The oxidation-reduction potential of aqueous soil solutions at the Mars Phoenix landing site

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[1]   Results from the Mars Phoenix mission Wet Chemistry Laboratory (WCL) are used to determine the oxidation-reduction potential (E_h) of the Phoenix WCL Rosy Red sample soil solution. The measured E_h of the Rosy Red sample in the WCL aqueous test solution was 253 ± 6 mV at a pH of 7.7 ± 0.1. Measured solution E_h changes correspond to changes in solution H^+ activity, which is controlled mainly by changes in headspace P_{CO2} and solution CO_3^{2-}, HCO_3^-, and CO_2 concentrations. If measured at a P_{CO2} of 8 mbar in water, rather than in WCL test solution, the E_h of the Rosy Red soil solution would be ~300 mV. The results of laboratory experiments using analog salt mixtures are compatible with the possible presence of low levels (ppm) of metal peroxides or other oxidants and indicate that levels of readily soluble ferrous iron in the soil are below 1 ppm. **Citation:** Quinn, R. C., J. D. Chittenden, S. P. Kounaves, and M. H. Hecht (2011), The oxidation-reduction potential of aqueous soil solutions at the Mars Phoenix landing site, *Geophys. Res. Lett.*, *38*, L14202, doi:10.1029/2011GL047671.

1. Introduction

[2]   The Wet Chemistry Laboratory (WCL), a component instrument of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) on the Mars Phoenix Lander, was used to perform, for the first time, a comprehensive chemical characterization of Martian soil in an aqueous solution. Prior to the Phoenix mission, the results of the aqueous Viking Biology Experiments indirectly indicated that soils at the landing sites contained unidentified soil oxidants [*Klein et al.*, 1976]. The Viking results led to inferences that Martian soils may be highly oxidizing and may contain species with high oxidation-reduction potentials (ORP) [*Zent and McKay*, 1994]. Direct measurements of aqueous Phoenix soil solutions using the WCL ion selective electrodes (ISE) revealed that the tested samples contained ~0.6% (by wt.) perchlorate (a strong oxidant at elevated temperatures) and had a pH of 7.7 ± 0.1 [*Hecht et al.*, 2009; *Kounaves et al.*, 2010a]. The results of the Phoenix Thermal Evolved Gas Analyzer (TEGA) confirmed the presence of perchlorate and measured calcium carbonate at 3 to 5% (by wt.), a finding that is consistent with the WCL pH measurements [*Boynton et al.*, 2009]. The pH of the Phoenix

soils is consistent with estimated pH of Viking soils [*Quinn and Orenberg*, 1993] and a reevaluation of the Viking Gas Chromatography-Mass Spectroscopy results is consistent with the presence of perchlorate in Viking soils [*Navarro-González et al.*, 2010]. However, although perchlorate is a strong oxidant, its stability (both thermally and in aqueous solution) precludes it as a direct explanation for the results of the Viking biology experiments or as a contributing species to the solution ORP.

[3]   In this paper, results from the Wet Chemistry Laboratory are used to determine the ORP of the Phoenix WCL Rosy Red sample soil solution. Rosy Red was a sample excavated from the top ~2 cm of surface material on sol 25 from the Burned Alive trench and delivered to the WCL on mission sol 30 [*Arvidson et al.*, 2009].

2. Methods

[4]   The WCL instrument description and previous WCL results have been published [*Kounaves et al.*, 2009, 2010a, 2010b; *Hecht et al.*, 2009; *Boynton et al.*, 2009]. One of the major goals of the WCL was to measure concentrations of soluble ions in the Martian soil. To accomplish this, an array of ion selective electrodes (ISE) was used to quantify the solution concentrations of ClO_4^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and H^+ after the addition of up to 1 cm^3 of soil to 25 mL of a dilute aqueous calibration solution [*Kounaves et al.*, 2009]. The WCL did not contain a standard reference electrode (e.g., Ag/AgCl); all ISE potentials were measured relative to a platinum ORP electrode and because of this, the raw ISE measurements were a combination of the ISE and ORP responses. ISE potentials were extracted from the raw data by referencing the measurement to one of two Li^+ ISEs electrodes (Li_A and Li_B) that were stabilized by an added background of 10^{-3} M $LiNO_3$ in the WCL calibration solution. Therefore, given a stable Li^+ ISE potential, the ORP of the soil solution relative to the Li^+ reference (ORP vs. Li^+) is the negative value of the measured Li^+ ISE potential (Li^+ vs. ORP).

