Measurements of Oxychlorine species on Mars

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\textbf{Abstract:} Mars landed and orbiter missions have instrumentation capable of detecting oxychlorine phases (e.g. perchlorate, chlorate) on the surface. Perchlorate (\textasciitilde 0.6 wt\%) was first detected by the Wet Chemistry Laboratory in the surface material at the Phoenix Mars Landing site. Subsequent analyses by the Thermal Evolved Gas Analyser aboard the same lander detected an oxygen release (\textasciitilde 465°C) consistent with the thermal decomposition of perchlorate. Recent thermal analysis by the Mars Science Laboratory’s Sample Analysis at Mars instrument has also indicated the presence of oxychlorine phases (up to 1.2 wt\%) in Gale Crater materials. Despite being at detectable concentrations, the Chemistry and Mineralogy (CheMin) X-ray diffractometer has not detected oxychlorine phases. This suggests that Gale Crater oxychlorine may exist as poorly crystalline phases or that perchlorate/chlorate mixtures exist, so that individual oxychlorine concentrations are below CheMin detection limits (\textasciitilde 1 wt\%). Although not initially designed to detect oxychlorine phases, reinterpretation of Viking Gas Chromatography/Mass Spectrometer data also suggest that oxychlorine phases are present in the Viking surface materials. Remote near-infrared spectral analyses by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument indicate that at least some martian recurring slope lineae (RSL) have spectral signatures consistent with the presence of hydrated perchlorates or chlorates during the seasons when RSL are most extensive. Despite the thermal emission spectrometer, Thermal Emission Imaging System, Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité and CRISM detection of hundreds of anhydrous chloride (\textasciitilde 10–25 vol\%) deposits, expected associated oxychlorine phases (>5–10 vol\%) have not been detected. Total Cl and oxychlorine data sets from the Phoenix Lander and the Mars Science Laboratory missions could be used to develop oxychlorine versus total Cl correlations, which may constrain oxychlorine concentrations at other locations on Mars by using total Cl determined by other missions (e.g. Viking, Pathfinder, MER and Odyssey). Development of microfluidic or ‘lab-on-a-chip’ instrumentation has the potential to be the next generation analytical capability used to identify and quantify individual oxychlorine species on future landed robotic missions to Mars.

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\textbf{Key words:} Perchlorate, chlorate, Mars, chlorine

\textbf{Introduction}

Perchlorate (\(\text{ClO}_4^–\)) was measured at the Mars Phoenix landing site using the Microscopy Electrochemistry and Conductivity Analyser Wet Chemistry Laboratory (WCL) (Hecht et al. 2009; Kounaves et al. 2010) and its presence, based on oxygen release, was also confirmed by the Phoenix Thermal Evolved Gas Analyser (Hecht et al. 2009). Based on the initial detection of perchlorate, spectral analysis using the Phoenix Surface Stereo Imager indicated a possible heterogeneous distribution of hydrated-perchlorate at the Phoenix landing site (Cull et al. 2010). Although in contrast, WCL data show a relatively uniform abundance in the samples analysed (Kounaves et al. 2010; Toner et al. 2014). Following the detection of perchlorate at the Phoenix site, a reanalysis of the Viking Gas Chromatography/Mass Spectroscopy (GCMS) data indicated the presence of oxychlorine phase like perchlorate at both Viking landing sites (Navarro-González et al. 2010). Results from the Sample Analysis at Mars (SAM) instrument suite on board the Curiosity rover suggest the presence of oxychlorine phases, likely perchlorate and chlorate (\(\text{ClO}_3^–\)), in Gale Crater (Glavin et al. 2013; Leshin et al. 2013; Archer et al. 2014; Ming et al. 2014; Freissinet et al. 2015). Remotely sensed infrared (IR) spectra acquired by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) are consistent with hydrated-chlorate or hydrated-perchlorate in recurring slope lineae (RSL) features on Mars (Ojha et al. 2015). These hydrated features appear to only be present during the summer.
Table 1. Total chlorine, perchlorate (ClO$_4^-$) and chloride (Cl$^-$) detected on Mars as determined by surface and orbital instrumentation.

<table>
<thead>
<tr>
<th>Mission</th>
<th>Soil/sediment</th>
<th>Detection method</th>
<th>Total Cl</th>
<th>Cl$^-$</th>
<th>ClO$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSL</td>
<td>John Klein mudstone$^d$</td>
<td>APXS</td>
<td>0.69 ± 0.03</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAM-EGA</td>
<td>–</td>
<td>–</td>
<td>0.39 ± 0.06$^n$</td>
</tr>
<tr>
<td>Cumberland mudstone$^d$</td>
<td>APXS</td>
<td>0.52 ± 0.02</td>
<td>–</td>
<td>–</td>
<td>0.12 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>SAM-EGA</td>
<td>1.19 ± 0.04</td>
<td>–</td>
<td>–</td>
<td>1.08 ± 0.04</td>
</tr>
<tr>
<td>Rosy red soil$^e$</td>
<td>WCL</td>
<td>0.05 ± 0.004</td>
<td>0.67 ± 0.007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phoenix</td>
<td>Sorceress 1 Soil$^e$</td>
<td>WCL</td>
<td>0.03 ± 0.001</td>
<td>0.68 ± 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sorceress 2 Soil$^e$</td>
<td>WCL</td>
<td>0.04 ± 0.001</td>
<td>0.62 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>Mars Reconnaissance orbiter</td>
<td>Recurring Slope Lineae$^f$</td>
<td>CRISM</td>
<td>–</td>
<td>–</td>
<td>Unknown</td>
</tr>
<tr>
<td>Mars odyssey</td>
<td>Chloride deposits$^{g,h}$</td>
<td>THEMIS</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mars express</td>
<td></td>
<td>OMEGA</td>
<td>10–25</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mars global surveyor</td>
<td></td>
<td>OMEGA</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mars Odyssey</td>
<td></td>
<td>THEMIS</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MER spirit</td>
<td>Gusev Soil$^{i,k}$</td>
<td>APXS</td>
<td>0.54–0.94 ± 0.08</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MER opportunity</td>
<td>Meridiani Soil$^{i,k}$</td>
<td>APXS</td>
<td>0.41–0.77 ± 0.06</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pathfinder</td>
<td>Ares Vallis Soil$^k$</td>
<td>APXS</td>
<td>0.55 ± 0.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VL1</td>
<td>Chryse Planitia Soil$^m$</td>
<td>XRF</td>
<td>0.7–0.9 ± 0.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VL2</td>
<td>Utopia Planitia Soil$^m$</td>
<td>XRF</td>
<td>0.3–0.6 ± 0.5</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

When the RSL are at their maximum spatial extent. Oxychlorine phases in this work refers to oxygen bearing Cl anions that fall into the series: hypochlorite (ClO$^-$), chloride (Cl$^-$), chlorate (ClO$_3^-$) and perchlorate (ClO$_4^-$). Hypochlorite and chlorite are typically thought of as intermediate phases involved in chlorate and perchlorate formation (e.g. Catling et al. 2010; Carrier & Kounaves, 2015) and may not accumulate in martian materials to the same level as perchlorate or chlorate. However, hypochlorite and chlorite in martian surface materials cannot be ruled out; therefore, oxychlorine will be the term used to account for all possible oxygen bearing Cl phases that may be present on Mars.

