

AQUEOUS CARBONATE CHEMISTRY OF THE MARTIAN SOIL AT THE PHOENIX LANDING SITE.

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Introduction: Phoenix landed on the northern plains of Mars May 25, 2008, in an area dominated by 1-2 m polygonal-patterned ground covered by several centimeters of loosely consolidated and cloddy soil above ice-cemented soil [1, 2]. An important component of the mission goals was to analyze the chemistry of the soils, at the surface and at depth. This will help us better understand the history of the water, the bi-habitability of the soil, the availability of chemical energy sources, and the general geochemistry of the site. To address such issues it is necessary to determine more than just the elemental composition of the soil. We must also understand the aqueous environment that might have been present during an earlier warmer and wetter period in Mars' history, and identify/quantify the soluble ionic components present in the soil. One property that is especially important is the pH of the soil, key to solution equilibrium and thus the aqueous chemistry of the soil. To this end, the Phoenix included four wet chemistry laboratories as part of the MECA instrument package.

The MECA Wet Chemistry Laboratory (WCL):

Each of the four WCLs on Phoenix (Figure 1) consist of a lower beaker lined with a variety of sensors and an upper actuator assembly for adding soil, water, reagents, and stirring. The beaker contains six membrane-based ion selective electrodes (ISE) for measuring Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , and NH_4^{+} , two ISEs for H^{+} (pH), an ISE whose selectivity is based on the Hofmeister series and is responsive primarily to ClO_4^{-} (and also NO_3^{-} if it were 1000 times greater), a Ba^{2+} ISE for titrimetric determination of SO_4^{2-} , two Li^{+} ISEs as reference electrodes, three crystal pellet ISEs for Cl^{-} , Br^{-} , and I^{-} , an iridium oxide electrode for pH, an electrode for conductivity, a Pt and two Ag electrodes for determination of Cl^{-} , Br^{-} , and I^{-} using chronopotentiometry (CP), and a Au electrode for cyclic voltammetry (CV). The WCL sensors and analytical procedures were calibrated and characterized on Earth before launch. A detailed description of the WCL hardware and its characterization can be found in reference [3].

The analyses on Mars were planned to take two sols. The first sol began by thawing and dispensing a 25 mL solution containing $1 \times 10^{-5} \text{M}$ concentrations of the detectable ions from a storage tank into the analysis beaker. After a couple of hours of equilibration, a

crucible of salts was added, raising the calibrant concentrations to about $3 \times 10^{-5} \text{M}$. Soon thereafter, approximately 1 cm^3 of soil was added. The solution was then monitored for the remaining portion of the sol and allowed to freeze at the end of the analysis.

The second sol analysis consisted of thawing the beaker for a couple of hours, adding a crucible containing 0.004 g of 2-nitrobenzoic acid, and then adding one or more of the three crucibles containing 0.1 g of BaCl_2 to titrate sulfate while monitoring with a Ba^{2+} -ISE. In some cases the barium crucibles were added separately on subsequent sols.

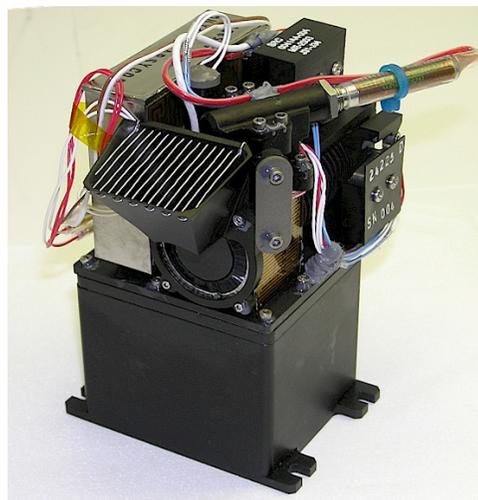


Figure 1. One of four Wet Chemistry Laboratories

Results and Discussion: Samples were successfully added and analyzed in three of the four WCLs. Soil was delivered to the fourth WCL, but its substantial cohesion prevented the sample from dispensing into the drawer and/or cell. One sample was collected from the surface (Rosy Red) and two from the top of the ice table approximately 5cm in depth (Sorceress 1 and Sorceress 2). All three samples contained the same ionic species and at similar concentrations. Since the results for all three samples were very similar, only the data for Rosy Red will be given here.

Responses from all the sensors indicated rapid dissolution of all the salts in the soil on the order of no greater than about 40-60 seconds. In most cases dissolution occurred within the response time of the ISE

sensors (~ 50 s). Such a rapid response would be expected from soil containing segregated salts as opposed to dissolution from a mineral matrix and points to a very likely previous aqueous history for the salts.

