Identification of the perchlorate parent salts at the Phoenix Mars landing site and possible implications

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Abstract

In 2008 the Phoenix Mars lander Wet Chemistry Laboratory (WCL) measured 0.6 wt% of perchlorate (ClO₄⁻) in the martian soil. A crucial question remaining unanswered is the identity of the parent salt phase(s) of the ClO₄⁻. Due to the ClO₄⁻ ion’s high solubility and stability, its distribution, chemical forms, and interactions with water, could reveal much about the aqueous history of the planet. Until now, the presence of Ca(ClO₄)₂ as a parent salt has been considered unlikely because based on its eutectic point and model calculations, highly insoluble calcium carbonates and sulfates would serve as sinks for Ca²⁺ rather than Ca(ClO₄)₂. Thus, the dominant ClO₄⁻ parent salt has been assumed to be a hydrated form of Mg(ClO₄)₂. Here we report on the results of a new refined analysis of the Phoenix WCL sensor data, post-flight experiments run on a flight-spare WCL unit, and numerous laboratory analyses. The results show that the response of the Ca²⁺ sensor is extremely sensitive to the counter ion of the ClO₄⁻ salt, and that addition of martian soil to the Phoenix WCL that contained only Mg(ClO₄)₂ or Ca(ClO₄)₂ would have produced a very different response than what was observed on Mars. A series of analyses were run with Ca²⁺ sensors and calibration solutions identical to those used on Phoenix, and with a Mars simulant formulation known to give the same results as on Mars. The response of the Ca²⁺ sensor at various ratios of added Mg(ClO₄)₂ to Ca(ClO₄)₂ gave the best fit to the Phoenix data with a sample containing ~ 60% Ca(ClO₄)₂ and 40% Mg(ClO₄)₂. These results suggest that the Ca(ClO₄)₂ in the Phoenix soil has not been in contact with liquid water and thus did not form by evaporation or sublimation processes. Had the highly soluble Ca(ClO₄)₂ come into contact with liquid water, then the presence of soluble sulfates would have, on evaporation formed only CaSO₄. The presence of Ca(ClO₄)₂ and Mg(ClO₄)₂ phases at roughly the CaCO₃ to MgCO₃ ratio suggests that since their production, the ClO₄⁻ phases have remained in a severely arid environment, with minimal or no liquid water interaction. The formation of the Ca(ClO₄)₂ and Mg(ClO₄)₂ is also consistent with the interaction of atmospherically deposited HClO₄ with Ca- and Mg-carbonates and may also contribute to CO₂ enrichment of ¹⁸O and may contribute in explaining why carbonates on the surface are at much lower levels than expected from an earlier global wet and warm period.
1. Introduction

The discovery by the Phoenix Mars lander Wet Chemistry Laboratory (WCL) of perchlorate (ClO$_4^-$) in the soil at the northern latitudes of Mars (Hecht et al., 2009; Kounaves et al., 2010), and by virtue of planet-wide dust storms most likely present globally, has altered our view of martian soil chemistry. A crucial question still remaining unanswered about the perchlorate is the identity of its parent salt phase(s). Due to the ClO$_4^-$ ion’s high solubility and stability, its distribution, chemical forms, and interactions with water, could reveal much about the aqueous history of the planet. Although stable under Mars ambient conditions, ClO$_4^-$ is the highest oxidized form of chlorine and is an indicator for the possible presence of other highly reactive oxidizing oxychlorine (ClO$_x^-$) species such as chlorite (ClO$_2^-$) and hypochlorite (ClO$^-$. The presence of oxychlorines such as ClO$_4^-$ and ClO$_3^-$ have broad implications for Mars’ aqueous geochemistry, astrobiology, human habitability, in controlling soil and global atmospheric water content (Catling et al., 2010; Hanley et al., 2012), and for the presence and detection of organics by the Curiosity rover and other missions (Navarro-González et al., 2010). The ability of perchlorate salts to depress the freezing point of water to the -70°C range is especially significant for possible formation of liquid brines under current Mars ambient conditions (Chevrier et al., 2009) and the present day formation of gullies (Malin et al., 2006) and seasonally recurring slope lineae (McEwen et al., 2011).

