THE PHOENIX MARS LANDER WET CHEMISTRY LABORATORY (WCL): UNDERSTANDING THE AQUEOUS GEOCHEMISTRY OF THE MARTIAN SOIL S. P. Kounaves, In-Situ Planetary Chemical Analysis Laboratory, Department of Chemistry, Tufts University, Medford, MA 02155 (samuel.kounaves@tufts.edu).

Introduction: In May of 2008, the Phoenix Mars Lander descended on the northern plains of Mars. The goals of the Phoenix Lander were, to acquire and analyze samples of soil and ice, to investigate the presence of water/ice, to determine the chemistry and mineralogy of the soil, to identify potential chemical energy sources available to support life, to analyze for organics, and to identify the potential of the geochemical environment to preserve paleontological evidence [1].

On the Phoenix deck were several instruments, including four Wet Chemistry Laboratory (WCL) units that were to perform the first wet chemical analysis of soil on Mars [2]. Each of the four WCL units, shown in Figure 1, consisted of a lower "beaker" containing an array of sensors to analyze the chemical properties of the soil/water mixture, and an upper "actuator" that added the soil, water, and reagents, and provided for stirring of the mixture. The array of sensors in the beaker consisted of solid state and PVC-membrane based *ion selective electrodes* (ISE) that analyzed for Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, Cl^-, Br^-, I^-, NO_3^-, pH, and $SO_4^=$, and special electrodes for conductivity and oxidation-reduction potential (E_h). Also included were anodic stripping voltammetry (ASV) for determination of heavy metals (e.g., Cu^{2+}, Cd^{2+}, Pb^{2+}), chronopotentiometry (CP) for independent determination of chloride, bromide and iodide, and cyclic voltammetry (CV) for identifying and analyzing possible reversible and irreversible redox couples. The actuator consisted of a 25mL titanium tank that contained deionized water plus ionic species at $\sim 10^{-5}$ M concentrations for the initial sensor calibrations, a drawer that would accept ~ 1 cm^3 of soil through a screened funnel from the robotic arm, and a stirrer motor. The actuator also included a reagent dispenser that held five "crucibles", a second calibration reagent, an acid, and three packed with $BaCl_2$ for the titrimetric determination of $SO_4^=$.

During surface operations, three ~ 1 cm^3 soil samples, one from the surface (Rosy Red) and two from the top of the ice table approximately 5cm in depth (Sorceress 1 and Sorceress 2), were successfully added and analyzed in three of the four WCLs. In general, the soluble equilibrium concentrations were found to be dominated by Mg^{2+}, and Na^+ at the mM levels, with sub-mM concentrations of Ca^{2+}, Cl^-, and K^+. The presence of these salts in addition to the moderate pH (7.7) and E_h (253mV), has broad implications for Mars' geochemistry and habitability. However, most surprising

Figure 1. The Wet Chemistry Laboratory (WCL) as part of MECA (left) and a single WCL unit (right.

was the discovery of 0.7% perchlorate (ClO_4^-), most likely present as either the Mg/Ca-$(ClO_4)_2$ salt [3,4]. The presence of such levels of perchlorate, and most likely on a global scale, has led to the realization that the mass spectrometer on Phoenix and on both 1974 Viking 1/2 landers would not have been able to detect any organics. This discovery has rekindled the possibility for the presence of both organics and life on Mars. Reviewed here are the major findings of the wet chemistry analyses performed by WCL and their implications for martian geochemistry and habitability.

The ionic species directly measured by the sensors and originally reported [3,4], were the soluble components and represented a portion of the total amount of any specific chemical elements present in the sample and did not reflect other species such as $CO_3^=$, HCO_3^-, and $SO_4^=$, that may have been present and were slowly or totally insoluble, or not measurable by any sensors. To better understand the identity of the added soil and its soluble mineral composition, equilibrium modeling of the soil/solution mixture with *Geochemist's Workbench®* (GWB) was used to provide guidance and for additional laboratory experiments with synthetic Mars samples.

The models and laboratory analyses have revealed 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. To differentiate between possible, probable, and confirmed chemistry, has require extensive formulation and testing with both simple aqueous leachate simulants and eventually more realistic Mars simulants. Recent additional data analyses have confirmed the presence of sulfate in the soil, the redox potential of the soil/water mixture, and the probable identity of the parent perchlorate salts.
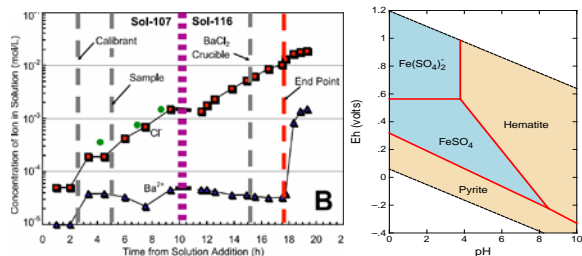
Figure 2. The titration for soluble sulfate on Mars by addition of barium chloride [5], and the E_h-pH diagram showing the phase stability fields for a soil-solution mixture based on Table 1 data and $10^{-3} > [Fe2+] > 10^{-9}$ [6] (left)

