

tice sites of calcium carbonate and affect Mars' soil geochemistry, and calcium carbonate can cement small soil grains and change the physical properties of the surface of Mars.

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- The onset temperature for this endothermic peak is similar to the calcite decomposition onset temperature of 738°C measured in the TEGA engineering qualification model (17). Other carbonates have decomposition temperatures that are lower than that of calcite.
- In a calibration run on the TEGA engineering qualification model with a known amount of calcite, we found the heat of transition to be 2550 J/g, which implies 2.4 mg of CaCO₃ in the Wicked Witch sample.
- Estimation of the concentration of calcium carbonate in the sample is uncertain because the mass of sample in the oven is not tightly constrained. We estimate that this error is on the order of ± 25%.
- The cause of this delay will be explored in planned laboratory experiments in the future. The plumbing temperatures are heated to greater than 35°C, so one would not expect CO₂ to condense out on any plumbing surfaces. The sol 70 run shows that this effect is not due to a background signal.
- A martian solar day has a mean period of 24 hours 39 min 35.244 s and is referred to as a sol to distinguish this from a ~3% shorter solar day on Earth.
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- A previous experiment suggested that carbonate could form in relatively dry Mars-like conditions as submicrometer coatings on soil particles (5). However, the results from this study cannot be extrapolated over time because the experiments did not proceed beyond a monolayer of carbonate. A more comprehensive experimental study under Mars-like conditions showed that, in a given time span, carbonate forms on the surface of basaltic particles in an amount that increases with the thickness of films of water around the particles (30, 31). Growth of more than a monolayer of carbonate occurs with logarithmic reaction kinetics. For damp or wet conditions (meaning 0.1 to 0.5 g H₂O per g soil, equivalent to 10² to 10³ monolayers of water), the number of CO₂-reacted monolayers of substrate, *L*, per particle is found empirically to follow the relationship (30, 32) $L(t) = D \log_{10}(1 + t/t_0)$ (Eq. 1). Here, the constant of proportionality *D* is ~1 monolayer CO₂/log₁₀t for powdered basalt, while *t*₀, which represents a time scale for CO₂ adsorption or dissolution in H₂O, is ~10⁻² to 10⁻³ days. Because the Phoenix site contains material that was likely ejected from the nearby Heimdall crater up to 0.6 billion years ago (27), or 2.2 × 10¹¹ (Earth) days ago, the number of monolayers reacting with CO₂ can be calculated from Eq. 1 as ~13 to 14. By stoichiometry, 1 mol of CO₂ generates 1 mol of carbonate, so it follows that the mass fraction, *F*, of carbonate produced under these “damp” or “wet” soil conditions would be $F = M \times [(L A_s/A)/N_A]$ (Eq. 2), where *M* is the molar mass of carbonate (100 g/mol for CaCO₃), *A*_s is the specific surface area of the particles, $A = 2 \times 10^{-19} \text{ m}^{-2} \text{ molecule}^{-1}$ is the area taken up by a CO₂ molecule in reaction with the surface (32), and *N*_A is Avogadro's number. Basalt glasses pulverized to 0.1 to 1 micrometer size have *A*_s ~1 to 10 m²/g (33), whereas 17 m²/g was estimated for Viking lander 1 soil (34). Substituting numerical values into Eq. 2 gives a carbonate mass fraction up to 20 wt % for continuously “wet” conditions. In contrast, under persistently dry or vapor conditions (meaning zero to a few monolayers of H₂O), the fraction of carbonate produced is smaller because the kinetic coefficient *D* is smaller. *D* was measured up to 0.07 monolayers CO₂/log₁₀t at 6.6 mbar and -15°C (24), giving up to 0.8 wt % in Eq. 2. Other values of *D* for dry or vapor conditions ranged from ~0.01 to 0.2, but high values occurred only at higher CO₂ pressures, up to 995 mbar (32).
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- We acknowledge the work of the Robotic Arm team in delivering the samples to TEGA and WCL and the contributions of the engineers, scientists, and managers who made these instruments and the analysis of their data possible, including H. Enos, C. Fellows, K. Harshman, M. Finch, M. Williams, M. Fitzgibbon, G. Droege, J. M. Morookian, V. Lauer, D. C. Golden, R. Chaney, H. Hammack, L. Brooks, M. Mankey, K. Gospodinova, J. Kapit, C. Cable, P. Chang, E. Coombs, and S. Stroble. The Phoenix Mission was led by the University of Arizona, Tucson, on behalf of NASA and was managed by NASA's Jet Propulsion Laboratory, California Institute of Technology, of Pasadena, CA. The spacecraft was developed by Lockheed Martin Space Systems, Denver.