During the summer of 2008, the Phoenix WCL analyzed three 1 cm$^3$ soil samples (Hecht et al., 2009; Kounaves et al., 2010a, 2010b; Quinn et al., 2011). Several of the measured ionic concentrations in the WCL reflected equilibrium values and not those of the species actually present as salts in the soil sample (Kounaves et al., 2010b). Thus, of those originally reported (Hecht et al., 2009) only Cl$^-$ (~0.4mM), ClO$_4^-$ (~2.5mM), K$^+$ (~0.4mM), and Na$^+$ (~1.4mM), were present both in the 25mL of solution and in the soil at equivalent concentrations. The measured concentrations in solution of Ca$^{2+}$ (~0.6mM), Mg$^{2+}$ (~3.3mM), and by titration SO$_4^{2-}$ (~5.5mM), are equilibrium concentrations controlled by the presence of solid calcite, magnesite, and epsomite/gypsum. The Ca$^{2+}$ and Mg$^{2+}$ from all added soluble salts came to chemical equilibrium within seconds and thus their concentrations do not reflect those of any other soluble salts comprised of these ions (Kounaves et al., 2010b).

The discovery of ClO$_4^-$ was significant, its concentration representing 0.5-0.7 wt% ClO$_4^-$ in the soil samples analyzed by the Phoenix WCL. The presence of the ClO$_4^-$ was also confirmed by its unique effect on the WCL Ca$^{2+}$ sensor (Kounaves et al., 2010a, 2009), and by the Thermal and Evolved Gas Analyzer (TEGA) (Boynton et al., 2009). More recently, the results from Curiosity's Sample Analysis at Mars (SAM) instrument also indicate the presence of a perchlorate of martian origin (Leshin et al., 2013; Glavin et al., 2013). The WCL analyses along with previous mission results (Gellert et al., 2004), indicate that Mg$^{2+}$, Ca$^{2+}$, Na$^+$, K$^+$, or Fe$^{2/3+}$, either singly or as a mixture, could be potential ClO$_4^-$ counterions, however several of these ions can be eliminated as viable candidates. The concentration of soluble Fe$^{2/3+}$ in the WCL solutions is insignificant and if present has been estimated at < 100 µM (~ 0.01 wt%) and would only constitute < 3% of a parent salt. Pre-flight characterization tests clearly showed that at higher concentrations soluble iron would have been detected by poisoning several of the WCL ion sensors and affecting the redox potential (Kounaves et al., 2010b; Quinn et al., 2011). The concentration of K$^+$ (~0.4mM), even if totally paired with ClO$_4^-$, would only constitute < 15% of a parent salt. The Na$^+$ (~1.4mM), if totally paired with ClO$_4^-$, would account for < 50% of the parent salt. On the other hand, from the results of the WCL and TEGA, Mg(ClO$_4$)$_2$ or Ca(ClO$_4$)$_2$ could constitute 100% of the perchlorate salt in the soil, either alone or in combination. Data, provided by the Phoenix Surface Stereo Imager (SSI) spectra further constrains the potential candidate cations to Ca$^{2+}$ and Mg$^{2+}$ (Cull et al., 2010). Finally, recent results from Curiosity's SAM Evolved Gas Analyzer (EGA) analysis of the Rocknest bedform material, and comparison with the laboratory SAM testbed, indicate that Ca-perchlorate is the best candidate over Fe- Mg-, Na- and K- perchlorates (Leshin et al., 2013).
Until now, it has been hypothesized that Ca(ClO₄)₂ is not a reasonable parent salt candidate because based on its eutectic point and model calculations, highly insoluble calcium carbonates and sulfates would serve as sinks for Ca²⁺ rather than Ca(ClO₄)₂ (Hanley et al., 2012; Chevrier et al., 2009; Marion et al., 2010). Thus, the dominant parent salt of the ClO₄⁻ has been assumed to be a hydrated form of Mg(ClO₄)₂. Here we report on a new refined analysis of the Phoenix WCL sensor data, post-flight experiments run on a flight-spare WCL unit, and numerous laboratory analyses. The objectives of this effort were to (1) constrain the ClO₄⁻ parent salts present in the Phoenix soil and (2) discuss the implications of the identified parent salts for the martian climate and geochemistry. The results show that the addition of martian soil to the Phoenix WCL that contained Mg(ClO₄)₂, Ca(ClO₄)₂, or a mixture, would have produced a different response from the Ca²⁺ sensor depending on the ratio of the two parent salts.