The occurrence of oxychlorine phases at widely spaced locations on Mars (Phoenix Landing site, Gale Crater and RSL features) suggests that oxychlorine phases may occur throughout the martian surface. The measurement of high chlorine (e.g. Clark et al. 1977; Rieder et al. 1997; Rieder et al. 2004; Gellert et al. 2006; Keller et al. 2006; Blake et al. 2013; Gellert et al. 2013) (Table 1) and chloride (Osterloo et al. 2008) concentrations all over Mars by orbital and landed instrumentation suggests that oxychlorine could be a component of these other chlorine detections. This is supported by the fact that oxychlorine phases are a component of the total Cl detected at that Phoenix and Gale Crater landing sites. IR spectroscopy and X-ray diffraction (XRD) analysis of Mars surface materials are capable of detecting oxychlorine phases such as perchlorate and chlorate. These techniques may thus be useful for identifying oxychlorine phases in locations where chlorine or chloride has been detected. Furthermore, where oxychlorine and chloride or chlorine have been determined, such relationships may be useful in constraining oxychlorine concentrations where only total chlorine or chloride data are available.

The goal of this review is to evaluate analytical techniques employed to detect and measure oxychlorine phases on Mars. The specific objectives of this review are to: (1) Discuss oxychlorine detection techniques employed on landed and orbital missions and their limitations; (2) Evaluate oxychlorine versus total Cl determinations from the Phoenix and Mars science laboratory (MSL) missions and how this relationship could be used to constrain oxychlorine levels at other sites (e.g. Viking, Mars Pathfinder, Mars Exploration Rovers, Mars Odyssey Gamma Ray Spectrometer (GRS)); and (3) Briefly discuss alternative analytical technology for detecting oxychlorine phases on future missions to Mars.

**Phoenix Lander WCL**

The WCL onboard the Phoenix Lander conducted the first analysis of soluble ionic species in the martian soil and resulted in the first direct detection of perchlorate on the martian surface. A detailed description of the Phoenix-WCL has been previously published (Kounaves et al. 2009) and is only briefly reviewed here. The WCL was consisted of an upper ‘actuator’ and a lower ‘beaker’ assembly. The actuator consisted of a titanium container that held 25 ml of deionized water plus ~10$^{-5}$ M concentrations of selected ionic species for initial
sensor calibrations; a drawer for accepting 1 cm$^3$ of soil through a screened funnel; a stirrer; and a reagent dispenser. The lower ‘beaker’ contained an array of sensors for determination of selected soluble ions, pH, and also solution properties such as electrical conductivity and redox potential ($E_{\text{h}}$).

Soil samples were successfully added and analysed in three of the four WCL cells, one from the surface on sol 30 (Rosy Red) and two from the top of the ice table ~5 cm in depth on sols 41 and 107 (Sorceress-1 and Sorceress-2). All three samples were found to contain ionic species similar to those generally measured on Earth, including mM levels in solution of Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, Na$^+$, K$^+$ and SO$_4^{2-}$, and a pH of ~7.7 (Kounaves et al. 2010). One ion-selective sensor in the WCL array, originally designated as a nitrate (NO$_3^-$) sensor, responds to a large number of anionic species with selectivity that follows the Hofmeister series (ClO$_4^->I^->SCN^-->$ ClO$_3^-->CN^-->Br^->BO$_3^{2-}->$ NO$_2^->Cl^-$). The response of this sensor to ClO$_4^-$ is three orders-of-magnitude greater than any other species. For all three WCL samples, a ~200 mV sensor response was observed (Fig. 1). The magnitude of this response exceeded the signal response limit, based on the sample size, for the possible concentrations of any other anionic species, with the exception of ClO$_4^-$. In other words, the sensitivity of the Hofmeister series electrode to anions other than perchlorate is insufficient to account for the magnitude of the sensor response. To definitively confirm the ClO$_4^-$ detection, laboratory analyses using flight-spare and/or identical sensors were used to eliminate all other possibilities. The concentration of ClO$_4^-$ in the Rosy Red, Sorceress-1 and Sorceress-2 soil samples have been reported ranging from 0.5 to 0.7 wt%; however recent reanalysis and refinements with decreased error (Fang et al. 2015) give solution concentrations of of 2.7, 2.2 and 2.5 mM, equivalent to 0.67, 0.68 and 0.62 wt% ClO$_4^-$ in the soil, respectively (Table 1).

In addition to measuring the concentration of the ClO$_4^-$ ion, the parent salt identity was determined by using the effect of the ClO$_4^-$ ion on the calcium (Ca$^{2+}$) sensor. A series of laboratory analyses at various ratios of added Mg(ClO$_4$)$_2$ to Ca(ClO$_4$)$_2$ demonstrated that the response of the Ca$^{2+}$ sensor would give the best fit to the WCL Mars data with a sample containing 60% Ca(ClO$_4$)$_2$ and 40% Mg(ClO$_4$)$_2$ (Kounaves et al. 2014a). The presence of Ca(ClO$_4$)$_2$ suggests that the soil at the Phoenix landing site has not been in contact with liquid water since formation. Subsequent dissolution of Ca (ClO$_4$)$_2$ in the presence of the soluble sulphates would have caused Ca$^{2+}$ to precipitate as insoluble CaSO$_4$ (Kounaves et al. 2014b) and the ClO$_4^-$ to reprecipitate as NaClO$_4$, KClO$_4$ and/or MgClO$_4$ (e.g. Marion et al. 2010; Toner et al. 2014). However, spectral analysis (0.455–1 μm) of the Phoenix soils is consistent with the presence of subsurface hydrated Mg-perchlorate patches that were interpreted to have formed by translocating Mg-perchlorate brines from the surface by liquid water thin films at low temperature (e.g. 206–245 K) (Cull et al. 2010). Mg-perchlorate deliquescents kinetics, although, may not be fast enough for the short periods of in which Mg-perchlorate brines are thermodynamically stable (Kounaves et al. 2014b). Nevertheless, more work is required to understand the possibility of post-depositional perchlorate translocation from the surface to the subsurface.

Even though the concentration of perchlorate present made it impossible to detect any other oxychlorine species like chlorate directly in the martian soil samples (Kounaves et al. 2010; Hanley et al. 2012), chlorate may be present in the Phoenix samples. Three recent discoveries, the presence of chlorate in the Mars meteorite EETA79001 (Kounaves et al. 2014b), the acquisition of orbital IR (1–3.92 μm) spectra consistent with the presence of hydrated Mg-chlorate (Ojha et al. 2015) and the formation of both ClO$_4^-$ and ClO$_3^-$ by UV on martian analogue CI-bearing mineral surfaces (Carrier & Kounaves, 2015), strongly support this possibility. The detection of chlorate in EETA79001 actually occurred at a molar concentration 2.8 × higher than perchlorate (Kounaves et al. 2014b). Furthermore, chlorates commonly occur with perchlorates in terrestrial deserts, which suggest that if oxychlorine formation processes on Earth and Mars are similar then chlorates may occur wherever there are perchlorates on Mars (Rao et al. 2010).
detected by presence of an endothermic transition and corresponding CO2 detection (Boynton et al. 2009).

The detection of evolved O2 by TEGA that began at 325°C and peaked at 465°C (Hecht et al. 2009) (Fig. 2(a)) is consistent with the presence of perchlorate in the Phoenix Landing site soil. Other O2 sources are possible, but the detection of perchlorate by the WCL instrument indicates that perchlorate is the likely O2 source. Perchlorate dehydration typically precedes its thermal decomposition (e.g. Marvin & Woolaver, 1945; Markowitz, 1963; Migdal-Mikuli & Hetmańczyk, 2008; Cannon et al. 2012).