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Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site

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The Wet Chemistry Laboratory on the Phoenix Mars Lander performed aqueous chemical analyses of martian soil from the polygon-patterned northern plains of the Vastitas Borealis. The solutions contained ~10 mM of dissolved salts with 0.4 to 0.6% perchlorate (ClO₄) by mass leached from each sample. The remaining anions included small concentrations of chloride, bicarbonate, and possibly sulfate. Cations were dominated by Mg²⁺ and Na⁺, with small contributions from K⁺ and Ca²⁺. A moderately alkaline pH of 7.7 ± 0.5 was measured, consistent with a carbonate-buffered solution. Samples analyzed from the surface and the excavated boundary of the ~5-centimeter-deep ice table showed no significant difference in soluble chemistry.

The elemental composition of the martian surface has been measured in situ by the two Viking landers (1), the Mars Path-

finder lander (2), and the two Mars Exploration Rovers, Spirit and Opportunity (3, 4) with the use of x-ray fluorescence spectrometry. Elemental

analysis does not, however, predict the solution chemistry of the soil (5), which is important because it is the soluble constituents that are of primary importance to biological activity, prebiotic organic synthesis, and the thermophysical properties of any liquid solution. The only prior aqueous experiments were by the Viking missions in 1976, but these focused on specific protocols

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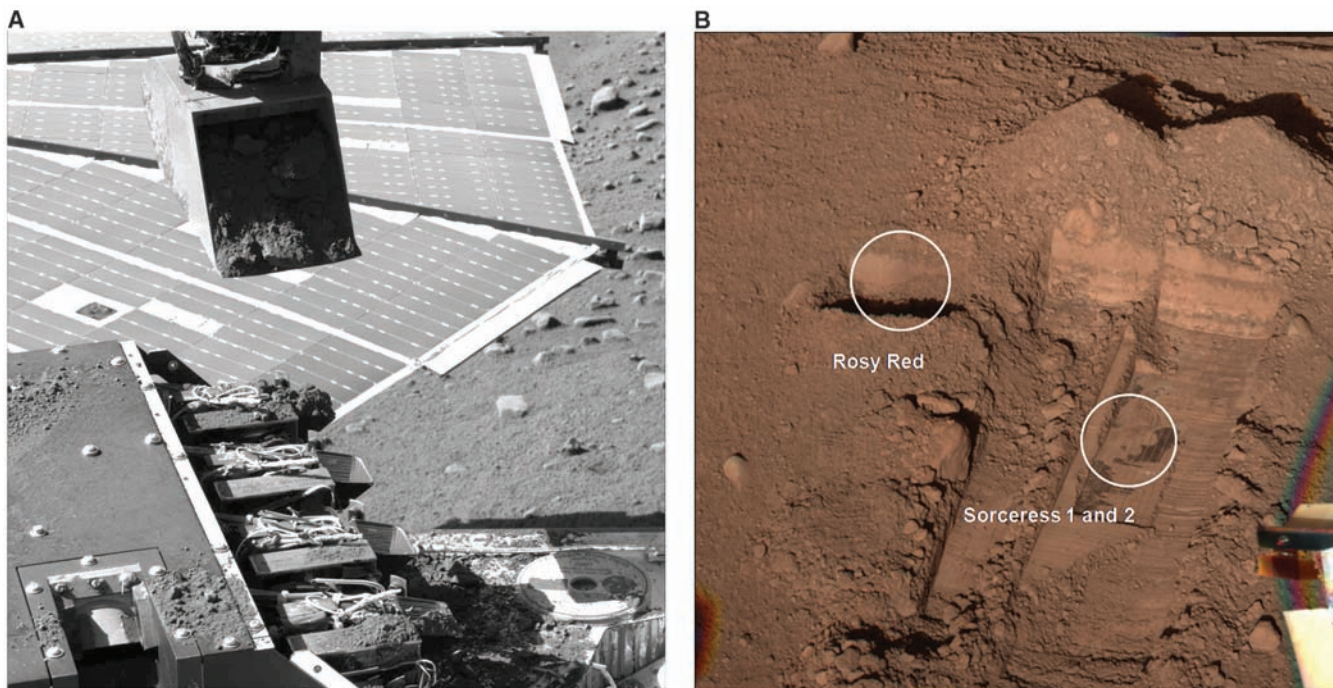


