



Soluble salts at the Phoenix Lander site, Mars: A reanalysis of the Wet Chemistry Laboratory data

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Abstract

The Wet Chemistry Laboratory (WCL) on the Phoenix Mars Scout Lander analyzed soils for soluble ions and found Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and ClO_4^- . The salts that gave rise to these ions can be inferred using aqueous equilibrium models; however, model predictions are sensitive to the initial solution composition. This is problematic because the WCL data is noisy and many different ion compositions are possible within error bounds. To better characterize ion concentrations, we reanalyzed WCL data using improvements to original analyses, including Kalman optimal smoothing and ion-pair corrections. Our results for Rosy Red are generally consistent with previous analyses, except that Ca^{2+} and Cl^- concentrations are lower. In contrast, ion concentrations in Sorceress 1 and Sorceress 2 are significantly different from previous analyses. Using the more robust Rosy Red WCL analysis, we applied equilibrium models to determine salt compositions within the error bounds of the reduced data. Modeling with FREZCHEM predicts that WCL solutions evolve Ca–Mg– ClO_4 -rich compositions at low temperatures. These unusual compositions are likely influenced by limitations in the experimental data used to parameterize FREZCHEM. As an alternative method to evaluate salt assemblages, we employed a chemical divide model based on the eutectic temperatures of salts. Our chemical divide model predicts that the most probable salts in order of mass abundance are $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ (meridianiite), $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$, KClO_4 , $\text{NaCl} \cdot 2\text{H}_2\text{O}$ (hydrohalite), and CaCO_3 (calcite). If ClO_3^- is included in the chemical divide model, then NaClO_3 precipitates instead of $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ precipitates in addition to $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. These salt assemblages imply that at least 1.3 wt.% H_2O is bound in the soil, noting that we cannot account for water in hydrated insoluble salts or deliquescent brines. All WCL solutions within error bounds precipitate $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ salts. These salts have low eutectic temperatures and are highly hygroscopic, which suggests that brines will be stable in soils for much of the Martian summer. © 2014 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Soluble salts on Mars readily interact with water and have wide-ranging implications for aqueous processes (Squyres et al., 2004; Haskin et al., 2005). A significant motivation for the exploration of Mars is the possibility that Mars harbored life early in its history or may have life

in the subsurface today (Beatty et al., 2005). Because life requires liquid water (Tosca et al., 2008; Davila et al., 2010), the search for life has focused on aqueous alteration minerals, such as salts, which are indirect tracers of liquid water (Boynton et al., 2009; Niles et al., 2013). Salts also have key properties that can stabilize liquid water in the cold and dry conditions of Mars, such as freezing-point depression (Brass, 1980; Kuz'min and Zabalueva, 1998; Squyres et al., 2004; Bibring et al., 2006; Fairén et al., 2009; Marion et al., 2010), slower evaporation rates due to reduced water activity (Sears and Chittenden, 2005;

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Altheide et al., 2009; Chevrier et al., 2009), and hygroscopicity (Zorzano et al., 2009; Davila et al., 2010; Gough et al., 2011). In addition, cryogenic salts can incorporate water and CO₂ into their crystal structure, which will influence water and CO₂ cycling between the Martian regolith and atmosphere (Clark, 1978; Kahn, 1985; Niles et al., 2013).

The quantitative identification of salts on Mars is the first step towards determining their origin and what they mean for the evolution and habitability of Mars. Both orbital spectra and *in situ* measurements have identified salts. Key salts detected from orbit include chlorides (Glotch et al., 2008; Osterloo et al., 2008, 2010; Ruesch et al., 2012), sulfates (Gendrin et al., 2004; Langevin et al., 2005; Murchie et al., 2009), and carbonates (Bandfield et al., 2003; Ehlmann et al., 2008; Niles et al., 2013). The Mars Exploration Rovers (MERs) detected Mg, Ca, and Fe sulfates (Squyres et al., 2006; Wang et al., 2006), indicative of past acidic conditions (Hurowitz et al., 2006), and also carbonates (Morris et al., 2010), characteristic of alkaline environments. Comparisons of elemental abundance measured by landers and rovers have led to the suggestion that the soil comprises a global unit, which is a mixture of weathered and unweathered basalt, salt, dust, and meteoritic material (Clark et al., 1982; McSween and Keil, 2000; Nelson et al., 2005; Yen et al., 2005). Hence, salt compositions measured in any one locality may have global implications for the evolution and habitability of Mars.