Following dehydration, Na-, K- and Ca-perchlorate thermal decomposition results in O2 evolution and chloride formation:

\[M^{m+}(\text{ClO}_4)_n\cdot n\text{H}_2\text{O}\rightarrow M^{m+}(\text{ClO}_4)_n + n\text{H}_2\text{O}\]  
(1)

\[M^{m+}(\text{ClO}_4)_n\cdot \text{MCl}_z + z\cdot 2\text{O}_2\]  
(2)

Mg and Fe perchlorates dehydrate as above but instead form oxides and release Cl2 gas.

\[2\text{M(ClO}_4)_2\rightarrow 2\text{MO} + 7\text{O}_2 + 2\text{Cl}_2\]  
(3)

Any residual water vapour remaining in the oven area can react with the Cl2 to from HCl.

\[2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HCl} + 2\text{O}_2\]  
(4)

Hydrated forms of perchlorate are thought to be stable under martian atmospheric conditions (e.g. Robertson & Bish, 2011) and evolved water detected by TEGA suggests that the perchlorate could have been hydrated, though adsorbed water and other hydrated minerals could have contributed to water detected by TEGA (Smith et al. 2009).

Perchlorate thermal decomposition is characterized by an exothermic transition (e.g. Acheson & Jacobs, 1970), yet no exothermic transition was observed by TEGA. The Phoenix soil possesses oxidized Fe phases that likely consist of nanophase iron oxides (Seelos et al. 2008; Goetz et al. 2010) which may have interacted with perchlorate and minimize the detection of the exothermic transition. Laboratory thermal analysis of K-perchlorate mixtures with hematite (Fe2O3) demonstrated that as more hematite was added, the intensity of the perchlorate decomposition exotherm decreased (e.g. Lee & Hsu, 2001). This suggests that interactions with Fe-oxide phases in the Phoenix material may have suppressed the perchlorate decomposition exotherm.

No evolved Cl masses (e.g. m/z 35 Cl, m/z 36 HCl, m/z 70 Cl2) were detected by TEGA suggesting that either the perchlorate was Na, Ca or K-perchlorate or that Cl was removed from the gas stream by Ni-bearing components of the TEGA (Lauer et al. 2009). The Na-, K- and Ca-perchlorates mostly decompose to chloride phases with limited evolution of Cl (e.g. Marvin & Woolaver, 1945; Markowitz, 1963) indicating that perhaps these perchlorates are responsible for the O2 release. However, laboratory analogue studies of the WCL ion selective electrode analyses were consistent with the presence of Mg-perchlorate and Ca-perchlorate (Kounaves et al. 2014a). This suggests that at least some HCl from Mg-perchlorate decomposition could have been detected. The possibility exists that the Ni composition of the TEGA ovens could have reacted.

Fig. 2. (a) Evolved oxygen release versus temperature from the Phoenix Lander TEGA analysis of the Baby Bear (TEGA-BB) sample and the SAM–EGA of Gale Crater Rocknest (SAM-RN), John Klein (SAM-JK) and Cumberland (SAM-CB) samples. (b) Evolved HCl from the SAM–EGA of the SAM-RN, SAM-JK and SAM-CB materials. No Cl phases were detected by TEGA.
with evolved Cl species to form NiCl₂ and scrubbed the Cl from the gas stream and inhibit detection by the TEGA mass spectrometer (Lauer et al. 2009).

**MSL-SAM instrument**

**Background**

The main objectives of the SAM instrument were to search for evidence of organics and evaluate the volatile bearing mineralogy in the Gale Crater sediments (Mahaffy et al. 2012; Glavin et al. 2013; Leshin et al. 2013; Freissinet et al. 2015). The SAM instrument is composed of three ovens connected to a quadrupole mass spectrometer (QMS), gas chromatograph (GC) and tunable laser spectrometer TLS. Soil, sediment or drilled material is acquired and deposited into sample cups (~45–135 mg) that is then transferred to one of two ovens. The material in the cup is heated to ~860°C at 35°C min⁻¹ in a 0.8 sccm He purge held at 25 mbar. Direct analysis of the volatiles released from the sample over the entire temperature range is achieved in an evolved gas analysis (EGA) mode where a fraction (~1:800 split) of the gas flow was analysed directly by electron impact ionization and QMS. A select temperature range of gas is sent to the GCMS for organic analysis (Glavin et al. 2013; Ming et al. 2014; Freissinet et al. 2015). The gas is concentrated on a hydrocarbon trap cooled to 5°C and subsequently desorbed by heating to ~300°C followed by GC separation (GC-5: XBT-CLP, Siltek-treated stainless steel metal-chlorinated pesticides columns, 30 m length, 0.25 mm internal diameter and 0.25 μm film thickness) before detection by the thermal conductivity detector (TCD) and the QMS (GCMS mode). The detailed description of the SAM-EGA and GCMS modes and instrument parameters can be found elsewhere (Mahaffy et al. 2012; Glavin et al. 2013).

**SAM-EGA results**

The SAM-EGA has detected O₂ and HCl releases in all samples reported to date suggesting the presence of perchlorate or chlorate in the Gale materials (Leshin et al. 2013; Glavin et al. 2013; Ming et al. 2014) (Fig. 2(a) and (b)). The Rocknest (RN) eolian deposit and John Klein (JK) and Cumberland (CB) mudstones all evolved O₂ and HCl during pyrolysis. However, laboratory analyses of pure perchlorate phases do not yield O₂ and HCl at temperatures entirely consistent with the Gale detections (Glavin et al. 2013; Leshin et al. 2013; Ming et al. 2014). Iron-bearing phases (e.g. hematite) when mixed with perchlorate or chlorate are known to lower perchlorate and chlorate decomposition temperatures (Rudloff & Freeman, 1970; Lee & Hsu, 2001). Iron-oxide phases detected by CheMin in the Gale sediments (Bish et al. 2013; Blake et al. 2013; Vaniman et al. 2014) suggest that such phases could lower the O₂ release temperatures.

The amounts of O₂ for RN, JK and CB translates to 0.1–1.1 wt% ClO₄²⁻ or 0.1–1.2 wt% ClO₃⁻ (Archer et al. 2014; Ming et al. 2014) (Table 1). The amount of HCl evolved (0.006–0.04 wt%) is much less than what is calculated to be stochiometrically possible from O₂ releases, for chlorate or perchlorate. This suggests the presence of perchlorate/chlorate phases that do not evolve HCl may be present. For example, pure magnesium and iron perchlorate evolve HCl upon thermal decomposition, whereas Ca, Na and K-perchlorate do not evolve HCl (Markowitz, 1963). The presence of natural geologic materials, on the other hand, may promote complex reactions with the perchlorate/chlorate phases. Such complex reactions could alter the evolution of Cl and/or formation of chloride phases which may cause HCl release characteristics to differ from what is expected of pure perchlorate phases.

**SAM–GCMS results**

The SAM/GCMS along with SAM-EGA detected chlorinated hydrocarbons produced during pyrolysis of the Rocknest fines that suggests the presence of oxychlorine compounds in the deposit (Fig. 3). Similar results were obtained after analysis of the drilled samples at Yellowknife Bay (John Klein and Cumberland) and Pahrump Hills (Confidence Hills) and those results are described in detail by Ming et al. (2014) and Freissinet et al. (2015).

The source of the chlorinated hydrocarbons was attributed to a reaction between martian oxychlorine and terrestrial organic contamination. Several chlorinated hydrocarbons including chloromethane (CH₃Cl), dichloromethane (CH₂Cl₂), trichloromethane (CHCl₃), a chloromethylpropene (C₃H₇Cl) and chlorobenzene (C₆H₅Cl) were identified by GCMS.