2. Analytical Methodology

The Phoenix WCL consisted of four identical units, each one composed of an upper actuator assembly with a drawer for adding soil, five reagent pellets, and a tank containing 25 mL of “leaching” solution (TS20), and a lower beaker assembly containing a stirrer, and an array of sensors for measuring the ionic species and parameters of the soil/solution mixture. The array included twelve ion-selective electrode (ISE) sensors for measuring Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺, Ba²⁺ (for SO₄²⁻), Cl⁻, Br⁻, and I⁻, two pH sensors, and a sensor originally intended for detecting NO₃⁻, but which is three orders more sensitive to ClO₄⁻ (Kounaves et al., 2009).

To confirm the observations made on Mars by the Phoenix WCL and during pre-flight characterizations with two flight-spare units on Earth, a new set of analyses were run using new Ca²⁺ sensors fabricated and calibrated identically to those used in the Phoenix WCL and previously described in detail (Kounaves et al., 2009). The test solutions for these analyses were prepared by adding the appropriate salts to 25 mL of D.I. water to give the TS20 and TS21M calibration solutions (Table 1) used on Mars and as previously described (Kounaves et al., 2009, 2010a). The TS20 solution acted as the leaching solution and also contained all the ionic species for providing the first calibration point for the sensors. The TS21M solution was the TS20 solution to which the first calibrant crucible had been added and gave the second point for calibrating the sensors. Both individual sensors and a test-bed unit with the WCL sensor array were used for the analyses. To ensure that the sensors were exposed to perchlorate for the first time when the sample was added, a new sensor was used for each analysis. This required a rather large number of Ca²⁺ sensors to be fabricated and characterized, since sensors often display different sensitivity and potential depending on many subtle factors, including membrane composition and fabrication procedures. The WCL test-bed, using the payload system electronics, was initially calibrated with a set of solutions containing all the ionic species ranging from 10⁻⁵ to 10⁻² M, identical to the preflight calibrations. All sensors were calibrated and responded as they had during preflight characterizations.

Unless otherwise indicated, the Mars simulant additions used in these analyses consisted of a solid mixture of the published salt composition for the Phoenix site soil (Kounaves et al., 2010b). Only salts that provided soluble ionic species either directly or through an equilibrium were used since the WCL sensors only measured the soluble ionic species in solution. Other components in the soil are not significantly soluble. Each addition to be made to 25 mL of the TS21M solution consisted of 40 mg calcite (pulverized Icelandic Spar, ≈4 wt% in the soil), 20 mg magnesite (pulverized magnesite from Pedra Preta Mine, Brazil, ≈2 wt% in the soil), 30 mg epsomite (reagent grade MgSO₄·7H₂O, Sigma Aldrich, ≈3 wt% in the soil), 0.8 mg KCl (reagent grade KCl, Sigma Aldrich, ≈0.04 wt% each in the soil), 3 mg NaHCO₃ (reagent grade NaHCO₃, Sigma Aldrich, ≈0.8 wt% in the soil), and the appropriate mole ratio amounts of Ca(ClO₄)₂ and/or Mg(ClO₄)₂ (reagent grade Mg(ClO₄)₂·6H₂O and Ca(ClO₄)₂·4H₂O, Sigma Aldrich) to give the 2.5 mM ClO₄⁻ concentration in solution. The combination of Mg- and Ca-perchlorate salts were added in various portions ranging from 100% Mg(ClO₄)₂ to 100% Ca(ClO₄)₂. Some analyses used the above simulant formulation, but included substitution or mixtures containing NaClO₄, NaClO₃, Ca(NO₃)₂, or CaCl₂. The conductivity of these solutions was approximately 1500 μS/cm, similar to what was measured on Mars for the Sorceress 1 and 2 soil samples. Unless otherwise
indicated, analyses were run using at a temperature of 5.0 ± 0.1°C, a $P_{CO_2}$ of ~ 8 mbar, and a stirring rate of ~ 100 rpm.

3. Results

Shown in Figure 1 for reference is the response on Mars of the Phoenix WCL Ca$^{2+}$ sensor after the first soil delivery to the two WCL units on sols 30 and 41. The presence of the ~0.6 wt % ClO$_4^-$ in the soil affected each sensor’s transduction mechanism, producing a -29 mV bias per decade of ClO$_4^-$ above 10$^{-5}$ M (Kounaves et al., 2010a, 2003). For the WCL ISE sensors, the transduction of the ionic concentration of a species present at the sensor/solution interface to a measurable potential is due to the selective partitioning of an ion from the aqueous phase into the sensor membrane via complexation by a carrier ligand known as an ionophore. The resulting charge separation is measured by the internal and external reference electrodes. (Kounaves et al., 2009). Processes or ionic species (other than the primary ion) which affect the partitioning or ionophore transport mechanism will alter the measured potential of the sensor.

