

Perchlorate in Martian soil: Evidence and implications. M.H. Hecht¹, D.C. Catling², B.C. Clark³, L. DeFlores¹, K. Gospodinova⁴, J. Kapit⁴, S. P. Kounaves⁴, D. W. Ming⁵, R. C. Quinn⁶, S. J. West⁷, S.M.M Young⁴, and the Phoenix Team. ¹Jet Propulsion Laboratory, California Institute of Technology (michael.h.hecht@jpl.nasa.gov), ²Department of Earth Sciences, University of Bristol, UK, ³Lockheed Martin, Denver, CO (ret.), ⁴Department of Chemistry, Tufts University, Medford, MA, ⁵NASA Johnson Space Center, Houston, TX, ⁶SETI Institute, Mountain View, CA, ⁷Invensys Process Systems, Foxboro, MA

Introduction: The Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) was one of two payload elements on the Phoenix Lander for analyzing soil excavated by the spacecraft robotic arm. A suite of four instruments (Figure 1), MECA comprises two microscopes (optical and atomic force) [1], a probe that is inserted into the soil to evaluate water in all phases by means of thermal, electrical, and relative humidity measurements (TECP) [2], and four single-use wet chemistry cells (WCL)[3] that are the primary subject of this report. Interest in soluble constituents that define the environment for microbial life drove the selection of an aqueous chemistry experiment for Phoenix. Microscopy and TECP results as well as results from the Thermal and Evolved Gas Analyzer (TEGA) also contribute to our understanding of the unusual aqueous chemistry the WCL results revealed.

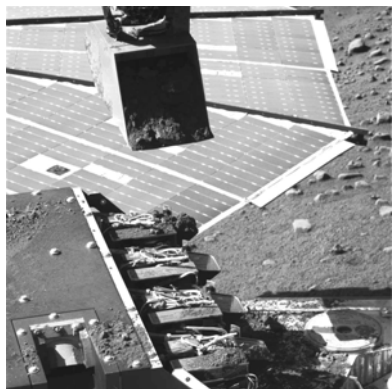


Fig. 1: MECA receiving a sample from the robotic arm. The four WCL cells are shown at right, the microscope entry port at lower left. The TECP is out of sight, folded above the scoop at the top of the picture.

Design of the WCL experiment was hampered by a nearly complete lack of knowledge of the likely soluble ions, range of concentration, solubilities, or even pH of the soil. A starting point was the known elemental composition of martian soils as determined by the Viking landers [4], Pathfinder [5], and MER [6,7]. Elemental composition, however, says little about solubility and only indirectly suggests the species of salt likely to be present. Nonetheless, a reasonable expectation was that the WCL would find largely sulfates, with measurable amounts of chlorides and small amounts of bromides. Carbonates were considered possible but were expected to be difficult to quantify because of limited solubility. Accordingly, the design was triply redundant with respect to chloride and pH measurement (potentially indicative of carbonate) and,

since sulfates cannot be directly sensed by ISEs, included a provision for titration with BaCl_2 .

The experiment: Elements of one WCL cell are shown in Figure 2. Ion selective electrodes were utilized for the WCL because of their ability to span orders of magnitude in concentration at the cost of some specificity. Following *in situ* calibration, up to 1 cm^3 of martian soil was delivered into 25 ml of an aqueous leaching solution and allowed to equilibrate while cation and anion concentration, pH, total conductivity, oxidation-reduction potential, and cyclic voltammetry were measured.

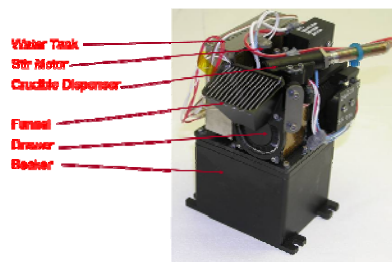


Fig. 2: One of four WCL cells showing the sampling port and actuators. Sensors line the interior of the black beaker

Results: Samples were collected and analyzed both from the surface and at the ice/soil boundary from the interior of a polygon (attempts to analyze a sample from a polygon boundary were unsuccessful). There were no statistically significant differences in the measured chemical species from sample to sample. In each sample the salts seemed to dissolve and stabilize in a matter of minutes.