![Fig. 3. SAM gas chromatogram showing the intensities (in counts per second) of the major masses of the chloromethanes and a chloromethylpropene detected in the second Rocknest sample run compared with the empty cup blank (shaded peaks) as a function of retention time in seconds. Each peak was identified by matching the mass spectrum generated from Gaussian fits of the QMS m/z values to mass spectra available in the NIST library (e.g. shown in inset). Peak identifications: 1, chloromethane; 2, dichloromethane; 3, trichloromethane; and 4, 1- or 3-chloro2-methylpropene. Figure from Glavin et al. (2013).](https://www.cambridge.org/core/terms)
above background levels with chloromethane abundances up to 2.3 nmol (≈2.3 parts-per-million assuming 50 mg sample) after pyrolysis of the Rocknest samples, but were not detected in the empty cup blank run analysed prior to the analysis of the Rocknest fines (Fig 3). Several products of N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), a chemical whose vapours were released from one of the derivatization cups inside SAM, were also identified in both the blank and Rocknest EGA and GCMS runs (Glavin et al. 2013). The evolution of the chloromethanes observed directly by EGA during pyrolysis was coincident with the increase in both O₂ and SO₂ releases detected and were attributed to nitrate thermal decomposition at similar temperatures as the main O₂ releases (Leshin et al. 2013; Ming et al. 2014; Stern et al. 2015). Nitrate thermal decomposition results in O₂ evolution, but the nmole levels of nitrates would not be expected to contribute significantly to the μmole O₂ detections. The detected high temperature (>500°C) SO₂ releases are consistent with sulphate thermal decomposition (Ming et al. 2014; McAdam et al. 2014) that can also evolve O₂. However, sulphate thermal decomposition occurring above 500°C is not a likely candidate for the main O₂ releases detected below 500°C. Hydrogen peroxide has been proposed to be a potential oxidant in the martian soil, but thermal decomposition of hydrogen peroxide occurs below 145°C and thus is not a candidate O₂ source in the Gale Crater sediments (Zent & McKay, 1994; Wu et al. 2010). Superoxides are another proposed source of O₂ but their instability in the presence of water (e.g. Yen et al. 2006) suggests that any O₂ related superoxides would have evolved with the main H₂O releases that occur below 200°C. The SAM-EGA and GCMS detections of O₂, HCl and a variety of chlorinated hydrocarbons produced during pyrolysis of the Rocknest scooped aeolian fines and in multiple drilled mudstone samples collected by Curiosity strongly argue for the presence of martian oxychlorine compounds such as perchlorates and/or chlorides.

**Viking GCMS**

The overall goal of the Viking GCMS analyses was to search for organics in the martian surface material. The detection of chlorinated hydrocarbons at the Viking Landing sites was thought to be derived solely from terrestrial contamination (Biemann et al. 1976, 1977). The detection of perchlorate at the Phoenix Landing site promoted a reevaluation of the Viking GCMS analysis, which suggested chlorinated hydrocarbon Cl could be derived from martian oxychlorine (e.g. ≤0.1 wt% perchlorate) in the Viking regolith (Navarro-González et al. 2010). Two regolith samples at each of the Viking Landing sites, Chryse Planitia (VL-1) and Utopia Planitia (VL-2), were analysed using thermal volatilization coupled to GCMS. The first VL-1 sample was acquired on Sol 8 and was primarily comprised of fine-grained material collected from 4 to 6 cm below the surface. A single ~100 mg fraction of this sample was delivered to GCMS oven number 1 analysed on sols 17 and 23 (Biemann et al. 1976). The second VL-1 sample was collected on sol 31 and consisted of coarse surface material located ~3 m from the sol 8 sample collection site. A single ~100 mg fraction of this sample was delivered to VL-1 oven 2 and analysed and on sols 32, 37 and 43. The first

This will be further discussed below. The much higher abundances of chloromethanes detected in the Rocknest soil by SAM compared with the abundances measured at the Viking sites is likely due to a significant terrestrial carbon background from MBSTFA in SAM that was not present in the Viking GCMS instruments.

The possibility that phases other than oxychlorine phases may be responsible for the detected O₂ are possible but unlikely. Nanomole levels of nitrogen-oxide (NO, NO₂ 30) were detected and were attributed to nitrate thermal decomposition at similar temperatures as the main O₂ releases (Leshin et al. 2013; Ming et al. 2014; Stern et al. 2015). Nitrate thermal decomposition results in O₂ evolution, but the nmole levels of nitrates would not be expected to contribute significantly to the μmole O₂ detections. The detected high temperature (>500°C) SO₂ releases are consistent with sulphate thermal decomposition (Ming et al. 2014; McAdam et al. 2014) that can also evolve O₂. However, sulphate thermal decomposition occurring above 500°C is not a likely candidate for the main O₂ releases detected below 500°C. Hydrogen peroxide has been proposed to be a potential oxidant in the martian soil, but thermal decomposition of hydrogen peroxide occurs below 145°C and thus is not a candidate O₂ source in the Gale Crater sediments (Zent & McKay, 1994; Wu et al. 2010). Superoxides are another proposed source of O₂ but their instability in the presence of water (e.g. Yen et al. 2006) suggests that any O₂ related superoxides would have evolved with the main H₂O releases that occur below 200°C. The SAM-EGA and GCMS detections of O₂, HCl and a variety of chlorinated hydrocarbons produced during pyrolysis of the Rocknest scooped aeolian fines and in multiple drilled mudstone samples collected by Curiosity strongly argue for the presence of martian oxychlorine compounds such as perchlorates and/or chlorides.

**Viking GCMS**

The overall goal of the Viking GCMS analyses was to search for organics in the martian surface material. The detection of chlorinated hydrocarbons at the Viking Landing sites was thought to be derived solely from terrestrial contamination (Biemann et al. 1976, 1977). The detection of perchlorate at the Phoenix Landing site promoted a reevaluation of the Viking GCMS analysis, which suggested chlorinated hydrocarbon Cl could be derived from martian oxychlorine (e.g. ≤0.1 wt% perchlorate) in the Viking regolith (Navarro-González et al. 2010). Two regolith samples at each of the Viking Landing sites, Chryse Planitia (VL-1) and Utopia Planitia (VL-2), were analysed using thermal volatilization coupled to GCMS. The first VL-1 sample was acquired on Sol 8 and was primarily comprised of fine-grained material collected from 4 to 6 cm below the surface. A single ~100 mg fraction of this sample was delivered to GCMS oven number 1 analysed on sols 17 and 23 (Biemann et al. 1976). The second VL-1 sample was collected on sol 31 and consisted of coarse surface material located ~3 m from the sol 8 sample collection site. A single ~100 mg fraction of this sample was delivered to VL-1 oven 2 and analysed and on sols 32, 37 and 43. The first

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VL-2 GCMS sample, a surface duricrust, was collected on sol 21 and a single ~100 mg fraction was analysed four times (sols 24, 26, 35 and 37) using VL-2 oven 2. The second VL-2 sample was acquired on sol 37 from under Badger Rock and a single ~100 mg fraction was analysed five times (sols 41, 43, 45, 47 and 61) using VL-2 oven 3 (Biemann et al. 1977) (Table 2).

The Viking GCMS instruments and sample analysis protocols (Biemann et al. 1974; Rushneck et al. 1978) differed substantially from both the Phoenix TEGA (Boynton et al. 2009) and MSL-SAM (Mahaffy et al. 2012) instruments, and consequently the results differed considerably. The TEGA and SAM instruments employed temperature ramps to perform sample thermal volatilization, in contrast, the Viking GCMS instruments utilized temperature steps (50, 200, 350 and 500°C) with thermal volatilization, in contrast, the Viking GCMS instruments employed temperature ramps to perform sample thermal volatilization, in contrast, the Viking GCMS instruments utilized temperature steps (50, 200, 350 and 500°C) with thermal volatilization was performed in a sealed sample cell (i.e. no flow) with either a H2 or 13CO2 filled headspace. After the volatilization step, carrier gas (H2) was diverted through the sample cell to inject the sample gases into the Viking GC column. Two other significant differences between the TEGA and SAM instruments and the Viking GCMS, both of which were used to protect the Viking MS from high pressure, were the use of a heated Ag–Pd diffusion tube to reduce the H2 purge gas pressure prior to the MS entrance and the use of a pressure sensitive effluent divider which acted to split and divert fractions of the carrier gas away from the MS as needed. For example as shown in Table 1, 20 : 1 ratio indicates that 20 parts were vented and one part of the gas from the GC column was sent to the MS.

