

**PHEEMS: A MARS SOIL REACTIVITY EXPERIMENT**, D. W. Ming<sup>1</sup>, D. C. Golden<sup>2</sup>, C. C. Liu<sup>3</sup>, A. D. Dawson<sup>4</sup>, and J. C. Hedgecock<sup>4</sup>, <sup>1</sup>SN2, NASA Johnson Space Center, Houston, TX 77058, douglas.w.ming1@jsc.nasa.gov, <sup>2</sup>Dual Inc., Houston, TX 77058, <sup>3</sup>Case Western Reserve University, Cleveland, OH 44106 and <sup>4</sup>Oceanering Space Systems, Houston, TX 77058.

**Introduction.** A Mars soil chemistry/reactivity experiment will answer important questions on the reactivity of the martian regolith and, hence, provide insight on the potential hazards of the regolith materials during a piloted mission to the surface. Our proposed Mars soil reactivity experiment consists of an array of chemical measurements made on the unconsolidated surface materials ("soils" and dust). These measurements include the determination of the hydrogen ion activity (pH), the redox potential (Eh), the electrical conductivity (EC), and composition of several soluble components (e.g.,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ). For simplification of terms, the experiment has been referred to as PHEEMS (pH, Eh, and EC of Martian Soils). The instrument is intent for lander and rover missions for the Mars Surveyor program (i.e., Mars 2001, 2003, and 2005 missions).

**Rational for the PHEEMS Instrument.** Contrary to the arguments made by Zent and McKay [1] against the use of Eh and pH for characterization of the martian regolith, we feel that there is a strong case for using these measurements. It is expected that important reactive components of the martian regolith materials will react very quickly in an aqueous medium because (i) the Mars surface materials have been shown to be highly reactive from Viking measurements, and (ii) the minerals suggested as being possible candidates in the Martian regolith are reactive in water, e.g., iron oxides, iron sulfates, phyllosilicates, evaporite-type minerals, and carbonates [2]. No doubt the surface materials on Mars are not in equilibrium with the current Mars environment, but that is to be expected as is the case for terrestrial soils.

The proposed methodology for the PHEEMS experiment involves the exposure of small quantities of martian regolith ("soil" or dust) to a finite volume of water. After a short period of time, soluble components will be sensed in solution with an array of microchemical sensors. The ionic species that go into solution will depend on the solubilities of the phases present in the regolith materials (e.g., NaCl, CaSO<sub>4</sub>, CaCO<sub>3</sub>, etc.) and on the reactivity with water (e.g., alkaline earth metal peroxides,  $\text{MO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{M}(\text{OH})_2$ , where M is an alkaline earth cation). The measurement of pH by itself may be the single most important measurement; it will provide mineralogical information. For example, a pH of 4 indicates the presence of free acids, generally from oxidation of sulfides or the presence of sulfates; a pH of 7.8 to 8.2 may indicate the presence of calcium carbonate; and a pH of 10 may indicate an alkaline metal carbonate system (e.g., evaporite basin). The measurement of the regolith's redox potential will provide valuable information to quantify the oxidation state. It is probable that several reactions (i.e., couples) will be controlling the redox potential in regolith materials and limit the ability to quantitatively interpret the value. However, based upon

our knowledge of terrestrial soils and materials, we will be able to provide qualitative information on the probable types of materials responsible for the redox potential of martian materials. The important aspect of the redox measurement will be the establishment of Eh-pH diagrams. These diagrams can give an excellent perspective on the relative stabilities of several minerals in a single diagram. The salinity (soluble salts) of the regolith will be determined by measuring the electrical conductivity of the solution. For example, high EC measurements (e.g., > 4mmho/cm) would indicate a high salinity and the presence of soluble salts. In addition to measuring the EC of the martian regolith, PHEEMS will determine the composition of soluble salts. An array of chemical microsensors will measure ionic species in solution, such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{AsO}_4^{3-}$ . The latter three toxic trace ionic species are of interest because of their potential health hazards during a piloted mission to Mars.