The total soluble sulfate $(SO_4^=)_T$ present in the soil was determined by addition of Ba^{2+} (as $BaCl_2$) to two samples, Rosy Red on sols 30/34 and Sorceress-2 on sols 107/116, and from a blank on sol 96. As shown in Figure 2, the concentration of the added Ba^{2+} in Sorceress-2 sample remained relatively constant until the end of sol 116 when it rapidly increased, indicating that it was no longer being precipitated by any $SO_4^=$ present in solution. At that point the $(SO_4^{2-})_T$ was equal to half of the ΔCl^-. The $SO_4^=$ in solution is thus 5.9 (± 1.5) mM, and equivalent to 1.4 (± 0.5) wt % $SO_4^=$ in the soil.

There are several sulfate mineral phases that are plausible candidates. These include K-, Na-, Fe-, Mg-, and Ca-sulfate. Soluble Fe-sulfate candidates can be eliminated since any $Fe^{2/3+} > 10^{-4}M$ would have been detected due to "poisoning" effects on the ISEs. Both K and Na were present at too low of concentration and would have only accounted for a minor fraction of their respective mineral phases. The most likely sulfate mineral phases in the soil are thus $MgSO_4$ or $CaSO_4$ (or a mixture of the two). Equilibrium calculations with GWB show that addition of $BaCl_2$, coupled with dissolution of $SO_4^=$, would have only resulted in an increase of Mg^{2+} and a decrease of Ca^{2+} if a $MgSO_4$ phase were added, as was observed during the sol 107 analysis. The addition of soluble $CaSO_4$ would have caused an increase in Ca^{2+} and no change in Mg^{2+}, which was not observed. This suggested that the major fraction of SO_4^{2-} was added as a $MgSO_4$ phase. The titration results and equilibrium modeling also allowed a more accurate assessment of other species and their concentrations. Table 1 shows the most likely composition of the martian soil at the Phoenix landing site. The level of dominant salts also has a direct bearing on the question of whether, under appropriate conditions, water activity on Mars could have been sufficient to support life. The WCL-derived salt composition indicates that if the soil at the Phoenix site were to form an aqueous solution by natural means, the water activity for a dilution of > ~ 0.015 g H_2O/g soil would be in a habitable range of known terrestrial halophilic microbes [5].

The comparison of the Mars soil with a simulant, formulated according to the results of the WCL and a GWB model, shows that when it is dissolved in water, yields ion concentrations almost identical to those observed on Mars. These results give confidence that the soluble composition and parent salts of the soil at the Phoenix site are reasonably constrained.

A long standing question about the martian soil has been its redox potential (E_h) on contact with water. The measured E_h of the soils in WCL solution has been recently reported to be $253 \pm 6mV$ at a pH of 7.7 ± 0.1. A difference between E_h and pH changes suggested a contribution from species not measured with the WCL, and experimental simulations confirmed that ppm soil levels of metal peroxides or similar oxidants could explain this difference. Although these soils contain high levels of ClO_4^- (a strong oxidant at temperatures > 200°C), and possibly low levels of more chemically reactive oxidants, the E_h of the soil is moderate and within the range of that expected for habitable soils [6].

The next generation Mars chemical analysis lab will build on the heritage and demonstrated success of the Phoenix WCL, and take advantage of recent improvements in both sensor and lab-on-a-chip technology. As part of an MER-class rover it will provide the ability to perform wet chemical analyses while ranging over a wide variety of geological surfaces, materials, soil chemistries, and over the lifetime of a long term mission. The sensor array and chemical analyses could be tailored to include parameters and substances of high priority to scientific analyses, sample return, and the health of future human explorers.

Table 1. Most Likely Species in Solution & Soil [5].

Species	Equilibrium Conc. in Solution (mM)	Conc. in Martian Soil (wt %)
$CaCO_3$ (calcite)	Saturated	3-5 (TEGA)
$MgCO_3$ (magnesite)	Saturated	≥1.8 (GWB)
$MgSO_4$ (epsomite)	Dissociated	3.3 (GWB)
ClO_4^-	2.5	0.6
Na^+	1.4	0.08
Cl^-	0.40	0.04
K^+	0.40	0.04
Mg^{2+}	6.4	–
SO_4^{2-}	3.9	–
HCO_3^-	5.4	–
$MgSO_4(aq)$	1.2	–
Ca^{2+}	0.75	–
$CaSO_4(aq)$	0.17	–

References: [1] Smith P. H. et al. (2009) *Science, 325*, 58-61. [2] Kounaves S. P. et al. (2009) *JGR, 114*, E00A19. [3] Hecht M. H. et al. (2009) *Science, 325*, 64-67. [4] Kounaves S. P. et al. (2010) *JGR, 115*, E00E10. [5] Kounaves S. P. et al. (2010) *GRL, 37*, L09201. [6] Quinn R. C. (2011) *GRL, 38,* L14202.