The use of H2 carrier gas in combination with the heated Ag–Pd diffusion tube prevented the detection of O2 (g) due to its reduction into H2O (g) prior to entry into the MS. This limitation, along with the lack of a direct EGA mode (i.e. direct MS injection), eliminates the ability to use O2 (g) release from the sample as a diagnostic for the presence of perchlorate or other oxychlorine species as was done with the TEGA (Boynton et al. 2009) and SAM data sets (Leshin et al. 2013; Glavin et al. 2013; Ming et al. 2014). These factors leave the detection of trace amounts of chloromethane (CH3Cl) in the VL-1 subsurface sample and trace amounts of dichloromethane (CH2Cl2) in both VL-2 samples as the sole GCMS evidence for the presence of volatile chlorine species in the Viking samples.

At the time of the initial Viking GCMS analyses, the possibility that the detected CH3Cl and CH2Cl2 might be of martian origin was recognized, however, the detection was attributed potential instrument contamination (Biemann et al. 1979). After the discovery of perchlorate during the Phoenix mission, the suggestion was made that the Viking GCMS CH3Cl and CH2Cl2 detection was due to the presence of perchlorate and organics indigenous to the samples (Navarro-González et al. 2010); an interpretation that was subsequently debated in the literature (Biemann & Bada, 2011; Navarro-González & McKay, 2011).

Chloromethane was detected during VL-1 sample analyses and dichloromethane was detected during VL-2 analyses (Table 2). The VL-1 subsurface sample analysis detected 15 ppb of CH3Cl during the first sample heating (200°C) on sol 17. No CH3Cl was detected during the second sample heating (500°C) on sol 23, and no CH2Cl2 was detected in either run. The position of the effluent divider at different times during the sample runs may offer a possible explanation as to why for CH3Cl was only detected in the first VL-1 sample run. During the first run of the subsurface sample, the effluent divider was in a 3 : 1 split at scan number 27 (which corresponds to the elution time of CH3Cl). In contrast, the effluent divider was in a 20 : 1 split ratio, indicating less gas from the GC column was sent to the MS detector, during scan 89 (corresponding to the elution time of CH2Cl2), which may have precluded the detection of CH2Cl2. Likewise, in the analyses of the

**Table 2. Viking 1 and 2 GCMS results for methyl chloride (CH3Cl) (scan 27) and methylene chloride (CH2Cl2) (scan 89)**

<table>
<thead>
<tr>
<th>Mission</th>
<th>Oven</th>
<th>Sample</th>
<th>Sol analysed</th>
<th>Purge gas</th>
<th>Temp. °C</th>
<th>CH3Cl Split</th>
<th>CH3Cl ppb</th>
<th>CH2Cl2 Split</th>
<th>CH2Cl2 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>VL1</td>
<td>1</td>
<td>Blank</td>
<td>Cruse</td>
<td>13CO2</td>
<td>500</td>
<td>3 : 1</td>
<td>15</td>
<td>ND</td>
<td>20 : 1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>Subsurface</td>
<td>17</td>
<td>13CO2</td>
<td>200</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>Subsurface</td>
<td>23</td>
<td>13CO2</td>
<td>500</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Surface</td>
<td>32</td>
<td>13CO2</td>
<td>350</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Surface</td>
<td>37</td>
<td>13CO2</td>
<td>500</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Surface</td>
<td>43</td>
<td>13CO2</td>
<td>500</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>VL2</td>
<td>2</td>
<td>Blank</td>
<td>Cruse</td>
<td>13CO2</td>
<td>500</td>
<td>3 : 1</td>
<td>15</td>
<td>ND</td>
<td>20 : 1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Duricrust</td>
<td>24</td>
<td>H2</td>
<td>200</td>
<td>20 : 1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Duricrust</td>
<td>26</td>
<td>H2</td>
<td>350</td>
<td>400 : 1</td>
<td>ND</td>
<td>ND</td>
<td>6–14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Duricrust</td>
<td>35</td>
<td>H2</td>
<td>500</td>
<td>400 : 1</td>
<td>ND</td>
<td>ND</td>
<td>6–14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Duricrust</td>
<td>37</td>
<td>13CO2</td>
<td>500</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2–6</td>
</tr>
<tr>
<td>VL2</td>
<td>3</td>
<td>Under Rock</td>
<td>41</td>
<td>H2</td>
<td>50</td>
<td>0 : 1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Under Rock</td>
<td>43</td>
<td>H2</td>
<td>200</td>
<td>400 : 1</td>
<td>ND</td>
<td>ND</td>
<td>0.04–0.08</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Under Rock</td>
<td>45</td>
<td>H2</td>
<td>350</td>
<td>400 : 1</td>
<td>ND</td>
<td>ND</td>
<td>10–20</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Under Rock</td>
<td>47</td>
<td>H2</td>
<td>500</td>
<td>400 : 1</td>
<td>ND</td>
<td>ND</td>
<td>&lt;4</td>
</tr>
</tbody>
</table>

(Biemann et al. 1976, 1977).
VL-1 surface sample the effluent divider was closed (carrier gas fully vented) during scan 27 and in a 20:1 split ratio during scan 28. These divider positions may have prevented the detection of low levels of CH₃Cl and CH₂Cl₂, generated from VL-1 samples, except when effluent divider was in the lower 3:1 split (i.e. during the first run of the subsurface sample at scan 27). Although an in-cruise blank run using the VL-1 oven 1 was performed no CH₄ or CH₂Cl was detected in this run. Despite a 0:1 split ratio at scan 87, no CH₂Cl₂ (Table 2) or other hydrocarbons were detected in the VL-1 blank run except for trace amounts of Freon-E (Viking cleaning solvent) (Biemann et al. 1976, 1977), which is an unlikely precursor to CH₂Cl₂.

Dichloromethane was detected in almost all VL-2 duracrust and Badger Rock sample runs; however, CH₂Cl₂ was not detected in any of the VL-2 runs. As was the case for the lack of CH₂Cl₂ detection in the VL-1 data, the lack of CH₂Cl₂ detection may possibly be explained by the position of effluent divider during the time of CH₂Cl₂ elution. At scan 89, which corresponds to the elution time of CH₂Cl₂ the effluent divider was in a 0:1 split ratio, that is all of the carrier gas was directed into the GC column for all runs except the fourth Badger rock run in which case the divider was in a 20:1 ratio position. While for most VL-2 runs the effluent divider was in a 400:1 split during scan 27, when CH₂Cl₂ would be expected to elute, thus making it difficult to detect CH₂Cl₂.

The apparent incomplete decomposition of perchlorate as indicated by the repeated detection of CH₂Cl₂ from each of the two VL-2 samples suggests that the proposed concentrations of perchlorate inferred from the Viking GCMS results should be considered a minimum. Because each Viking sample was analysed multiple times, the total amount of CH₂Cl₂ detected from the VL-2 duracrust sample was 14–32 ppb and the total amount detected from the VL-2 Badger Rock sample was ~34–64 ppb. Furthermore, the detectable levels of CH₂Cl₂ detected in the final run for each VL-2 sample indicates that not all of the volatile chlorine was released (i.e. the CH₂Cl₂ did not go to zero). Likewise, the 15 ppb of CH₂Cl₂ detected in the VL-1 subsurface run should be considered a minimum because only two runs were performed. The partial decomposition of perchlorate is consistent with the SAM and TEGA results that show relatively slow perchlorate decomposition kinetics occurring over an extended heating period as indicated by O₂ and Cl (measured as HCl) evolution over a wide temperature range from the Gale samples sample (Fig. 2).