Fig. 1. (A) The Phoenix robotic arm is poised to deliver a sample to one of the four WCL cells. The sample previously delivered to the cell on the far end did not successfully pass through the screen, and this cell was used as a blank. The single chute in the foreground is for the delivery of samples to the microscopes. The SSI image is from sol 102; the length of the box is 35 cm. (B) The three successful WCL samples were acquired by the Phoenix robotic

arm and delivered from the locations shown in this image. The picture is a mosaic of two SSI images acquired on sol 31 at wavelengths of 600, 530, and 480 nm to approximate RGB color. The first WCL sample (Rosy Red), from the small divot on the left, consisted primarily of surface material. The second and third samples (Sorceress 1 and 2) were acquired by scraping at the ice-soil boundary from the large trench on the right (Snow White).

seeking to detect metabolic processes indicative of life (6, 7), and only evolved gases were analyzed.

The Phoenix spacecraft (8) landed in the northern plains of Mars on 25 May 2008 carrying several soil analysis instruments, among them a Wet Chemistry Laboratory (WCL). The four single-use cells (9) comprising the WCL were part of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) instrument suite (10, 11). Samples from the landing site, which was dominated by several centimeters of a loosely consolidated regolith above a hard, icy sheet of permafrost, were excavated by a robotic arm. The WCL analyzed three of those samples (Fig. 1).

Using ion-selective electrodes (ISEs) (12), the WCL measured solution concentration of the cations Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , and Na^+ ; the H^+ ion (pH); and the halide ions, Cl^- , Br^- , and I^- . A Hofmeister anion ISE was intended to monitor nitrate from a LiNO_3 reference electrolyte that was part of the leaching solution, but was ultimately used for perchlorate detection (13). Other electrodes measured total conductivity and oxidation-reduction potential, performed cyclic voltammetry (in part to detect soluble iron), and redundantly measured halide concentration with chronopotentiometry. Deployable BaCl_2 crucibles were included to detect sulfate by titration using a Ba^{2+} ISE.

Each WCL analysis was designed to extend over two nonconsecutive martian solar days (sols) (14), with up to 10 hours of operation during each sol. On the first sol, 25 ml of an aqueous leaching solution containing micromolar levels

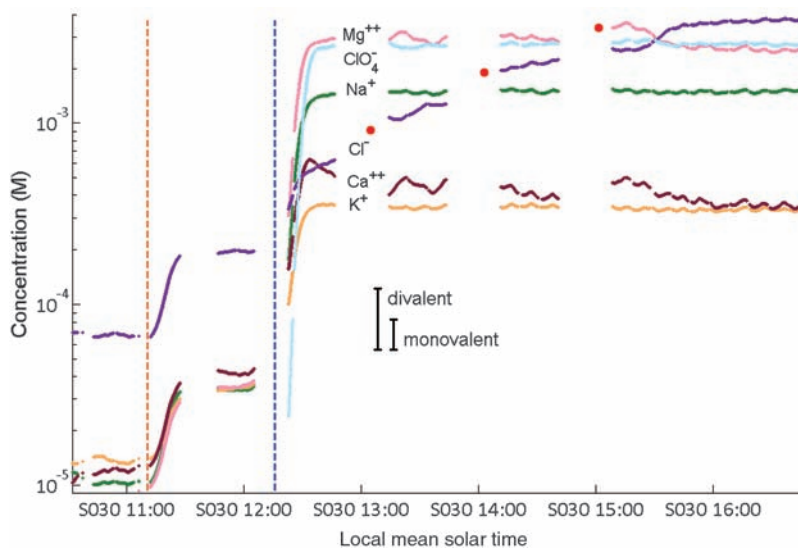


Fig. 2. Sensor response for the analysis of a 1-cc sample (Rosy Red on sol 30) after delivery to 25 ml of solution in the WCL. The responses of the sensors are shown after filtering, determination of activity from the calibration, and conversion to solution concentration with the Debye-Hückel formula. The first vertical dashed line marks delivery of a crucible containing calibration salts; the second dashed line marks the sample addition. Red circles are chloride measurements using chronopotentiometry. The time axis is labeled by sol and local mean solar time. The small error bar is typical for monovalent ions, and the larger error bar is for divalent ions (relative errors are smaller). The slow increase in Cl^- is attributed to a source within the WCL assembly, not the martian soil. For ClO_4^- , a small contribution due to interference from NO_3^- in the leaching and calibration solutions has been subtracted.