The response observed on Mars is in contrast to what would be expected if the soil contained a soluble Ca-salt and no ClO$_4^-$ had been added. Figure 2 shows the response of the calcium sensor in a laboratory flight-spare WCL immediately after addition of the Mars simulant, but without ClO$_4^-$ present. The sensor in response to the Ca$^{2+}$ released from the calcite shows a ~ +20 mV increase compared to the TS21 calibration solution. The signal levels off at the Ca$^{2+}$ concentration controlled by the CaCO$_3$ equilibrium (~0.7 mM) and the CO$_2$ concentration in the WCL headspace (3 mbar).

Figure 3 shows the response of the Ca$^{2+}$ sensor in one of the flight-spare WCL units after addition of a simulant containing the salts identified on Mars and Mg(ClO$_4$)$_2$ equivalent to the 2.5 mM ClO$_4^-$ measured on Mars. The behavior after the addition is drastically different than that observed on Mars for the sol 30 and 41 samples. This response had been observed in later laboratory analyses on Earth, but lacking resources to pursue further, was discounted because it did not affect the quantitative determination of Ca$^{2+}$ and was considered an artifact.

As described above for the ISE transduction mechanism, the response of the Ca$^{2+}$ sensor observed on Mars requires at a minimum the presence of 2.5 mM ClO$_4^-$ and a highly soluble source(s) of Ca$^{2+}$ (Kounaves et al., 2010a; Bühlmann et al., 1998). Other highly-soluble sources for the Ca$^{2+}$ could include CaCl$_2$, Ca(ClO$_4$)$_2$, and Ca(NO$_3$)$_2$. However, CaCl$_2$ would be present at insufficient concentration, since only 0.4 mM Cl$^-$ was measured by WCL. Both Ca(ClO$_4$)$_2$ and Ca(NO$_3$)$_2$ would also be present at insignificant amounts since the WCL solution electrical conductivity and charge balance account for the major portion of the known anionic species measured. In order to better constrain the possible ratios of the Ca- to Mg-perchlorates, and ensure that the different Ca$^{2+}$ used did not bias the results, a series of analyses were run with each using a new Ca$^{2+}$ sensor and calibration solution identical to those used on Phoenix, and with a Mars simulant formulation shown to give the same results as on Mars (Kounaves et al., 2010b). Figure 4 shows representative results for the response of the Ca$^{2+}$ sensor at various ratios of added Mg(ClO$_4$)$_2$ to Ca(ClO$_4$)$_2$. The sample containing ~ 60% Ca(ClO$_4$)$_2$ and 40% Mg(ClO$_4$)$_2$ shows the best fit to the Phoenix data. At a 50/50 mixture, the effects of the Ca$^{2+}$ have disappeared and the effects of the ClO$_4^-$ from the Mg(ClO$_4$)$_2$ salt are evident.

4. Discussion

The presence of Ca(ClO$_4$)$_2$ has been considered unlikely based on evaporation and sublimation models showing that highly insoluble calcium carbonates and sulfates (e.g., calcite and gypsum) act as sinks for Ca$^{2+}$ rather than a highly soluble species such as Ca(ClO$_4$)$_2$ (Hanley et al., 2012; Marion et al., 2010). If these models are accurate, our results lead to the conclusion that the Ca(ClO$_4$)$_2$ in the Phoenix soil has not been in contact with liquid water and thus did not form by evaporation or sublimation processes. Had the highly soluble Ca(ClO$_4$)$_2$ come into contact with liquid water, then the presence of ~ 1.3% soluble sulfates (Kounaves et al., 2010b) would have, on evaporation or sublimation, formed CaSO$_4$.
and not Ca(ClO₄)₂. It is possible that ClO₄⁻ salts could also form by gas-solid reactions (Catling et al., 2010), and though at such low temperatures they might be inhibited, kinetic time scales are probably much faster than geologic time scales. On the other hand, it is clear that they would be very difficult to form without at least a molecular film of water. In the case of a carbonate alteration process, the ClO₄⁻ salts could be formed within such a film but would be isolated from other salts such as sulfates and thus unable to react.