The possibility that the organic sources of the chlorinated hydrocarbons detected with the Viking GCMS instrument were of martian origin has been questioned (Biemann & Bada, 2011; Navarro-González & McKay, 2011). The organic sources for the chlorinated hydrocarbons detected by SAM–GCMS have been attributed to terrestrial and martian sources (Glavin et al. 2013; Freissinet et al. 2015). Chlorobenzene was not detected by the Viking-GCMS but was detected by SAM analyses. The SAM chlorobenzene detection was attributed to the reaction of martian perchlorate thermal decomposition products with both hydrocarbon contamination generated by Tenax sample preconcentrators in the GC system, and to indigenous martian organics (Glavin et al. 2013; Ming et al. 2014; Freissinet et al. 2015). Although benzene contamination may be a poor chlorobenzene precursor (Freissinet et al. 2015), the Viking data provides no evidence for the presence of indigenous aromatic organics that may serve as a chlorobenzene precursor (e.g. aromatic carboxylic acids). Additionally, dichloroalkanes were not detected in the Viking GCMS runs, however, they were detected in the SAM runs and, as was the case for the SAM chlorobenzene detections, attributed to both terrestrial organic contaminants and indigenous martian organics (Freissinet et al. 2015). Similarly, trichloromethane sourced from martian perchlorate-Cl reacting with terrestrial background hydrocarbons was detected by the SAM–GCMS but not detected by Viking-GCMS. Independent of the origin of the hydrocarbon component (contamination or indigenous to Mars) of the detected CH₃Cl and CH₂Cl₂, the lack of the detection of chlorine in the Viking GCMS blank runs, as with the MSL-SAM data (Glavin et al. 2013) strongly suggests a martian origin for the chlorine that is consistent with presence of perchlorate and possibly other oxychlorine species.

**Mars science laboratory Chemistry and Mineralogy (CheMin) instrument**

The CheMin instrument on MSL performs XRF and X-ray fluorescence (XRF) on scooped soil and drilled rock samples (Blake et al. 2012, 2013; Bish et al. 2013; Vaniman et al. 2014). Samples are sieved to <150 µm before delivery into a disc-shaped sample cell 8 mm in diameter and 175 µm thick. CheMin uses a Co X-ray source and operates in transmission geometry. A collimated X-ray beam strikes the sample cell, while the sample is agitated by piezoelectric vibrations to achieve different orientations of the grains. Diffraacted X-ray photons are detected by a cooled charge coupled device in a two-dimensional (2D) array. The 2D ring patterns are integrated circumferentially to obtain conventional 1D diffraction patterns. CheMin’s angular range is ~5–50°2θ with 0.3°2θ full-width at half-maximum resolution at 25°2θ. These large instrumental peak widths (relative to laboratory X-ray diffractometers) limit the ability to accurately determine minor crystalline phases, so that the detection limit of CheMin is ~1–3 wt%.

Abundances of crystalline phases and crystal structures of these phases are determined by the Rietveld refinement method (e.g. Young, 1993), whereas abundances of amorphous, poorly crystalline, and phyllosilicate phases (i.e. poorly ordered phases) are determined by the FULLPAT full-pattern fitting method (Chipara & Bish, 2002). SAM data suggest that the abundances of oxychlorine compounds in the Gale Crater sediments are near the detection limit of CheMin (Leshin et al. 2013; Ming et al. 2014); however, Rietveld refinements of CheMin data from the Rocknest, John Klein and Cumberland samples have not unequivocally identified oxychlorine minerals (Bish et al. 2013; Vaniman et al. 2014). Akaganitee, β-Fe₃O(OH,Cl), has been detected in CheMin data of John Klein and Cumberland, but for this discussion, akaganite will not be included as an oxychlorine phase.
Comparisons of laboratory EGA data to SAM data from Rocknest, John Klein, and Cumberland suggest that Ca, Mg and/or Fe perchlorates are possible oxychlorine compounds that contribute to the O2 and HCl signals (Leshin et al. 2013; Glavin et al. 2013; Ming et al. 2014). Perchlorate minerals can have several hydration states, dependent on relative humidity (RH) and temperature conditions. A range of perchlorate hydration states for Mg-perchlorate, for example, were evaluated at temperatures and RH relevant to Mars and it was determined that Mg(ClO4)2·6H2O would be the most stable phase on the martian surface (Robertson & Bish, 2011). Hydrated Mg-perchlorate [Mg(ClO4)2·6H2O] and Ca-perchlorate [Ca (ClO4)2·4H2O] were included in Rietveld refinements of CheMin data of Rocknest (Bish et al. 2013) and John Klein and Cumberland (Bish, personal communication); however, these phases refined to zero indicating that these hydrated perchlorates are not present.

Visual comparisons of the XRD patterns of additional perchlorate and chlorate phases available in the International Centre of Diffraction Data (ICDD) library to the CheMin XRD patterns from Rocknest, John Klein, and Cumberland do not support the presence of crystalline perchlorate or chlorate minerals (Fig. 4). Considering the low abundance of oxychlorine phases in samples from Gale crater and the high background in CheMin data from a significant amorphous component, only the strongest XRD lines of oxychlorine minerals would be detectable in CheMin data. The strongest peaks of some oxychlorine minerals, including Fe(II)-perchlorate·6H2O, anhydrous Ca-chlorate, anhydrous Na-perchlorate, Na-perchlorate·H2O and anhydrous Na-chlorate overlap peaks of common basaltic igneous minerals, so that it would be difficult to detect them in many soils and sediments on Mars (Fig. 4). Strong peaks of other oxychlorine minerals occur at angles lower than common basaltic minerals, so that they could be more easily detected, including Fe(III)-perchlorate·9H2O, Ca-perchlorate·6H2O, Ca-chlorate·2H2O and Mg-chlorate·6H2O. Investigations of these regions of CheMin XRD patterns from Rocknest, John Klein and Cumberland show no evidence for these phases (Fig. 4).

Although oxychlorine minerals may be at the detection limit of CheMin, the detection limit is dependent upon the crystallinity of the phase in question and the positions of the strongest XRD lines of that phase. If the oxychlorine phase is poorly crystalline, so that its XRD peaks are broad, then its detection limit with CheMin is much greater than 1–3 wt% (e.g. Bish et al. 2013). The low ionic potential of perchlorate and chlorate ions in solution and the very low eutectic temperatures of both perchlorate and chlorate salts may help them precipitate from solution as amorphous phases in martian soils (Toner et al. 2014). If the oxychlorine phase in the Gale sediments is completely amorphous, then it would be indiscernible from other amorphous materials and would contribute to the amorphous hump (i.e. broad, convex-upward background) observed in all CheMin analyses to date (e.g. Rampe et al. 2014).

The possibility of a mixture of chlorate and perchlorate also presents a challenge to the CheMin detection of oxychlorine phases in the Gale sediments. The chlorate anion is the most stable intermediate species of the oxidation of chloride to perchlorate (e.g. Hanley et al. 2012), and concentrations of perchlorate and chlorate can be equivalent in desert soils on Earth (Rao et al. 2010). The subdivision of the oxychlorine concentrations as detected by SAM into equal portions of perchlorate and chlorate would easily cause the individual perchlorate and chlorate abundances to fall below the detection limits of CheMin.