[5]   The overall stability of the Li^+ ISEs was confirmed by comparison to the NH_4^+ ISE response, which showed only a small change after sample addition due to a known cross-selectivity to K^+. Therefore, the E_h (ORP referenced to the standard hydrogen electrode) of the WCL soil-solution can be determined from the measured change in Li^+ potential relative to the known E_h of the calibration solution prior to the addition of the soil sample.

[6]   The ORP and pH of the WCL calibration solution (Table 1) was measured in the laboratory using commercial ORP (Orion, model 977800) and pH (Orion, model 911600) electrodes. Laboratory measurements were obtained at room temperature and corrected using the Nernst equation to a

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Table 1. Cation and Anion Content of the Mars Phoenix Samples, the Phoenix Salt Analog and the WCL Mars Calibration Solution

Soluble Ion	Mars Samples[a] (moles/~1 cc)	Mars Analog (moles/80 mg)	Mars Calibration Solution[b] (M)
Na^+	3.23E-05	3.23E-05	3.40E-05
K^+	7.42E-06	7.42E-06	3.40E-05
Ca^{2+}	1.28E-05[c]	5.89E-04[c]	4.20E-05
Mg^{2+}	7.31E-05	7.31E-05	3.47E-05
NH_4^+	8.63E-07	NA	3.40E-05
Li^+	NA	NA	1.00E-3
Ba^+	NA	NA	3.80E-5
Cl^-	9.67E-06	9.67E-06	1.90E-04
ClO_4^-	5.83E-05	5.83E-05	NA
NO_3^-	NA	NA	1.00E-3
SO_4^{2-}	1.34E-04[d]	1.34E-04[d]	NA
CO_3^{2-}	3–5% as Ca[c,e]	5.15E-04[c]	3.40E-5

[a]*Kounaves et al.* [2010a].
[b]*Kounaves et al.* [2009].
[c]Saturated $CaCO_3$ solution.
[d]*Kounaves et al.* [2010b].
[e]*Boynton et al.* [2009].

WCL cell temperature of 8.4°C [*Kounaves et al.*, 2010a]. The ORP of the calibration solution was measured after purging with a N_2:CO_2 mixture (99.2%:0.8% by volume) to establish an initial 8 mbar partial pressure of CO_2 (P_{CO2}) in the test cell, corresponding to the approximate P_{CO2} during initial calibration on Mars. This gas purge removed dissolved O_2 from the calibration solution and established a pH of 5.5 ± 0.1, which was pH of the WCL cell0 calibration solution prior to the addition of the Phoenix WCL Rosy Red sample on Mars.

[7] The composition of the Phoenix salt analog used for laboratory simulation of the flight results was based on the measured Rosy Red soluble ion concentrations [*Kounaves et al.*, 2010a] and is shown in Table 1 (listed as moles/cc of Mars soil). To simulate the addition of the Phoenix soil to the WCL test cell on Mars, 80 mg of the analog salt mixture per 25 cc of calibration solution was used. Simulations using the analog salt mixture were carried out in 18 MΩ H_2O in place of the WCL calibration solution to determine the contribution of calibration solution nitrate to the measured sample solution E_h. The reported Phoenix WCL ISE measurements were processed as described by *Kounaves et al.* [2010a] and ORP values are reported as E_h (i.e., referenced to standard hydrogen electrode potentials). The reported error for the laboratory measurements represent standard deviations determined from replicate experiments.

3. Results

[8] Figure 1 shows the E_h of the Rosy Red WCL solution on sol 30 as determined from the cell0 Li^+_B ISE. No significant differences in ORP as measured with either the Li_A or the Li_B electrodes were observed. E_h of the WCL solution was determined by referencing the measured ORP (vs. Li^+) prior to sample addition to the laboratory determined E_h calibration value of 363 ± 6 mV for the WCL calibration solution at a pH of 5.5 ± 0.1.