As extremely arid conditions are approached, it becomes more difficult to eliminate residual brines. The humidity and temperature measured by the Phoenix Temperature and Electrical Conductivity Probe (TECP) (Zent et al., 2010) showed several instances where the liquid stability field crossed the eutectic points of Ca- and Mg- perchlorate (~196 and ~206 K, respectively) and thus deliquescence would have been possible. However, even though thermodynamically liquids could form at such low temperatures, they are most likely kinetically hindered because of insufficient time and the extremely low partial pressure of water. Recent deliquescence studies have been carried out at relatively high temperature and relative humidity (Gough, R. V., et al., 2011). Deliquescence kinetics are dependent on available water (pressure) and temperature. Although thermodynamically favored, it is not clear if the kinetics allow “enough time” for deliquescence to occur. Another issue (as compared to crystal nucleation) is the nucleation of brine films on the surface of crystals. The very early stage is adsorption of water molecules on the surface of crystals which is strongly dependent on water vapor and temperature. Thus, even if favored, the timescale during which the liquid phase would be stable is only a matter of a few hours (Chevrier et al., 2009), and might not be enough if the deliquescence kinetics are relatively slow.

Even though it has been proposed that Mars’ northern polar site is prone to higher temperatures (and thus liquid water) during extreme obliquity cycles (Lasker et al., 2002), our findings point to an extremely arid environment at this location, very likely since the formation of the Heimdal Crater ejecta blanket ~600 Myrs ago (Heet et al., 2009). There are locations on Mars where the presence of current liquid water has been suggested by the formation of such features as active gullies (Malin et al., 2006), dune and slope streaks (Kereszturi et al., 2010; Kreslavsky et al., 2009), and seasonally recurring slope lineae (McEwen et al., 2011), however, in some cases alternate mechanisms for their formation are possible and in general definitive evidence is still lacking. It is also possible that at such locations Ca(ClO₄)₂ is not present.

Our conclusions of extreme prolonged aridity are also supported by two other lines of evidence. First, the Phoenix microscopy data indicates a single method of production for particles < 11 μm and that they are primarily produced by aeolian weathering under very dry conditions. The production time for a soil with 6% phyllosilicates by volume is up to 400 kyr, however, if we assume that < 0.05% by volume of the Phoenix soil is < 2 μm, this implies that the soil has been exposed to liquid water for a total of << 5 kyr, insignificant in comparison to the ~600 Myr age of the site (Heet et al., 2009). There is also substantial geomorphological evidence for cryoturbation and lack of aeolian features at the site, implying that the soils are locally derived and mixed with a small fraction of windblown dust (Heet et al., 2009). Thus, at minimum, a fraction of the soil may have been transported, but along with the local soil, was never exposed to liquid water. Secondly, the degree of aridity at the Phoenix site can also be inferred by comparison with the level and homogeneity of ClO₄⁻ in the soils of two different locations in the McMurdo Dry Valleys (MDV) of Antarctica, the highly arid University Valley (UV) at ~2000 m elevation vs. the often-wet Taylor Valley at ~100 m. The ClO₄⁻ in UV is found homogeneously at the ppb levels throughout the valley in both horizontal and vertical directions. This is in contrast to TV where the ClO₄⁻ is hard to find and splotchy, often found at only one depth and absent in pits only a meter away (Kounaves et al., 2010c; Stroble et al., 2012). These results are consistent with the Phoenix site being significantly more arid and for a much greater period of time, as evidenced by the relatively high concentration of ClO₄⁻ (6×10⁶ ppb) on Mars compared to University Valley (600 ppb). This is especially stark when noting the Phoenix site age (likely ≥600 Myr) in contrast to that of UV (~1.2 Myr).

Although Mg- and Ca-carbonates are expected to be present on the martian surface as alteration products from a presumed thicker ancient CO₂ atmosphere and liquid water, their quantity, form, and distribution, has been difficult to ascertain. Measurements by the Mars Global Surveyor’s Thermal Emission Spectrometer (TES) (Bandfield et al., 2003), and the Mars Reconnaissance Orbiter’s (MRO)
Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) (Ehlmann et al., 2008), indicate levels in the 2-5 wt% range and dominated by magnesite. Calcium carbonate may have been present but was not detectable at < 5 wt%. The Mars Express Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) did not detect any carbonates above its detection limit of 4 vol% (Bibring et al., 2006). On the surface, the Mars Exploration Rover Spirit in Gusev crater, identified outcrops with 16-34 wt% magnesium-iron carbonate (Morris et al., 2010).