**IR spectroscopy**

Perchlorates and chlorates have diagnostic spectral features throughout the visible/near-IR (VNIR; ~0.35–2.5 μm) and mid-IR (~5–50 μm). The VNIR features of perchlorates have been characterized using reflectance spectroscopy techniques similar to those used by VNIR spectrometers on remote sensing platforms in orbit around Mars (Morris et al. 2009; Cull et al. 2010; Bishop et al. 2014; Hanley et al. 2015). Mid-IR studies of perchlorates and chlorates (Miller & Wilkins, 1952; Pejov & Petraševski, 2002; Bishop et al. 2014; Hanley et al. 2015) have utilized reflectance and absorption spectroscopic techniques, which differ substantially from mid-IR emission spectroscopy technique employed at Mars. All of these studies demonstrate that oxychlorine salts have numerous diagnostic spectral features in the mid-IR. These studies show that the anion (ClO4− or ClO3−), cation (Na+, Mg2+, Ba2+, Ca2+, K+, etc.) and hydration state all cause systematic variations in the mid-IR spectral properties, making mid-IR spectroscopy a useful diagnostic tool for oxychlorine...
Hydrated Na perchlorate displays two strong bands at 1.43 and 1.93 µm, with additional weaker bands between 1.00 and 2.33 µm (Fig. 5(a)). Hydrated Na chlorate has a more complex spectrum, with major bands at 1.43 and 1.92 µm, with additional weaker bands at between 0.97 and 2.42 µm. The large number of bands may be due to several hydration states being present in the sample. Regardless, it is clear from these data and those of others (e.g. Morris et al. 2009; Cull et al. 2010; Bishop et al. 2014), that perchlorates are best identified in the VNIR wavelength region by the positions and shapes of their various H2O vibrational bands. The major perchlorate/chlorate hydration bands at ~1.4 and 1.9 µm are noted as overlapping with other H2O or OH bands from other hydrated phases including sulphates and phyllosilicates, which are also known to occur on Mars. Although the band shapes and exact positions may vary between oxychlorine species, the potential presence of other hydrated phases (e.g. sulphates, phyllosilicates) indicates that care must be taken when determining the presence or absence of oxychlorine from remotely sensed VNIR data.

Figure 5(b) shows mid-IR emissivity spectra of hydrated Na perchlorate and chloride acquired on VSL’s Nicolet 6700 FTIR spectrometer modified to collect emissivity spectra by removing the glowbar IR source and exposing the interferometer to a custom-built environmental chamber. Samples were heated to 80°C and spectra were collected in an environment with CO2 and H2O vapour removed. Spectra were referenced to a blackbody calibration target heated to 70°C and 100°C and were calibrated using the methods of Ruff et al. (1997). A total of 256 spectra of each sample were averaged to create the final spectra.

The major features in the mid-IR emissivity data are due to ClO4 bending and stretching modes. The positions and shapes of the Na perchlorate spectrum are generally similar to those reported in the reflectance data by Bishop et al. (2014). The hydrated Na chlorate spectrum has fewer strong features than perchlorate at long wavelengths (12.5–50 µm; 200–800 cm⁻¹), but has a strong split ClO₃ stretching mode at 1000 cm⁻¹. The multiple strong spectral features of chlorates and perchlorates in the mid-IR make them good candidates to be identified in thermal emission remote sensing data sets if their concentrations are high enough anywhere on the martian surface (≥5–10 vol%).

IR evidence consistent with presence of hydrated perchlorate and/or chloride has been detected in select locations on Mars by orbital and landed IR analyses. The Phoenix Landers Surface Stereo multispectral visible/IR (0.45–1.00 µm) imager has detected an IR hydration feature consistent with the presence of hydrated perchlorates in discrete, concentrated patches at the Phoenix landing site (Cull et al. 2010). The Mars Reconnaissance Orbiter’s CRISM instrument has also detected hydration features in the VNIR range (6–18 m pixel⁻¹ spatial resolution) consistent with the presence of hydrated perchlorate and chloride at several locations associated with martian RSL features (Ojha et al. 2015).

Anhydrous chloride salts have also been remotely detected from orbit using both mid-IR and VNIR instruments (Fig. 6). Chloride salt deposits were initially identified in mid-IR Thermal Emission Imaging System (THEMIS)
multispectral images (~100 m pixel\(^{-1}\) spatial resolution) (Osterloo et al. 2008). These detections were subsequently supported by observations made at VNIR wavelengths with the CRISM instrument (Murchie et al. 2009; Wray et al. 2009; Glotch et al. 2010) and the Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) instrument (Ruesch et al. 2012). Anhydrous chloride salts have no features at either VNIR or mid-IR wavelengths. At VNIR wavelengths, CRISM and OMEGA ratio spectra of chloride salt-bearing surfaces are spectrally featureless, with a distinct red slope (Fig. 6). This spectral behaviour was confirmed in the laboratory, using physical mixtures of halite and flood basalt particulates (Jensen & Glotch, 2011). At mid-IR wavelengths, chloride salts are spectrally featureless and have an emissivity less than unity. This leads to distinct blue spectral slopes observed in THEMIS and thermal emission spectrometer (TES) data (Osterloo et al. 2008, 2010; Glotch et al. 2010) and laboratory emissivity spectra (Glotch et al. 2013, 2016). Recently acquired mid-IR emissivity spectra of the Jensen & Glotch (2011) halite/basalt sample suite, in combination with a hybrid light scattering/Hapke radiative transfer model has constrained the salt abundance at Martian chloride deposits to \(~10\text{–}25\text{ vol}\%\), with the remaining component being the regional silicate regolith (Glotch et al. 2013, 2016).

Despite the orbital IR detections of hydrated-perchlorate and hydrated-chlorate in select martian RSL features, chlorate or perchlorate have not been identified in the chloride bearing regions by IR remote sensing instruments orbiting Mars (Glotch et al. 2010; Osterloo et al. 2008, 2010). This is in stark contrast to hyperarid deserts (e.g. Atacama Desert, Antarctic Dry Valleys), where halide salts and silicates are often mixed or layered with various other phases such as nitrates, perchlorate and chloride phases (e.g. Sutter et al. 2007; Rao et al. 2010; Jackson et al. 2015). Furthermore, the detection of oxychlorine phases at the Phoenix and Gale Crater landing sites suggests that where Cl concentrations are high as in these martian chloride deposits, perchlorates/chlorates should be present, but have yet to be detected by orbital IR analyses. As will be discussed below, the oxychlorine/total Cl ratio has been shown to vary between and within landing sites. Thus it is likely that concentration of oxychlorine phases in these chloride bearing regions is below orbital IR detection limits.

**Total Cl versus oxychlorine relationships**

The detection of oxychlorine species at the Phoenix, Gale Crater, RSL features and arguably at the Viking landing sites suggests that oxychlorine formation on Mars is likely a
global process. Chlorine analysis of sediments at the Phoenix and Gale Crater landing sites suggests that global martian Cl should contain an oxychlorine-Cl component that can range from 10 to 86 mol% of total measured Cl. The average soluble perchlorate and chloride concentration in the three sample solutions analysed by WCL at the Phoenix landing site was $2.5 \pm 0.1$ and $0.4 \pm 0.2$ mM, respectively (Fang et al. 2015).

The molar oxychlorine-Cl amount in the Phoenix soils could therefore be $\sim 86\%$ of the total chlorine in the sample. Gale Crater total Cl as determined by the Alpha Proton X-ray Spectrometer (APXS) and oxychlorine as determined by SAM-EGA indicate that the oxychlorine-Cl molar fraction is lower relative to the Phoenix landing site and varies from $\sim 10$ to 40% of total Cl (Archer et al. 2015). This suggests that if the molar Cl in oxychlorine is only 10% of the total Cl in a 25 vol% chloride bearing region, then the oxychlorine phases could occur below the THEMIS detection limits ($\sim 5–10$ vol %).

