NEXT GENERATION WET CHEMICAL ANALYSIS LABORATORY FOR MARS SAMPLE RETURN AND HUMAN HAZARD EVALUATIONS

S. P. Kounaves[1], A. D. Aubrey[2], J. M. Bauer[3], M. H. Hecht [2], K. M. McElhoney[1], G. D. O'Neil[1], R. C. Quinn[4]. [1]Department of Chemistry, Tufts University, Medford, MA, 02155, (samuel.kounaves@tufts.edu), [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 91109, [3]Draper Laboratory, 555 Technology Drive, Cambridge, MA, 02139, [4]SETI Institute, Mountain View, CA

Introduction: The 2007 Phoenix Mars Lander [1] included four Wet Chemistry Laboratory (WCL) units [2] that accepted martian soil from the robotic arm, mixed it with water, and analyzed it for selected soluble inorganic species and other parameters. In addition to finding and measuring the soluble concentrations in the soil of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4^=$, the electrical conductivity, reduction-oxidation potential (E_h), performing chronopotentiometry (CP) for Cl^-, Br^-, and I^-, and cyclic voltammetry (CV) for redox couples, the results included the discovery that most of the soluble chlorine at the Phoenix landing site was in the form of ClO_4^-, and that the soil/water mixture resulted in a moderately alkaline pH of almost eight due to buffering by carbonates [3-7].

In keeping with the Planetary Decadal Survey [8] and the MEPAG Mars scientific goals [9], it is clear that the path forward for both Mars sample return (MSR) and human exploration, be undertaken with sufficient understanding of the martian environment so as to minimize the risks to the Mars program and humans. To fulfill the current strategic knowledge gaps in this area requires that the martian soil be chemically characterized to the maximum extent possible to identify soluble chemical species that may undergo potentially harmful interactions if they come into contact with the skin or lungs of the crew, or critical life support and other mechanical/electrical systems. In addition, a chemical analysis prior to caching for MSR could provide invaluable data on species that may be unstable during subsequent storage and transport.

Here we describe the next generation Mars wet chemistry laboratory that, in addition to the analyses performed by the Phoenix WCL [2], extends the capability to dozens of soil samples without increasing the demand on spacecraft resources, and extends the quantitative chemical aspects of the analyses.

The Next Generation WCL: With support from NASA's PIDD and ASTID programs, we have built on the heritage and successful performance of the Phoenix WCL and designed and assembled an instrument for use on a future MER or larger class mission, along with sample caching [10], that would provide the ability to perform wet chemical analyses at multiple locations over the rover's trajectory and lifetime. This next generation Mars chemical analysis lab (MCAL) is comprised of two subsystems. The front end consists of a number of individual mini-WCL units (Figure 1) but with improved calibration, reagent addition, and additional sensors, including redundancy, better reproducibility and a wider selection of chemical species and conditions. For example, instead of using calibration pellets composed of pressed salts as the Phoenix WCL did, it allows for addition of liquid reagents to ensure rapid dissolution and equilibration of any added reagent. This portion of the instrument enables both instantaneous and long term chemical equilibrium monitoring of the soil/water mixture and will provide data that can be compared to that previously returned by the Phoenix WCL.

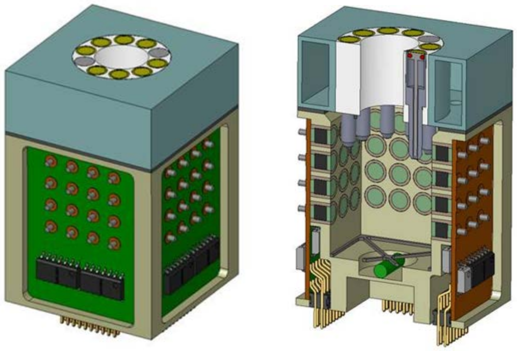

Figure 1. While the new analytical cells build on the heritage and demonstrated success of the Phoenix WCL, they are half the mass/volume and take advantage of recent improvements in technology, allowing 3X the sensors.

The mini-WCL based system hardware is built on a "modular" concept so that it can be adjusted to facilitate the specifications set by a future payload. For this reason, it is configured on a grid system that can be anything from a 1 x 4 grid (as the Phoenix WCL) to, for example, a 10 x 10 grid, where 100 individual units can be present. Each mini-WCL unit consists of a beaker where the sensors are housed and can hold 1 cc of soil and 7 mL of a leaching solution, as well as an "actuator assembly" which incorporates the leaching solution tank, sample and liquid calibration delivery mechanisms (Figure 1). Above the grid of beakers is a movable gantry system for sample delivery from an external sample mechanism as shown in Figure 2. Each beaker contains three walls of ion selective sensors in a 4 x 4 grid and a fourth beaker wall is reserved for other sensors to be determined at a later date (e.g., conductivity, pH, Eh, CP, CV, ASV, etc). The use of nanoporous carbon as a replacement for the hydrogel used in the Phoenix WCL [2] yielded sensors that were approximately 3mm while having stable potentials, increased lifetimes, and excellent sensitivity to increases in species' ionic activity.