[9] Within 15 minutes after soil addition, the WCL solution ORP decreased by 110 mV and after one hour, the E_h of the soil-solution was 253 ± 6 mV. A 120 mV decrease in the pH ISE potential, corresponding to a 2.2 pH unit increase, was measured upon soil addition. After soil addition, minor changes in E_h that tracked changes in the soil-solution pH were
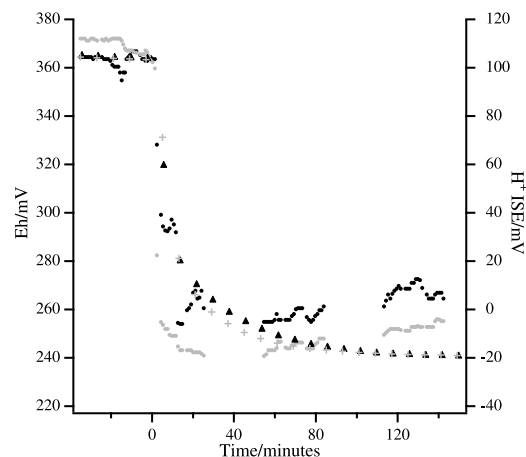

Figure 1. The E_h of the Mars Rosy Red WCL solution on sol 30 of the Phoenix mission (black dots) with the pH ISE mV response (gray dots). Also shown is the laboratory measured E_h of Phoenix analog salt mixture (black triangles) with the pH ISE mV response (gray crosses). Sample addition occurs at zero minutes.

observed. Also shown in Figure 1 are the results of a laboratory simulation of the Rosy Red E_h and pH ISE response using the Mars analog salt mixture listed in Table 1 and commercial pH and ORP electrodes. The measured E_h changes in WCL calibration solution upon addition of the salt mixture correspond to changes in H^+ activity, which is controlled mainly by changes in CO_3^{2-}, HCO_3^-, and CO_2 concentrations on formation of a calcium carbonate saturated solution. In general, the laboratory simulations using the salt mixture in Table 1 match the flight data Li^+ ISE (ORP) and H^+ ISE (pH) responses recorded for the Rosy Red sample on Mars. However, the measured E_h of the Rosy Red sample is ~10 mV higher than theoretically expected based on the observed 2.2 unit change in pH. For the analog salt mixture, the E_h and pH (mV) responses are identical.

[10] Figure 2 shows solution E_h and pH upon addition of the analog salt mixture to both WCL calibration solution and 18Ω H_2O. Due to carbonate content (Table 1), the solution
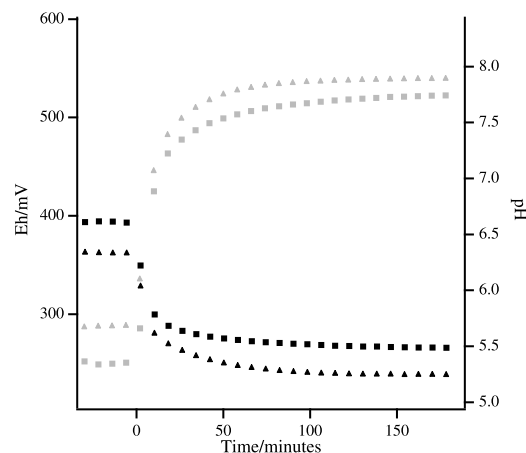

Figure 2. Analog salt mixture Eh (black) and pH (gray) measured in WCL calibration solution (triangles) and in 18MΩ H2O (squares). Analog salt mixture addition occurs at zero minutes.
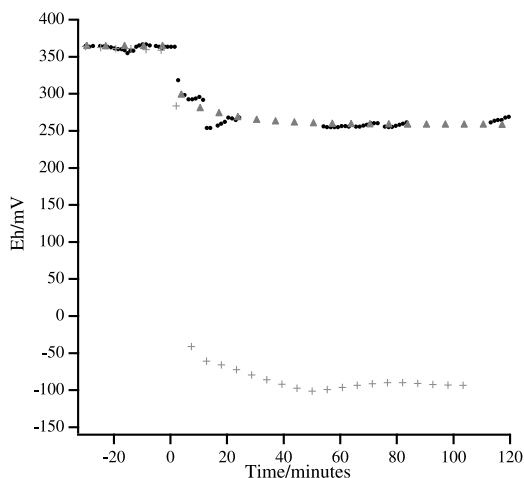
Figure 3. E_h (gray crosses) of the analog salt mixture containing the equivalent of 10 ppm of ferrous iron (as ferrous sulfate), and the E_h (gray triangles) of the analog salt mixture containing 16 ppm O_2 (as calcium peroxide), assuming a 1 gram sample Rosy Red sample. Also shown is the Eh of the Mars Rosy Red WCL solution on sol 30 of the Phoenix mission (black circles). Sample addition occurs at zero minutes.

pH of the CO_2 purged calibration solution is higher than the pH of the purged water. Correspondingly, due to differences in pH, the ORP of the water is higher than that of the calibration solution prior to the addition of the analog salt mixture. Accounting for the slight differences in pH, the E_h of the analog in calibration solution is ~16 mV lower than the E_h of the analog in water solution. Overall, the difference in E_h between the solutions is small and lies only slightly outside the experimental measurement error, indicating that the contribution of the calibration salts (including nitrate) to the measured soil solution ORP on Mars is small.