Most relevant are the soil analyses of the Phoenix TEGA sampled from the same locations as WCL and reported to contain Ca and Mg carbonate minerals as 3-6 wt% calcite, dolomite, or ankerite, and 1-2 wt% magnesite or siderite, in any combination or intermediate compositions (Boynton et al., 2009; Sutter et al., 2012). However, caution must be used since the exact ratio of the Ca/Mg-carbonates may have been skewed by the release of low temperature CO2 by other sources such as organics and/or perchlorate reactions with calcite and not just Mg-or Fe-carbonate (Cannon et al., 2012). Taking all of this into account, TEGA gives Ca:Mg ratios that range from about 3:2 to 6:1.

The above processes all suggest that over millions of years, deposited HClO4, with even only molecular films of H2O present, would react with Ca- and Mg-carbonates minerals such as calcite and magnesite to produce the corresponding perchlorates (4HClO4 + CaCO3 + MgCO3 → Ca(ClO4)2 + Mg(ClO4)2 + 2H2O + 2CO2). Such a scenario would then initially result in perchlorate parent salts approximately resembling the ratio of the predominate carbonate minerals, and would remain nearly so if no interaction with water and sulfates occurred. The best fit data reported here for the Ca/Mg-perchlorate ratio 3:2 (Fig. 4), lies within the lower range of the TEGA results for the Ca:Mg ratio of 3:2 to 6:1. This observed similarity of the perchlorate and carbonate ratios would support the hypothesis that there has been no significant interaction of these salts with water, at least at the Phoenix site, perhaps since the Heimdal crater impact. One might also speculate that such a process may play a role as a global mechanism for the CO2 cycle in the martian atmosphere, and could explain why carbonates in the dust and surface are at such low levels, having been “neutralized” by millions-billions of years of acidic HClO4 deposition.

If a substantial fraction of the martian atmospheric CO2 was formed by reaction of HClO4 with CaCO3, then it should contribute to the oxygen isotopic composition of the atmospheric CO2 and would thus result in enriched 18O. This would be expected since the CaCO3 was most likely precipitated by low-temperature reactions of aqueous CO2 with Ca2+ released from parent basaltic minerals (Boynton et al., 2009). Recent isotopic measurements by the Phoenix (Niles et al., 2010) and Curiosity (Webster et al., 2013) show a martian atmospheric CO2 with a δ18O enrichment of +31‰ and +48‰, respectively. Even though the H2O + CO2 ↔ H2CO3 equilibrium by itself would be sufficient to provide isotopic exchange with H2O and result in fractionation of oxygen isotopes and strongly enrich CO2 in 18O, under severely arid conditions the contribution via reaction (1) above could contribute to the enrichment.

5. Conclusion

The reanalysis of the WCL calcium sensor behavior on Mars, and numerous laboratory experiments on WCL flight and testbed sensors, provide strong evidence that the soil samples analyzed by the Phoenix WCL contain ~ 3:2 ratio of Ca(ClO4)2 to Mg(ClO4)2 phases. This result is contrary to current hypotheses that Mg(ClO4)2 is the dominant phase and that Ca(ClO4)2 would be absent based on its eutectic point and models showing that insoluble Ca-carbonates and sulfates would serve as sinks for Ca over highly soluble Ca(ClO4)2. Recent results from Curiosity also indicate that Ca(ClO4)2 provides the most reasonable match with the SAM data. Even though a reliable association between the duration of aridity and the presence of the ClO4 may be difficult and could only be accurately determined if the rate of ClO4 deposition was known, our results also led to the conclusion that the soil at the landing site may have not interacted with liquid water of any form, perhaps for as long as 600 Myr. Two other lines of evidence also provide strong support; the observations from the Phoenix optical and atomic force microscopy of particle size distribution (PSD) indicating the soil has been exposed to liquid water for < 5,000 years; and data from the highly arid and consistently sub-zero 1.2 Myr soils of University Valley, showing the distribution of atmospherically deposited ClO4 in those soils is easily mobilized and altered by molecular
water films. This makes it highly improbable that the $\text{ClO}_4^-$ in the martian soil would have remained immobilized and unreacted for 600 Myr. The presence of $\text{Ca(ClO}_4)_2$ and $\text{Mg(ClO}_4)_2$ phases at roughly the CaCO$_3$ to MgCO$_3$ ratio suggests that since their production, the $\text{ClO}_4^-$ phases have remained in a severely arid environment, with minimal or no liquid water interaction. The formation of the $\text{Ca(ClO}_4)_2$ and $\text{Mg(ClO}_4)_2$ is also consistent with the interaction of atmospherically deposited HClO$_4$ with Ca- and Mg-carbonates and may also contribute to atmospheric CO$_2$ enrichment in $^{18}$O and carbonates on the surface and explain why it is at much lower levels than would have been expected as a result of an earlier global wet and warm period.