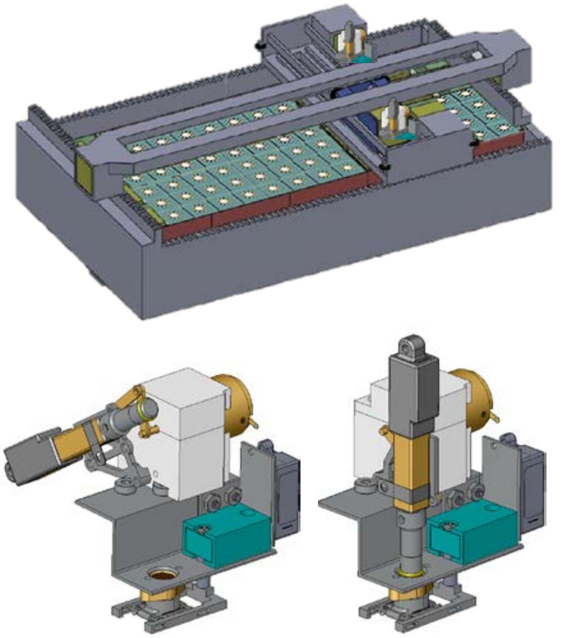

Figure 2. The integrated system (top) will be able to perform complex analyses on a large number of soil samples but easily be accommodated on a MER class rover. The soil can be accepted from a MER type robotic arm and transferred to each cell via an actuator (bottom).

The modular grid type system will allow for analysis of the larger number of samples that would be collected during a rover type mission. It also allows for customization depending on payload mass/size and provides for adaptability to a variety of future missions, both terrestrial and extraterrestrial. We also see the possibility that future decreases in sensor size would allow for an even greater density of sensors and/or beakers.

The second part of the MCAL system, shown in Figure 3, is a microfluidic lab-on-a-chip chemical analyzer (LCA) that can interface to each beaker and withdraw a small microliter aliquot of solution from each beaker. This is a powerful addition to the system used on the Phoenix WCL, since it will allow additional monitoring of the solution equilibrium chemistry as dissolution of salts and minerals in the sample proceed over time. It also adds the capability to perform a number of complex analytical flow-through procedures such as serial dilution, pre-and-post sensor calibration, titrations, and pH control of the solution. The LCA will use similar or the same sensors used in the beaker so that it can continue monitoring the same chemical processes that began in the beaker when the soil was initially added. The number of samples processed through the LCA and the complexity of the analyses during a mission is limited only by the consumables available. The LCA is in its 3rd year of development and integration with the MCAL is foreseen in the coming year.

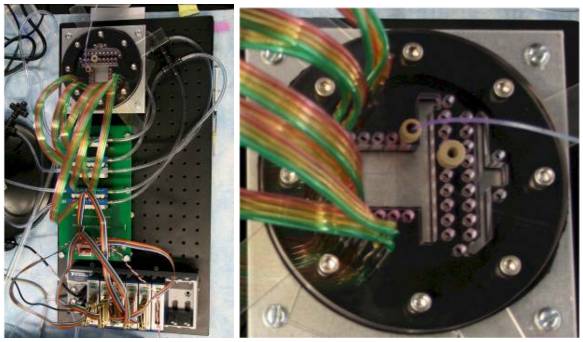

Figure 3. Prototype of a microfluidic system for processing monitoring of solution equilibrium chemistry as dissolution of salts and minerals in the sample proceed over time..

Summary: The next generation Mars chemical analysis lab (MCAL) builds on the heritage and demonstrated success of the Phoenix WCL, and takes 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 can be tailored to include parameters and substances of high priority to both sample return and human health. It is being developed with the view to allowing a scalable payload that will match a variety of requirements and possess the flexibility for use on any type of future mission.

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. et al. (2011) *GRL*, *38*, L14202. [7] Boynton, W. V. et al. (2009) *Science*, *325*, 61-64. [8] Planetary Science Decadal Survey (2012) Vision and Voyages, NRC Press. [9] MEPAG (2010) Mars scientific goals, objectives, investigations, and priorities: 2010. [10] Ehlmann, B. L. et al. (2012) Concepts and Approaches for Mars Exploration Workshop, Houston TX, (This Volume)