[11] Two examples of the sensitivity of WCL E_h measurements to the presence of redox active couples are shown in Figure 3. One of the analog salts used in the experiment (Figure 3) contains the equivalent of 10 ppm of ferrous iron (as ferrous sulfate) in the Mars Rosy Red sample, assuming that a one gram (1 cc) sample was delivered to the WCL cell on Mars. Upon addition of the iron containing salt mixture, the E_h of the solution decreased to -66 ± 5 mV (pH 7.7 ± 0.1) in comparison to 253 ± 6 mV (pH 7.7 ± 0.1) for the Mars Rosy Red sample. The second analog salt (Figure 3) contained the equivalent of 16 ppm O_2 added as calcium peroxide. After addition of the peroxide containing salt mixture, the E_h of the solution decreased to 257 ± 6 mV (pH 7.7 ± 0.1) in comparison to 253 ± 6 mV (pH 7.7 ± 0.1) for the Mars Rosy Red sample.

4. Discussion

[12] The E_h of the Rosy Red sample-solution was determined to be 253 ± 6 mV at a pH of 7.7 ± 0.1 and 8.4°C. Overall, E_h of the Rosy Red soil-solution is a function of the carbonate and P_{CO2} controlled hydrogen ion activity. In general, the redox potential of an aqueous system can be described by the Nernst equation:

$$E_h = E^\circ - \frac{RT}{nF} \ln \frac{a_{red}}{a_{ox}} - \frac{mRT}{nF} \ln [a_H^+] \qquad (1)$$

where E° is the standard half-cell reduction potential, R is the universal gas constant, T is temperature, F is Faraday's constant, n is the moles of electrons transferred, m is the moles of protons transferred, and a is activity of contributing components in solution. As can be seen from equation (1), E_h will decrease with decreasing H^+ activity (increasing pH). Upon addition of the Rosy Red sample to the WCL calibration solution the pH shifted from 5.5 ± 0.1 to 7.7 ± 0.1, which for a system at 8.4°C (the Rosy Red cell temperature) that displays ideal Nernstian behavior, would result in a 123 mV decrease in E_h. The pH dependence of the measured soil-solution E_h can be clearly seen over the 40 to 140 minute time interval shown in Figure 1. After the soil was added to the WCL cell, a maximum pH of 7.7 ± 0.1 was quickly reached, after which, the pH slowly decreased as indicated by the positive slope (increasing H^+ concentration) recorded by the H^+ ISE. This response is mirrored in the measured E_h and indicates pH control of the soil-solution E_h. The measured pH (and E_h) of the calibration solution and the soil solution is dependent on the P_{CO2} in the WCL cell headspace. Prior to launch, the WCL calibration solution was sealed under an 8 mbar P_{CO2} atmosphere and, after arriving on Mars, the solution was dispensed after the empty WCL sample cell had equilibrated with the Martian atmosphere. After the calibration solution was dispensed, the P_{H2O} in the sealed WCL cell (~11 mbar at 8.4°C) exceeded the external atmospheric pressure and the cell P_{CO2} was reduced from an initial ~8 mbar by displacement with $H_2O(g)$ induced by repeated venting of the cell. Based on laboratory tests, the predicted P_{CO2} in the WCL headspace (resulting from cell venting and CO_2 desorption from solution) just prior to sample addition was ~2 mbar. This P_{CO2} level is consistent with the measured pH of 7.7 ± 0.1 and the presence of a saturated calcium carbonate solution in the WCL cell. Following the initial rapid change in pH and E_h upon soil addition, there is a slow decrease in soil solution pH and a corresponding increase in E_h that has been attributed to the addition of reagent $BaCl_2$ [*Kounaves et al.*, 2010a].