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**References**


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Table 1
Composition of WCL leaching solution with concentrations of ionic species in TS20 prepared preflight and concentrations of ionic species in solution after addition of calibrant to TS20 solution on Mars, equivalent to preflight TS21M solution.

<table>
<thead>
<tr>
<th>Solution Ionic Species</th>
<th>TS20 Leaching Solution</th>
<th>TS21M Calibrant Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration [mol/L]</td>
<td>Concentration [mol/L]</td>
</tr>
<tr>
<td>Li⁺</td>
<td>1.00×10⁻³</td>
<td>1.00×10⁻³</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.00×10⁻⁵</td>
<td>3.40×10⁻⁵</td>
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<td>NH₄⁺</td>
<td>1.00×10⁻⁵</td>
<td>3.40×10⁻⁵</td>
</tr>
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<td>K⁺</td>
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<td>1.94×10⁻⁴</td>
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<tr>
<td>NO₃⁻</td>
<td>1.03×10⁻³</td>
<td>1.10×10⁻³</td>
</tr>
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</table>
Fig. 1. After an initial addition of 25 mL of TS20 solution containing $1 \times 10^{-5}$ M Ca$^{2+}$ and a mixed salt pellet to raise concentration to $4.2 \times 10^{-5}$ M Ca$^{2+}$, the soil sample was added and the sensors monitored for the remaining portion of the martian sol. Shown is the response for (a) WCL cell-0 FU020 on sol 30 and (b) WCL cell-1 FU018 on sol 41. In contrast to the positive response expected for the Ca$^{2+}$ sensor (Fig. 2), the presence of the ClO$_4^-$ in the martian soil at ~ 0.6 wt% produced a negative offset.
Fig. 2. Response of the calcium sensor in a flight-spare WCL unit after addition of a Mars simulant which did not contain any ClO$_4^-$ . The sensor in response to the Ca$^{2+}$ released from the calcite shows a ~ +20 mV increase compared to the TS21 calibration solution. The signal levels off at the Ca$^{2+}$ concentration controlled by the CaCO$_3$ equilibrium (~0.7mM) and the CO$_2$ concentration in the WCL headspace (3 mbar).

Fig. 3. Addition to a WCL flight-spare unit of 25 mL of TS20 solution containing 1×10$^{-5}$ M Ca$^{2+}$, a mixed salt pellet to raise concentration to 4.2×10$^{-5}$ M Ca$^{2+}$, and a Mars simulant containing 1.25 mM Mg(ClO$_4$)$_2$, under conditions similar to those present on Mars. Unlike the response on Mars, the flight-spare response of the Ca$^{2+}$ sensor showed an initial sharp negative spike. The signal eventually reaching a plateau controlled by the Ca-carbonate equilibrium.
Fig. 4. Initial positive and negative spikes result from Ca\(^{2+}\) and/or ClO\(_4^-\) in solution by rapid dissolution of the Ca(ClO\(_4\))\(_2\), and/or Mg(ClO\(_4\))\(_2\), respectively. With only Ca(ClO\(_4\))\(_2\) added, sensor instantaneously responds to the increase of Ca\(^{2+}\) and then to the ClO\(_4^-\). Signal levels off at the potential dictated by the CaCO\(_3\) equilibrium. With only Mg(ClO\(_4\))\(_2\), sensor responds negatively to increase of ClO\(_4^-\) and then equilibrates to the potential dictated by the concentration of Ca\(^{2+}\) from CaCO\(_3\).