Oxychlorine and total Cl data from the Phoenix and Gale landing sites may be used to constrain oxychlorine levels at sites where only total Cl data is available. Total chlorine has been determined for a wide variety of locations from orbit by the GRS on the Mars Odyssey spacecraft (Keller et al. 2006) as well as in situ by every landed mission to date (Table 1). Chlorine concentrations determined from orbit by the GRS were for a 440–540 km diameter footprint in the top meter that occurred roughly between 45°S and 45°N latitude (Boytont et al. 2002; Keller et al. 2006). The Viking missions utilized XRF spectroscopy to examine scooped samples for total Cl (Clark et al. 1977). The Mars Pathfinder, Mars Exploration Rover and Mars Science Laboratory missions utilized APXS to determine in situ total chemistry including Cl of soil, sediment and rock (e.g. Rieder et al. 1997; Brückner et al. 2003; Rieder et al. 2004; Clark et al. 2005; Gellert et al. 2006; Morris et al. 2006; Ming et al. 2008; Blake et al. 2013; Gellert et al. 2013; Arvidson et al. 2014) (Table 1).

The fraction of oxychlorine relative to total chlorine can vary from site to site (10–95%) as is evident in the Phoenix and Gale data sets, which can make it difficult to ascertain what oxychlorine value to apply to a particular site with no oxychlorine measurements. However, knowledge of the type of material in which the oxychlorine was detected may provide constraints as to where a particular oxychlorine concentration can be applied elsewhere on Mars. The Rocknest eolian deposit in Gale Crater, for example, has eolian features (coarse-grained, indurated, bright dust-coated surface over darker finer sediment) and total chemistry similar to coarse-grained eolian deposits observed at both MER landing sites (Blake et al. 2013). The similarity of eolian materials between the MER and Gale landing sites could be argued as the result of global process that also leads to similar oxychlorine concentrations at in all soil and windblown sediments. The Rocknest oxychlorine component consists of $\sim 36\%$ of total chlorine (Archer et al. 2015), which suggests that a similar fraction of oxychlorine-Cl may be present in the coarse-grained eolian deposits at the MER landing sites.

Oxychlorine species are likely to be globally distributed but the amount of oxychlorine as a percentage of total chlorine will likely vary from location to location. However, if two spatially different sites have materials with similar geologic properties (e.g. geochemistry, mineralogy, particle size distribution), then the oxychlorine-total Cl ratio of one site could potentially be used to constrain the oxychlorine concentration at the other site that has a known total Cl concentration.

**Measurement challenges and alternative oxychlorine analytical techniques**

The characterization of oxychlorine in martian sediments can be challenging because of the low (<1 wt%) oxychlorine concentrations, difficulty in identifying the oxychlorine species present, and ensuring evolved O$_2$ as detected by EGA is attributed to oxychlorine. XRD and IR analysis detection limits for oxychlorine are $>1$ wt% and $>5–10$ vol%, respectively. EGA while useful in detecting low oxychlorine concentrations (e.g. 0.1 wt% Table 1) can encounter difficulty in identifying which oxychlorine phases is present (e.g. chloride versus perchlorate). The temperature in which O$_2$ is evolved can be used to identify which oxychlorine species is present; however, Fe phases in the sample can alter oxychlorine decomposition temperatures causing difficulties in identifying oxychlorine species. Furthermore, EGA of other gases, total chemistry (e.g. APXS), and/or XRD data may be required to rule out other non-oxychlorine sources of evolved O$_2$. The WCL ion-selective sensor has provided the only direct detection of oxychlorine as perchlorate in the martian soil. However, chloride and nitrate could also have been present in the soil but were not detected because all three anions are only detectable by that ion-selective sensor. The presence of perchlorate in this case, inhibited the detection of the chloride and nitrate. Future analysis of Mars soils or sediments with ion-selective sensors could continue to encounter this problem especially if lower concentrations of nitrate, perchlorate, and chloride are present. The ion-selective sensor, in this case, would not be able to determine the proportion of perchlorate, chloride and nitrate present in the sample. A potential solution to this problem would be to use an array of ISEs comprised of individual sensors where each possess different selectivity to the various oxyions. For example, using $3 \times 3$ ISEs with ionophores of different selectivity for each of ClO$_4^-$, ClO$_3^-$ and NO$_3^-$ would then allow for use of a chemometric identification method of the individual responses and determination the respective concentrations.

The development of microfluidic devices also offers another suitable alternative for identifying and quantifying oxychlorine on future landed robotic missions to Mars. Several microchip based systems, which include isotachophoresis (ITP), ITP-capillary electrophoresis (ITP-CE), capillary electrophoresis (CE) and ion chromatography (IC) on a chip are being developed for terrestrial purposes (e.g. Evenhuis et al. 2004; Haddad et al. 2008). The reader is referred to the relevant literature for more detailed account of research and development of anion solution analysis using microchip technology (e.g. Murrihy et al. 2001; Evenhuis et al. 2004; Haddad et al. 2008). Briefly, the main purpose in developing this ‘lab-on-a-chip’
technology for terrestrial needs is that less time, less sample and less reagents along with lower power requirements are required for analyses (Evenhuis et al. 2004). These attributes coupled with small instrument size are desirable for planetary instrumentation. The requirement of soil solution extracts for analysis can add a layer of complexity to overall instrument design that does not exist for IR, EGA and Chemin like XRD instruments. However, these microfluidic devices can detect much lower anion concentrations (~0.1 wt%) than IR and XRD techniques. Furthermore, microfluidic devices have the potential to more easily than EGA, to discriminate between chlorite (ClO\(_2^-\)), chloride, and perchlorate phases without interferences from each other and other solution constituents (Evenhuis et al. 2004).

**Summary**

Chlorine was first detected on the surface of Mars by the Viking Landers at concentrations only found in arid environments on Earth. The species of Cl has long thought to be in chloride form (e.g. Clark & Baird, 1979). The Phoenix Lander’s WCL analysis; however, yielded the surprising result that more than 86% of the soluble Cl consisted of perchlorate. The Phoenix Landers’ TEGA instrument detected an evolved O\(_2\) release from the Phoenix soil which supported the WCL perchlorate detection. The MSL rover’s SAM instrument has also detected the presence of evolved O\(_2\), HCl and chlorinated hydrocarbons consistent with the presence of perchlorate and/or chloride salts. Further evaluation of the Viking GCMS data suggests that martian oxychlorine phases may have been detected in the Viking soils.

Perchlorate or chloride salts have not been detected in Gale crater by CheMin. The lack of detection for oxychlorine phases could be attributed to several factors: (1) The oxychlorine phases could be poorly crystalline; (2) the oxychlorine abundance could be split between chlorate and perchlorate which drives the concentrations of these two species below the CheMin detection limits; and/or (3) the oxychlorine phases are at CheMin detection limits but are obscured by other basaltic phases present.

Orbital IR analysis has detected evidence consistent with the presence of hydrated perchlorate and chloride in areas possessing RSL features. The co-occurrence of oxychlorine phases with Cl suggests that where ever Cl is detected the perchlorate or chlorate should be present. However, no evidence of perchlorate or chlorate has been observed especially in the anhydrous chloride enriched regions (up to 25 vol%) of Mars. Perhaps a physical/chemical mechanism may be operating that inhibits the formation or persistence of detectable oxychlorine in these chloride-rich regions.

Although the surface oxychlorine concentrations detected thus far by landed missions are below the orbital IR detection limits, a targeted search for oxychlorine phases in chloride rich regions may yield positive identification if abundances occur at the 5–10 vol% level. There are challenges in detecting oxychlorine phases by remote IR observations; however, oxychlorine/total Cl ratios obtained from the landed MSL and Phoenix missions has the potential to constrain oxychlorine levels at other locations where total Cl values have been or will be determined.

The development of microfluidic devices or ‘lab-on-a-chip’ technology may offer a suitable alternative for identifying and quantifying oxychlorine on future landed robotic missions to Mars. The small instrument size coupled with sensitivity to low anion concentrations, and the ability to identify individual oxychlorine species without interferences from other anions make microfluidic devices an attractive technology. Such instrumentation has the potential to make significant advance in understanding the distribution and concentration of oxychlorine species and other soluble anions (e.g. nitrate, sulphate, phosphate, fluoride and chloride) on Mars.

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**References**