of calibrant ions was thawed and delivered to the sensor-lined beaker, which was maintained at a temperature of 5° to 10°C. A standard addition of

soluble salts provided a second calibration point (except for the sample Sorceress 1, where the addition apparently failed), and then up to 1 cm^3 of

soil was added and allowed to equilibrate with the solution as it was stirred and monitored. Results from the two calibration solutions were compared to prelaunch data to determine an intercept (pivot) voltage for the logarithmic scale and to verify that there were no significant changes from the predetermined slope. The nominal slope at 25°C is 59/n mV per decade of concentration, where *n* is the ion charge. A systemic error estimated at less than ±5 mV, resulting from the determination of the slope and pivot voltage, corresponds to a 20% error in concentration for monovalent ions and 50% for divalent ions (15).

All sensors responded promptly upon addition of soil to the solution (Fig. 2 and Table 1). Allowing for variable sample sizes (for Sorceress 1 the sample drawer was only two-thirds to three-fourths full), the differences among the samples were not significant. The most striking response was the increase of the Hofmeister lipophilicity series anion sensor signal by three orders of magnitude, attributed to the perchlorate ion at an average concentration level of 2.4 (±0.5) mM (16). The concentrations of Mg²⁺, Na⁺, and K⁺ in the solution increased over the initial calibrant concentrations by an average of 3.3 (±1.7), 1.4 (±0.3), and 0.39 (±0.08) mM, respectively. The Ca²⁺ signal decreased from its calibration level, a behavior characteristic of the Ca²⁺ ISE in the presence of perchlorate (17, 18). The true level of Ca²⁺ was estimated as 0.60 (±0.3) mM from laboratory calibration of the Ca²⁺ sensor in the presence of the measured concentration of perchlorate. For Cl⁻, an increase of 0.47 (±0.09) mM relative to the calibrant level was observed upon soil addition. Over the course of the experiment the Cl⁻ level appeared to slowly increase, but the observation of similar behavior in an empty cell suggests that leakage from the BaCl₂ crucibles is the most likely explanation (19). Thus, we only attribute to mineralogical chloride the prompt increase in Cl⁻ after soil addition.

The pH of all three samples at the partial pressure of CO₂ of the sample cell (~3 mbar) was 7.7 (±0.5). Although Mars rover results led to inferences of widespread acidic soil (20), Viking data analysis suggested a pH consistent with the WCL result (21). The pH of the soil solution was not measurably affected by addition of 4 mg of 2-nitrobenzoic acid, with a p*K*_a of 2.2; this result indicates that the soil provides pH buffering at ≥1 mM, most likely by calcium carbonate in the soil (22). The leaching solution itself is unbuffered.

The measurement strategy of the WCL experiment was to identify as many major anions and cations as possible, and to measure the overall conductivity of the sample solution in order to identify gaps. Discrepancies among cation, anion, and conductivity measurements imply the presence of unmeasured ionic species. The activity-weighted concentrations of only the measured ions predict conductivity of about one-half the measured total solution conductivity (Table 1), which suggests that any unmeasured constituents are of comparable or lower concentrations than those measured directly. Although charge balancing in complex fluids can

be problematic, comparison of the charge concentration associated with anions and cations suggests that the missing species are anions. Bicarbonate could account for this entire deficit, but soluble sulfate is also a candidate. Measurements by Viking Lander 1 (1), the Mars rovers (23–25), and near-infrared spectroscopy of the martian surface (26, 27) suggest a soil sulfur content of 5 to 9 weight % SO₄, at a uniform molar ratio for S:Cl of 4:1. Although it cannot be assumed that soils encountered by Phoenix and by the Mars rovers are the same, the complete absence of sulfate at the Phoenix site would nonetheless be surprising. If the entire anion deficit were sulfate, it would constitute ~0.8% of the total sample mass, so if sulfate is present in the soil at higher concentrations, it must be in a sparingly soluble form such as CaSO₄.