The fortuitous inclusion of an ISE sensitive to the Hofmeister series, intended to monitor nitrate in the calibration salts, allowed detection of the perchlorate ion at a solution concentration of approximately 2 mM (this quantity of perchlorate would overwhelm any other signal, making the identification unambiguous). By comparison, the Cl^- concentration was less than 0.5 mM. Additional confirmation was offered by a negative offset in the Ca^+ signal, an unusual anion-cation sensor interference unique to perchlorate [8,9]. In at least one sample TEGA observed a mass 32 peak with a 325°C onset, a response consistent with oxygen evolved from decomposition of perchlorate [10].

After correction of the Ca^{++} signal for the perchlorate effect, the approximate concentration of the cations Mg^{++} , Ca^{++} , Na^+ , and K^+ in solution (within a factor of two) was found to be 4.4, 0.3, 2.3, and 0.4

mM respectively, averaged over three samples. The relative concentrations suggest that most of the ClO_4 is likely associated with Mg^{++} , Na^+ , or both, though solution equilibria may skew the cation distribution. The excess of cations over directly sensed anions implies the presence of additional anions. At the measured pH of 8.3 ± 0.5 only a small amount of the detected carbonate is soluble [11], leaving sulfate as the likely counter-ion for the remainder of the Na^+ and Mg^{++} .

Discussion: Perchlorates are highly water soluble and extremely inert in solution (they are commonly used as supporting electrolytes). Though no heterogeneity was seen by Phoenix, the affinity for water suggests that concentrated deposits of perchlorate should mark historical liquid water. Once concentrated, the presence of perchlorate increases the plausibility of pools of liquid, since perchlorate salts with divalent cations are deliquescent, and some saturated solutions have freezing points in the range of the martian frost-point (around -70°C) [12,13].

Using $\text{Mg}(\text{ClO}_4)_2$ as an example, it can be seen in Figure 3 that the range of temperature and pressure measured by the TECP [14] (presumably typical of summer conditions at these latitudes) overlaps the branch of the phase diagram representing the hexahydrate and the octohydrate. Environmental conditions to the right of this line would be required to produce the liquid super-eutectic state, presuming that the water vapor flux into the soil is sufficient to saturate the perchlorate at the given temperature.

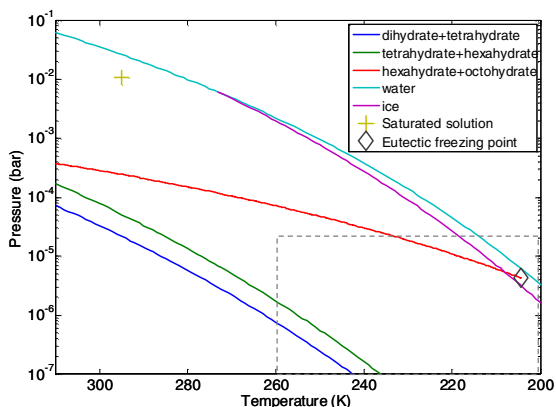


Fig. 3: Phase diagram of $\text{Mg}(\text{ClO}_4)_2$ extrapolated from [12] with water and ice for reference. Eutectic freezing point from [13]. The dashed box indicates the range of water partial pressure and temperature measured in soil by TECP [14].

Though technically an oxidant, perchlorate is highly stable at ambient martian or terrestrial temperatures and is unlikely to cause oxidation of organics (though it may confound attempts to detect organics thermally as was attempted by Viking and by the Phoenix TEGA experiment). Certain terrestrial mi-

croorganisms not only survive perchlorate but can utilize it as an energy source [15] coupled with a suitable reduced nutrient. Saturated brines of perchlorate and other salts can have very low water activity, so an adequate source of H_2O would be needed to support metabolic activity

While rare on Earth, natural perchlorates are found in the Atacama desert [16] and other arid locations [17], though typically at concentrations orders of magnitude lower than those found on Mars. Occasional findings of perchlorate at the parts per thousand level are likely due to concentration by evaporation. Terrestrial perchlorates result from photochemical processes in the atmosphere, and it is likely that the source of the perchlorate on Mars is similar [18].

Ultimately, the significance of perchlorate derives from the chemical potential energy stored in large quantities in a stable form. This energy can be utilized by microbes or by humans, and it is responsible for the remarkable affinity of perchlorate for water, evidenced by its solubility, deliquescence, and freezing point depression. If the total perchlorate budget on Mars were comparable to the chloride budget on Earth, it is intriguing to consider a history where shallow oceans of divalent perchlorate salt brines buffer the global frostpoint at temperatures not dissimilar to Mars today.

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