**Proposed PHEEMS Instrument.** In the past 10 years, the fabrication and reliability of chemical microsensors have vastly improved and the design of the PHEEMS microsensor array is based upon well established sensor technology [3,4,5,6,7]. The chemical microsensor array is fabricated by silicon-based microfabrication and micromachining processing and electrochemical sensing techniques. The voltammetric chemical microsensor array was chosen for several reasons. The array is solid-state, fabricated from metals and metal oxides; therefore, it can withstand the temperature and pressure extremes expected during Mars missions. Another important aspect of these chemical microsensors is their small size and mass. The sensor array has a low energy consumption requirement that allows it to operate effectively over the mission time period. Solid-state sensors are easy to clean and calibrate. Additionally, because of the electrochemical nature of the materials used for fabrication of the sensors, amperometric stripping techniques are used to eliminate any interferences from other ions in solution. The PHEEMS instrument will have two sensor array chips that will be placed into a low-temperature furnace (<100°C). Each chip has a physical dimension of 0.20" x 0.20" x 0.03". The two chips will provide redundant measures for these parameters. On one side of the chip, the array consists of sensors capable of measuring pH; redox potential, electrical conductivity; and temperature. On the other side, a three-electrode configuration electrochemical sensor will be used to determine the concentrations of the selected specific ions. The sensor output is an electrical signal such as current, potential, or conductivity that can be interfaced to a data collection system. The expected sensitivities and ranges for the sensors in the PHEEMS instrument are listed in Table 1.

A consumables package accompanies the microsensor array. Consumables for the instrument include wa-

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ter, N<sub>2</sub>, and a calibration solution. At the start of a run, an empty sample oven crucible will be placed inside the low-temperature oven maintained at a constant temperature (e.g., 20°C). Calibration solution will be dispensed into the sample crucible and N<sub>2</sub> will be flowed into the calibration solution at constant pressure (e.g., 50 mb). Chemical sensor measurements will be performed at several time intervals (e.g., 1 minute, 10 minutes, and 1 hour). Following calibration and cleaning, regolith samples (approximately 0.1 g) will be dispensed into a sample oven crucible. The sensor block and lid will be placed on the crucible and the oven will be operated at a constant temperature. Water (0.5-2.5 ml) will be dispensed into the crucible and nitrogen gas will be flowed into the solution containing the sample. Chemical sensor measurements will be performed at several time intervals. Additionally, evolved gases may be flowed to an evolved gas analyzer during or after the reaction.

**Table 1. Expected sensitivities and ranges for chemical microsensors**

Measurement	Sensitivity	Range
pH	0.1	0 to 14
EC (mmhos/cm)	0.02	0.02 to 10
Eh (mV)	10	-3000 to +3000
Cl <sup>-</sup> (mg/L)	0.8	0.8-30000
SO <sub>4</sub> <sup>2-</sup> (mg/L)	0.8	0.8-20000
Fe <sup>2+</sup> (mg/L)	0.8	0.8-1000
Fe <sup>3+</sup> (mg/L)	0.8	0.8-1000
Cd <sup>2+</sup> (mg/L)	0.3	0.3-10
Pb <sup>2+</sup> (mg/L)	0.3	0.3-10
AsO <sub>4</sub> <sup>3-</sup> (mg/L)	0.3	0.3-10

**PHEEMS Prototype Instrument.** A prototype PHEEMS instrument has been developed at the NASA Johnson Space Center. The prototype instrument used commercially-available chemical microsensors to measure pH, redox potential and electrical conductivity. A suite of Mars analog soils and one Lunar Breccia were analyzed by the PHEEMS prototype on very small sample sizes. The prototype required only 0.1 g samples and 0.5 ml of water to achieve nearly the sample accuracy (within 5% accuracy) as in experiments where standard laboratory procedures and equipment were used (Table 2).