Independent evidence for perchlorate was provided by the Thermal and Evolved Gas Analyzer (TEGA) (Fig. 3) (22). Although oxygen, sulfur, and hydrazine (from thrusters) are candidate fragment ions for mass 32, the observed temperature range (325° to 625°C) is consistent with O₂ evolu-

tion by the thermal decomposition of perchlorate salts, as demonstrated both in a laboratory testbed (28) and by literature values (29). Hydrazine would evolve at lower temperature, and no other S fragments (e.g., ³²S¹⁶O₂⁺, ³²S¹⁶O⁺) were detected during the ramp.

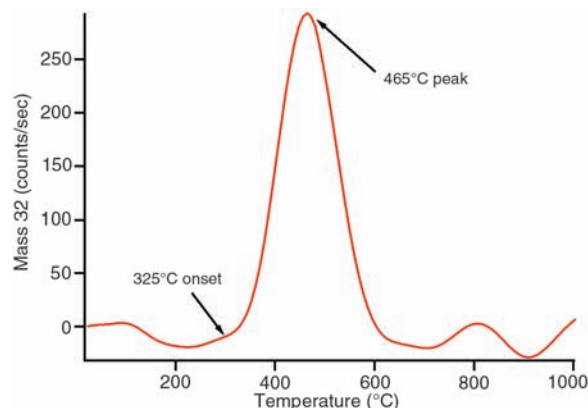
The characteristics of perchlorate salts derive largely from the chemical energy stored in the highly metastable, fully oxidized molecule, which at high temperature is used for rocket fuel and generation of breathing oxygen. At low temperature, in aqueous solution, most perchlorates are soluble and do not readily react or precipitate. This affinity for water suggests that a history of liquid water would be indicated by sharp gradients in evaporitic perchlorate salt concentration. The homogeneous perchlorate concentration found at two depths at the Phoenix site argues against such a history. If liquid water were present in the past, aeolian mixing, cryoturbation, or subsequent influx of perchlorate have since obscured the record.

The distribution of cations in the solution suggests that at least some of the perchlorate in

Table 1. Ion concentration determined shortly after addition of each of the three samples. Quantities in the last seven rows are derived from concentrations. Concentration error is ±20% (monovalent ions) or ±50% (divalent ions). Total charge includes Li⁺ and NO₃⁻ from the leaching solution. The Sorceress 1 sample volume was smaller than the others (i.e., more dilute) by an estimated 25 to 35% and is therefore not included in the average. The pH reading from Sorceress 2 was comparable to the others, but noisy. Note that measured conductivity also includes ions from the leaching solution.

	Rosy Red	Sorceress 1	Sorceress 2	Average
Na ⁺ (mM)	1.4	1.10	1.4	1.4
K ⁺ (mM)	0.36	0.17	0.39	0.38
Ca ²⁺ (mM)	0.55	0.42	0.6	0.58
Mg ²⁺ (mM)	2.9	2.20	3.7	3.3
Cl ⁻ (mM)	0.6	0.24	0.47	0.54
ClO ₄ ⁻ (mM)	2.6	2.10	2.2	2.4
Conductivity (μS/cm)	NA	1000	1400	1400
pH	7.7	7.6	—	7.7
Equivalent conductivity at 25°C (μS/cm)	NA	1370	1900	1900
ClO ₄ ⁻ mass (mg)	6.50	5.25	5.50	6.00
Conductivity at 25°C (calculated, μS/cm)	815	636	918	866
Total cation charge (mM)	9.66	7.51	11.39	10.53
Total anion charge (mM)	4.30	3.44	3.77	4.04
Anion deficit, if monovalent (mM)	5.36	4.07	7.62	6.49
Anion deficit, if divalent (mM)	2.68	2.04	3.81	3.25

Fig. 3. Evolved mass 32 (O₂) analysis for the Baby Bear surface sample from TEGA. The curve is the difference between the first high-temperature ramp and the second-day reheat for the high-temperature ramp.



the soil is in the form of $Mg(ClO_4)_2$ or $Ca(ClO_4)_2$. Alkaline earth perchlorate salts have a strongly exothermic affinity for water, are deliquescent, and have eutectic freezing points in the range of $-70^\circ C$ (30, 31). The dynamics of thermally driven exchange of water vapor between the buried ice and the overlying perchlorate-rich soil may make a wet super-eutectic solution possible at certain temperatures, possibly explaining the time-varying cohesiveness of the soil at the Phoenix site (32). If, as was found by Phoenix, most of the chlorine on Mars is in the form of perchlorate, it lends support to the conjecture that low-temperature brines, stable at or below the present-day mean martian frost-point, may be responsible for contemporary liquid-mediated processes such as gully formation (33).