[13] The observed decrease in the ORP electrode response upon addition of the Rosy Red sample was ~110 mV, which is slightly less than what is expected based on the measured pH change (Figure 1). One possible explanation for this behavior is a small contribution to the E_h by an oxidized soluble soil component. This possibility is shown in Figure 3 as demonstrated by the addition of ppm levels of peroxide to the Phoenix salt analog mixture. However, Figure 3 is not meant to suggest that the WCL data indicates the presence of peroxide, it is only meant to show that the possibility of low levels of peroxides or other oxidizing species can not be excluded based on the measured ORP of the solution. As shown in equation (1), the solution E_h depends on a weighted average of oxidized and reduced species in solution and does not measure a specific redox couple. However, in general, E_h will increase with an increase in the activity of oxidized species and decrease with an increase in the activity of reduced species.

[14] Despite the presence of nitrate in the WCL calibration solution, the difference between the E_h of the analog Phoenix salt mixture measured in water was small compared to measurements made in calibration solution (Figure 2). If measured under Mars P_{CO2} conditions in the WCL using water rather than WCL test solution, the expected E_h of the Rosy
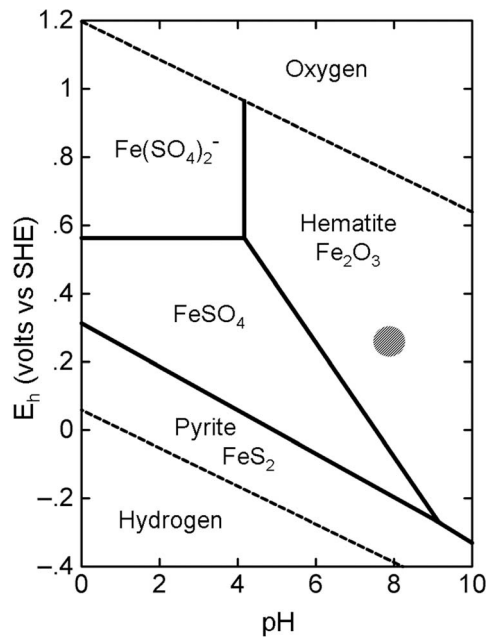
Figure 4. Eh-pH diagram showing the phase stability fields at 8.4°C based on the Mars soil sample ion concentrations given in Table 1 and $10^{-3} > [Fe^{2+}] > 10^{-9}$.

Red soil solution would ~300 mV, which is slightly higher than the WCL measured value.

[15] The general sensitivity of E_h measurements to small concentrations of reduced iron can be seen in Figure 3. After the addition of sample to the WCL cell, the stability of soil species will depend on the soil-solution pH and E_h. Under the Rosy Red sample solution conditions, with a pH of 7.7 and E_h of 253 mV, thermodynamically Fe^{2+} (aq) is unstable and iron would predominately be present as sparingly soluble Fe^{3+} species. However, as can be seen in Figure 3, under the WCL test conditions oxidation of Fe^{2+}(aq) is slow, allowing the detection of very low levels (<1 ppm) of soluble ferrous iron. This result is consistent with modeled (Geochemist's Workbench®) phase stability fields, which based on the ion concentrations in Table 1 (and $10^{-3} > [Fe2+] > 10^{-9}$) predict hematite as the stable iron bearing species for a soil solution at the WCL measured pH and E_h values (Figure 4).

5. Conclusions

[16] The E_h behavior of the Mars Rosy Red sample can, in general, be reproduced in the laboratory using a salt mixture that quantitatively replicates the sample's soluble ion content as measured on Mars. Observed changes in E_h are dominated by the formation of a saturated carbonate solution upon sample addition and corresponding headspace P_{CO2} and solution CO_3^{2-}, HCO_3^-, and CO_2 concentrations. A slight difference (~10 mV) between the measured solution E_h and

pH changes, suggests the possibility of a contribution(s) to the system ORP from a species that was not measured with the WCL ISEs. Experimental simulations show that ppm soil levels of metal peroxides or similar oxidants could explain this difference. However, other explanations are possible, since E_h measurements are non-specific and do not provide a means for species identification. Highly redox active species, such as soluble Fe^{2+}, if present, are below detectable levels (<1 ppm). Although Phoenix soils contain significant levels of perchlorate (a strong oxidant under certain conditions), and possibly low levels of more chemically reactive oxidants, the E_h of the soil is moderate and firmly in the range expected for habitable soils.

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