The concentrations of the individual ionic species measured are shown in Table 1. The soil lechate is dominated by ClO_4^- , Mg^{2+} , and Na^+ at mM levels, with sub-mM concentrations of Ca^{2+} , Cl^- , and K^+ . Several discoveries, such as ClO_4^- [4], were unexpected and hold significant implications for several Mars related issues. The ionic species in Table 1 are soluble components measured directly by the sensors, and as discussed below, may only represent a portion of the total amount of any specific chemical element present in the sample and/or solution. In addition, other species such as CO_3^{2-} , HCO_3^- , and SO_4^{2-} , are inferred from these results, modeling, and other parameters. The pH (measured by two ISE and an IrO-based sensor) and conductivity of the solution, were 8.3 ± 0.5 and $1100 (\pm 200) \mu\text{S}/\text{cm}$, respectively. Except for sensor drift and other understood artifacts, the indication is that very little or no other soluble ionic species were released into the solution during the subsequent several hours, and in some cases days, of monitoring.

Table 1 - WCL Results for Rosy Red

| Ionic Species | Concentration in Cell, mM | %wt * |
|--|--|-------|
| Ca^{2+} | 0.40 (± 0.2) | - |
| Cl^- | 0.45 (± 0.5) | 0.04 |
| ClO_4^- | 3.0 (± 1) | 0.75 |
| K^+ | 0.30 (± 0.1) | 0.03 |
| Mg^{2+} | 2.5 (± 1) | - |
| Na^+ | 1.5 (± 0.5) | 0.10 |
| | | |
| pH | 8.3 (± 0.5) | |
| Cond | 1100 (± 200) $\mu\text{S}/\text{cm}$ | |
| * Assumes 1g sample and $1\text{g}/\text{cm}^3$ density. | | |

Analysis and interpretation of the data is still ongoing, but currently the modeling and lab experiments using WCL flight like EQM units lead us to believe that the solution chemistry is most likely controlled by CO_3^{2-} , HCO_3^- , and CO_2 in a solution saturated with MgCO_3 and/or CaCO_3 . In addition to not knowing $[\text{Ca}]_T$ and $[\text{Mg}]_T$ (the total concentration of Ca and Mg in the sample), the values for SO_4^{2-} , P_{CO_2} , and pH have large enough error bars so that it makes it difficult to model $[\text{Ca}]_T$ and $[\text{Mg}]_T$ and obtain a unique mathematical solution. Equilibrium modeling and very preliminary experiments appear to support that the solution is saturated in one or both of these species.

In addition to the pH itself, evidence for the presence of a buffering system also comes from the observed effects on pH after addition of the acid containing crucible. On being dispensed, the 4mg of 2-nitrobenzoic acid ($\text{pK}_a=2.2$) did not cause any observable change in the pH. In addition to the WCL results, the TEGA results also indicate the presence of a significant amount of a carbonate, most likely calcite [5,6].

Equilibrium modeling of the measured and inferred composition of the soil/solution mixture in WCL with MINEQL and GWB has been used to provide guidance for further laboratory experiments with synthetic Mars samples. The models indicate a very complex system with the final species distribution dependent on several variables, including ionic strength, pH, precipitation, ion adsorption, the partial pressure of the CO_2 in the WCL headspace, and the rate of equilibration.

The current models and lab experiments lead to several possible end-results depending on assumed P_{CO_2} (usually between 0.1 and 1 mbar due to CO_2 remaining in the WCL headspace on degassing after the drawer openings) and the presence (or not) of SO_4^{2-} . The models accurately predict the measured concentrations for Ca^{2+} , Mg^{2+} , and pH, but do so with several possible compositions. To differentiate between possible, probable, and confirmed, will require extensive formulation and testing with both simple aqueous lechate simulants and eventually more realistic geological Mars simulants.

Conclusions: In addition to the pH, conductivity, and soluble ionic species, as listed in Table 1, the results provide strong evidence that the salts contained in the soil sample delivered to WCL have previously interacted with water and contain high levels of carbonates. The compositional similarity of all samples (surface to 5 cm ice table) shows a lack of any chemical gradients.

The carbonate results to date clearly show the need for more extensive laboratory work and equilibrium modeling. Planned or underway are several experiments with a variety of minerals, salts, and conditions. In an iterative process, the chemical equilibrium modeling provides both soluble ion concentrations and/or constraints, that will allow us to better predict formulation of a Mars simulant in high fidelity with that added to the WCL on Mars.

References: [1] Arvidson et al. (2009) *LPSC XL*, this volume. [2] Arvidson et al. (2008) *JGR*, 113, E00A03 doi:10.1029/2007JE003021. [3] Kounaves et al. (2008) *JGR*, 113, doi:10.1029/2007JE003084. [4] Hecht et al. (2009) *LPCS XL*, this volume. [5] W. Boynton et al. (2009) *LPCS XL*, this volume. [6] B. Sutter. (2009) *LPSC XL*, this volume.