The deliquescent properties of perchlorate salts may also play a role in controlling soil and atmosphere water content. Hydrogen levels measured by Odyssey's Gamma Ray Spectrometer (GRS), corresponding to several percent of water in martian surface soil over large swaths of equatorial Mars, have been attributed to hydrated salts (34). Subsequently, the concentration of chlorine was mapped and found to correlate with the hydrogen (35). In the form of $Mg(ClO_4)_2$, perchlorate in equilibrium with the martian atmosphere would be coordinated as a mixture of hexahydrate and octahydrate, depending on temperature and humidity (30), such that the mass of water would be 3 to 4 times that of the chlorine, a value similar to the GRS ratios. At the Phoenix site, perchlorate in this form would take up and release more water with temperature than the entire peak summer column density in the atmosphere, which suggests that it may even be a factor in zonal control of atmospheric humidity.

Several microorganisms on Earth are known to harvest energy by anaerobic reduction of the perchlorate molecule (36, 37). Under martian conditions, perchlorate does not readily oxidize organics (although the presence of perchlorate salts may indicate a vigorous oxidant-forming chemistry in the martian atmosphere or on the surface), but the low water activity associated with such a strongly desiccating substance may inhibit many forms of life. The high-temperature oxidizing properties of perchlorate will, however, promote combustion of organics in pyrolytic experiments, compromising the ability of Phoenix's TEGA experiment to readily detect organics (38) and possibly affecting the Viking mass spectrometer experiments (39).

If perchlorate on Mars has a photochemical origin similar to that on Earth (40), and if the chlorine directly originates from volcanic gas, then perchlorates are likely to be characteristic only of later geologic time because on early Mars volcanism would have produced a reducing atmosphere (41). Perchlorate may be favored at high latitudes if ice is important as a reaction surface for adsorbed species or if its formation depends on ozone, which is barely detectable in the tropics but is abundant in the spring-winter circumpolar regions (42, 43).

In summary, aqueous chemical analysis of martian soil has revealed that most of the soluble chlorine is in the form of perchlorate. This find-

ing has possible relevance to water sequestration, control of soil and atmospheric humidity, gully formation, habitability, and resource use for human exploration.

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- Following the Nernst equation, the ISE voltage response is logarithmic in concentration over several orders of magnitude of concentration, making ISEs well suited for analysis of a solution of unknown composition. Most of the ISEs in the WCL use polyvinyl chloride membranes doped with ionophores that respond predominantly to one ionic species. In a complex mixture, the ISEs may respond to more than one species. Processing of the signal requires the use of selectivity coefficients to deconvolve the response.
- The relative sensitivity of the Hofmeister series ISE to perchlorate over nitrate is 1000:1, and substantial quantities of perchlorate will overwhelm any other signal. If, as was observed, >1 mM perchlorate accounts for the observed signal, it would require >1000 mM nitrate to produce the same response. This would correspond to more than the mass of the entire sample.
- A martian solar day has a mean period of 24 hours 39 min 35.244 s and is referred to as a sol to distinguish this from a $\sim 3\%$ shorter solar day on Earth.
- The slope of the Nernst relationship is consistent with preflight calibration, but the reference (pivot) point can shift and must be calibrated relative to the reference solution. The 5-mV error is a conservative estimate of the accuracy of that calibration and combines the effects of noise and drift. It does not reflect a standard deviation.
- Possible sources of perchlorate contamination, such as pyrotechnic devices, have been systematically eliminated as explanations for the signal. The only source of perchlorate sufficient to produce the measured level in soil would be the third-stage rocket engine, which is many levels of protection removed from the lander and uses ammonium perchlorate (which was not detected by the WCL). The lander retrorockets use hydrazine as fuel.
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