One of the most oxidized samples with a high EC and pH was sample HWMK12, which was obtained from just below the summit of Mauna Kea in Hawaii (Table 2). The high EC and pH indicate the ready release of alkali and/or alkaline earth metals (e.g., in this case Na<sup>+</sup>) and suggests an evaporite-type environment. Sample HWMK12 is a weathered basaltic tephra [8]. The 2-line ferrihydrite is a mineral characteristic of oxidative weathering of Fe(II)-containing minerals and it is a residual mineral after extensive oxidation and leaching. The environment for oxidative weathering of this nature would have a solution pH close to neutral, a high Eh, and a low EC. This type of soil reactivity measurement might be expected in ancient Mars flood plains (although the redistribution of materials via dust storms will have to be considered). The Lunar breccia

79135 is a fresh basalt containing highly reduced materials; e.g., metallic Fe. The soil reactivity of this material has a Eh in the reducing range and a low EC, which would be expected for a solution in contact with slow dissolving glasses and minerals. Although some of the materials considered as candidates for the "superoxide" in the Martian regolith are not shown in Table 2, we would expect the most dominant redox couple to initially control the Eh. For example, if H<sub>2</sub>O<sub>2</sub> is present in the martian surface materials or forms by reaction of water with peroxides, then, the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O couple will control the redox potential and the solution Eh is expected to be around 1780 mV.

We are currently building a data base for a wide range of Mars analog materials. With the addition of the detection of soluble ions, we expect to be able to differentiate the soil reactivity of nearly all of the possible analog materials and, eventually, for Mars "soil" and dust. The measurement of Eh, pH, EC, and specific soluble ions on a Mars robotic mission will provide a great detail of information on the chemical nature (i.e., reactivity) of the sample and provide information on past environmental (i.e., climatic) conditions and processes of regolith formation.

**Table 2. Soil reactivity (pH, redox, and EC) of 9 Mars soil simulants and one lunar breccia using a prototype PHEEMS instrument. Sample locations and mineralogies of palagonitic materials (HWMK11, HWMK12, HWMK13, PN-9, HWMK600) are described in Golden *et al.* [8,9] and Morris *et al.* [10]. 2LFH is 2-line ferrihydrite. 6LFH is 6-line ferrihydrite.**

Sample Name	pH	Eh (mV)	EC (mmhos/cm)
HWMK11	7.8	200	0.55
HWMK12	8.2	250	1.20
HWMK13	8.1	240	1.00
PN-9	6.7	240	0.21
HWMK600	7.4	210	0.50
2LFH	7.2	250	0.10
6LFH	6.5	255	0.10
Nanophase hematite	6.9	255	0.10
Washington nontronite	7.8	255	0.50
Lunar Breccia 79135	6.2	100	0.21

**References.** [1] Zent, A.P., and McKay, C.P. (1992) LPI Rpt. 92-04, 41-42. [2] Gooding, J.L. (1978) *Icarus*, 33, 483-513. [3] Liu, C.C., and Cha, C.S. (1994) In *Chemical Sensor Technology*, Vol. 5, M. Aizawa (ed.), Kodansha Ltd, Tokyo. [4] Shoji, S. *et al.*, (1994) In *Chemical Sensor Technology*, Vol. 5, M. Aizawa (ed.), Kodansha Ltd, Tokyo. [5] Sze, M.J. (1994) *Semiconductor Sensors*. John Wiley & Sons, Inc., NY. [6] Shao, *et al.* (1994) *Electroanalysis*, 6, 245-249. [7] Savinell, R.F., *et al.* (1989) *Plating and Surface Finishing*, 40-44. [8] Golden, D.C., *et al.* (1993) *J. Geophys. Res.*, 98, 3401-3411. [9] Golden *et al.*, (1998) *LPSC 29*, This Volume. [10] Morris, R.V., *et al.* (1993) *Geochem. Cosmochim. Acta*, 57, 4597-4609.