence (RH increases) and efflorescence (RH decreases) [15], both processes are identical from a thermodynamic point of view. Thus, for a fixed temperature, we calculate the evaporation of binary mixture at an initial molar ration and record the first salt to precipitate and the associated water activity (= DRH at equilibrium). Then, we repeat the step for various mol ratios. This method can be used with various numerical codes (FREZCHEM in particular for deliquescence below 0ºC).

**3- Thermodynamic properties of Na- hypochlorite and Na- chlorite:** From literature data [16, 17, 18], we have constructed stability diagrams of hypochlorite and chlorite salts for NaClO and $NaClO_2$ as shown in Figure 1. From these data we can determine the Pitzer parameters to be included in the various thermodynamic databases.

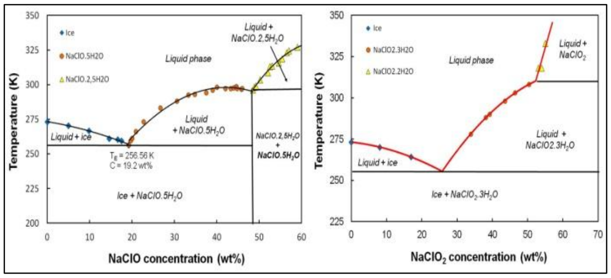


**Figure 1.** Stability diagrams of sodium hypochlorite (left) and sodium chlorite (right). The lines are polynomial fits of the data.

**Results and Discussion:**

**1- Freezing and Evaporation modeling:** Modeling the WCL solutions via FREZCHEM and GWB show domination of chlorate salts specially Mg-chlorate in all runs. In addition, there is a major absence of Ca perchlorate in the simulations which give a clue of either Ca-perchlorate remained isolated from other salts or that we have a very arid environment. Our freezing simulations also show precipitation of the highly hydrated salts such as meridianiite ($MgSO_4.11H_2O$) and $MgCl_2.$ $12H_2O$ indicated freezing route, while deposition of the low hydrated slats as anhydrite, epsomite, $Mg(ClO_3)_2{\cdot}4H_2O$ and $Mg(ClO_4)_2{\cdot}H_2O$ indicated evaporation (Fig 2).

**2- deliquescence and efflorescence of binary salt mixtures of perchlorate and chlorides:** Certainly, like for eutectic temperatures, the deliquescence of binary salt mixtures are lower than for individual salts. Our modeling results show that the $RH_{eut}$ (eutonic concentration) for the binary salt mixture is systematically lower than the DRH (deliquescence relative humidity) of each individual salt at a fixed temperature. Therefore, we observe that presence of a little amount of a more deliquescent salt such as $CaCl_2$ cause aqueous solution to form at a RH value far below the DRH of the less deliquescent salt as $Ca(ClO_4)_2$ (Fig. 3). Where at temperature of 253 K, the $RH_{eut}$ of $Ca(ClO_4)_2.8H_2O/CaCl_2.6H_2O$ mixture was found to be 23.2% RH. Future work will focus on other relevant salts, and comparing our modeling results to experiments focusing on binary mixtures.

**3- Thermodynamic properties of Na- hypochlorite and Na- chlorite:** From the established stability diagrams of both Na-hypochlorite and Na-chlorite, we can extract the Pitzer parameters for each anion – cation couple. Later we can include these parameters in thermodynamic model databases. We are currently calculating the Pitzer parameters for sodium hypochlorite / chlorite from freezing temperatures.

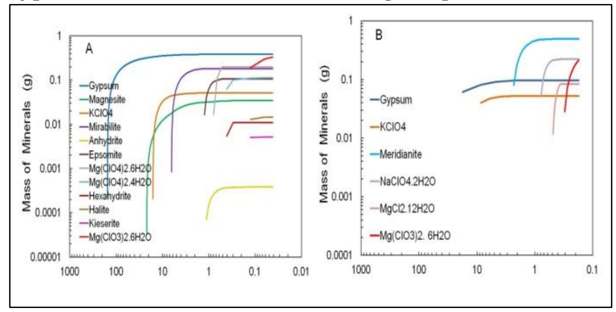


**Figure 2:** Minerals precipitated via evaporation pathway using GWB (A) and freezing pathway (B) using FREZCHEM

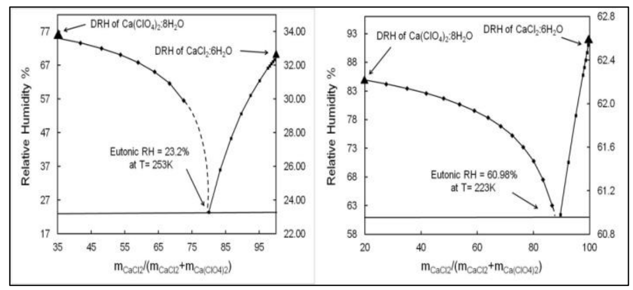


**Fig 3**: Deliquescence phase diagrams of $Ca(ClO_4)_2/CaCl_2$ binary salt mixtures at 223 and 253 K using GWB model. Scales on vertical axes are for each salt and mole ratios on the horizontal axes.

**References:**

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