The first direct measurements of soluble salts on Mars were made by the Wet Chemistry Laboratory (WCL) experiment on the Phoenix Lander (Boynton et al., 2009; Hecht et al., 2009; Kounaves et al., 2010a). Soluble salts were measured by adding dry soil to liquid water heated to a temperature between 5 and 10 °C, and analyzing the dissolved ions using an array of Ion Selective Electrodes (ISEs) (Kounaves et al., 2010a). The WCL experiment identified an alkaline soil solution consistent with previous pH inferences of 7.4–8.7 for soils in the Viking Lander biology experiments (Quinn and Orenberg, 1993). Phoenix also found some soluble sulfate (~1–2 wt.%), which can be compared to 5–9 wt.% total sulfate in typical soil inferred from previous landers (Kounaves et al., 2010b). This suggests that most of the soil sulfate resides in insoluble or sparingly soluble forms. One of the most interesting findings of the WCL experiment is that most of the soluble chloride is present as perchlorate (ClO₄⁻) (Hecht et al., 2009; Kounaves et al., 2010a). Perchlorates are among the most hygroscopic salts (Besley and Bottomley, 1969; Gough et al., 2011) and have eutectic temperatures as low as -75 °C (Dobrynina et al., 1980; Pestova et al., 2005), which could stabilize liquid water on present-day Mars (Marion et al., 2010).

To determine both the soluble ion chemistry and solid salt precipitates on Mars, thermodynamic models have been used, such as FREZCHEM (Marion et al., 2003, 2009, 2010, 2011). FREZCHEM suggests that a variety of parent salts are present at the Phoenix site, including calcite (CaCO₃), gypsum (CaSO₄·2H₂O), meridianiite (MgSO₄·11H₂O), NaClO₄·2H₂O, KClO₄, and Mg(ClO₄)₂·6H₂O, and that a small fraction of liquid water is stable down to about -60 °C as Mg–ClO₄-rich brine (Marion et al., 2010). However, equilibrium model predictions are sensitive to

the initial WCL chemistry that is input into the model. This deserves further attention because the Phoenix WCL analysis is characterized by relative errors in concentration between about 20–50% due to high levels of noise and anomalous signal fluctuations (Hecht et al., 2009; Kounaves et al., 2010a,b; Quinn et al., 2011). As a result, many different solution compositions are possible within error bounds.

To better understand the soluble chemistry at the Phoenix site, we reanalyzed data from the WCL experiment using improvements to the original analyses of Hecht et al. (2009) and Kounaves et al. (2010a,b) that include Kalman optimal smoothing, corrections for ion-pairs, and corrections for calibrant salts. It is important that an independent reanalysis is done because the WCL results are the only direct measurements we have of the soluble soil chemistry on Mars. With our revised ion concentrations and uncertainty estimates for the WCL aqueous solution, we apply the geochemical model FREZCHEM and a chemical divide model to determine probable parent salt compositions in the Phoenix soil, i.e. the original salt precipitates in the soil that dissolved to form the WCL solution.

2. OVERVIEW OF THE WCL EXPERIMENT

The operation and construction of the WCL experiment has been described in detail (Kounaves et al., 2009), as well as methods used to analyze the WCL data (Hecht et al., 2009; Kounaves et al., 2010a,b; Quinn et al., 2011). Briefly, the WCL instrument consists of four 40 ml beakers (labeled cells 0 to 3), each containing an array of Ion Selective Electrodes (ISEs) and other sensors for the analysis of Ca²⁺, Mg²⁺, Ba²⁺, Na⁺, K⁺, NH₄⁺, H⁺ (pH), Cl⁻, ClO₄⁻, Br⁻, I⁻, conductivity, cyclic voltammetry, anodic stripping voltammetry, and chronopotentiometry. There are three ISE sensors for measuring pH (pH_a, pH_b, and pH_{irid}). Above each WCL beaker is a 36 ml tank containing 25 ml of leaching solution with the following dissolved ions: Ca²⁺ = Mg²⁺ = Ba²⁺ = Na⁺ = K⁺ = NH₄⁺ = HCO₃⁻ = 10 μM, Cl⁻ = 50 μM, Li⁺ = 1 mM, and NO₃⁻ = 1.03 mM. During operation, the leaching solution was thawed and ejected into the WCL beaker, which is stirred by an impeller. Following this, a crucible containing salts for calibration of the ISEs was deposited into the leaching solution, bringing the solution to the composition: Ca²⁺ = 42 μM, Mg²⁺ = 34.7 μM, Ba²⁺ = 38 μM, Na⁺ = K⁺ = NH₄⁺ = HCO₃⁻ = 34 μM, Cl⁻ = 190 μM, Li⁺ = 1 mM, and NO₃⁻ = 1.1 mM. After analysis of the calibration solution, ~1 cm³ of soil sample was deposited into the WCL beaker and the sensor array was monitored over several hours. Once this initial analysis phase was finished, the heater shut down and the soil-solution was allowed to freeze in the WCL beaker. A second major phase of the WCL analyses began by thawing the frozen soil-solution in the WCL beaker. To this thawed soil-solution was added 4 mg of 2-nitrobenzoic acid to test for pH buffering in the soil, followed by three crucibles containing 0.1 g of BaCl₂ for titrimetric determination of soil SO₄²⁻. For some cells, additional thawing/freezing, soil sample addition, and sample analysis cycles were performed.

To provide context for this paper, an overview of key WCL events during the Phoenix mission operations is

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