Effect of Hydration State of Martian Perchlorate Salts on Their Decomposition Temperatures During Thermal Extraction

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Abstract
Three Mars missions have analyzed the composition of surface samples using thermal extraction techniques. The temperatures of decomposition have been used as diagnostic information for the materials present. One compound of great current interest is perchlorate, a relatively recently discovered component of Mars’ surface geochemistry that leads to deleterious effects on organic matter during thermal extraction. Knowledge of the thermal decomposition behavior of perchlorate salts is essential for mineral identification and possible avoidance of confounding interactions with organic matter. We have performed a series of experiments which reveal that the hydration state of magnesium perchlorate has a significant effect on decomposition temperature, with differing temperature releases of oxygen corresponding to different perchlorate hydration states (peak of O₂ release shifts from 500 to 600°C as the proportion of the tetrahydrate form in the sample increases). Changes in crystallinity/crystal size may also have a secondary effect on the temperature of decomposition, and although these surface effects appear to be minor for our samples, further investigation may be warranted. A less than full appreciation of the hydration state of perchlorate salts during thermal extraction analyses could lead to misidentification of the number and the nature of perchlorate phases present.

Plain Language Summary
Missions to Mars look for evidence of organic molecules using thermal extraction techniques. Certain minerals, perchlorate salts, on the Martian surface break down during this heating, releasing oxygen and causing the combustion and destruction of both themselves and any organic matter which may have been present. Previously, the parent salts of these perchlorates have been identified by the temperature at which they release oxygen. However, our work shows that the hydration state of these minerals can affect the temperature of oxygen release just as much as the perchlorate cation. Consequently, incorrect identification of mineral species may occur if hydration state is not taken into account and a mixture of hydration states of one type of perchlorate may be mistaken for a mixture of perchlorate salts. Our findings are important for Mars as the hydration state of the minerals may change throughout the Martian year because of large variations in humidity and temperature.

1. Introduction
Our understanding of Martian geochemistry has been enhanced by experiments performed on Mars missions. Many important advances have come from the results of thermal extraction experiments that transform solid materials available on the Martian surface to volatile products for analysis. The original life detection experiments performed by the Viking landers in 1976 failed to detect organic matter (Biemann et al., 1977; Klein et al., 1976), diminishing hopes that the planet hosted life. Further examination of the data suggested a highly oxidizing surface (Navarro-González et al., 2010; Zent & McKay, 1994). In 2008 the Wet Chemistry Laboratory on board the Phoenix Lander measured ~1 wt % perchlorate (ClO₄⁻) in the soil (Hecht et al., 2009; Kounaves et al., 2010, 2014). Since 2012, the Mars Science Laboratory (MSL) Sample Analysis at Mars (SAM) instrument has performed numerous thermal extraction analyses on Mars that have confirmed the ubiquitous presence of perchlorate salts (Blake et al., 2013; Leshin et al., 2013; Ming et al., 2014) and provided evidence of their deleterious effect on the detection of organic compounds. The release of oxygen and chlorine from perchlorates and their role in combustion and chlorination of organic matter has been recognized from the presence of chlorinated hydrocarbons during analysis on Mars (Blake et al., 2013; Glavin et al., 2013), and in laboratory studies on Earth (Miller et al., 2016). Since thermal extraction methods are the preferred technique for detection of organic compounds on Mars, their use in the presence of...
perchlorate salts will continue to present challenges, for example, when applied to soil samples on the forthcoming ExoMars mission (Barnes et al., 2006).

Understanding the data from thermal extraction experiments involves examination of the temperature at which thermal decomposition begins, maximizes, and completes to produce a profile that is diagnostic for the materials present. Temperature profile-based interpretations rely on an understanding of the behavior of the material present. Diagnostic temperature profiles have been used to understand variation in parent salt cation composition for perchlorate and sulfate salts (Glavin et al., 2013; Leshin et al., 2013; Lewis et al., 2015; Ming et al., 2014). The molecular weight of organic matter can also be indicated by the mineral-induced decomposition temperature and range of release (Sephton et al., 2014). Hence, the literature reveals that although interactions between organic matter and perchlorate and sulfate salts can reduce the diagnostic quality of information, the detection of organic compounds by thermal decomposition in the presence of oxidizing species is still amenable to effective interpretation.

One factor which may currently be underappreciated is that the Martian surface materials are in constant interaction with the atmosphere and thus any consequent chemical changes may influence their decomposition characteristics during thermal extraction. Perchlorate salts, for example, can exist in several hydration states (Gough et al., 2011; Krivtsov et al., 1987; Nikolakakos & Whiteway, 2015; Nuding et al., 2014; Robertson & Bish, 2011; Willard & Smith, 1922). The influence of atmospheric water on the hydration state of perchlorates on Mars has been recently recognized as a mechanism for inducing surface fluid flow features (Chevrier & Rivera-Valentin, 2012; Dundas & McEwen, 2015; Heinz et al., 2016; Ojha et al., 2015). Hydration of perchlorate salts involves chemical change (Nuding et al., 2014; Robertson & Bish, 2011) and can be expected to influence their thermal decomposition behavior. Thermal decomposition profiles are thus not only indicators of chemical composition but can also be reflective of transient environmental conditions.

In this study we have examined the thermal decomposition profiles of magnesium perchlorate (Mg(ClO$_4$)$_2$), which has been oven-dried for varying lengths of time, using thermal extraction by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). This analytical technique has been used before to simulate the response of materials to thermal extraction protocols on Mars missions (e.g., Lewis et al., 2015; Sephton et al., 2014). We examine whether the variation in the thermal decomposition profiles of different hydration states of Mg(ClO$_4$)$_2$ is enough to lead to misidentification of the perchlorate parent salt cation composition and find that future interpretations of thermal decomposition profiles of perchlorate containing samples should consider the hydration state of these important Martian salts.

2. Methods

2.1. Samples for Pyrolysis

The Mg(ClO$_4$)$_2$·aq (Fisher Scientific UK Ltd.) was heated in the low relative humidity environment of the drying oven at 110°C. At weeks 3, 4, and 5 samples of Mg(ClO$_4$)$_2$·aq were removed from the oven. The Mg(ClO$_4$)$_2$·aq samples were powdered using a pestle and mortar and loaded as four subsamples into quartz pyrolysis tubes supported by a quartz wool plug. The loaded tubes were left exposed to absorb atmospheric water, under ambient laboratory conditions (around 20–25°C and 50–60% RH (with respect to liquid water)), for different amounts of time (0, 24, 48, and 72 h) to allow progressive hydration to generate an additional three samples each for weeks 3, 4, and 5. Samples were weighed before and after hydration to allow the calculation of the water (wt %) added to the Mg(ClO$_4$)$_2$. To establish a baseline response, one sample was pyrolysed without dehydration in the oven or further exposure to the atmosphere.

2.2. Pyrolysis-Gas Chromatography-Mass Spectrometry

For analysis, each sample was placed inside the platinum coil of a Chemical Data Systems 2500 pyroprobe under helium carrier gas and heated at a rate of 20°C m s$^{-1}$ to the target temperature where it was held for 15 s. Target temperatures ranged from 200 to 1000°C in 100°C increments. For identification of any generated products the pyrolysis unit was coupled to an Agilent Technologies 6890 gas chromatograph coupled to a 5,973 mass spectrometer (GC-MS) and the interface held at 150°C. The GC injector was held at 200°C and operated in split mode (50:1) with a column flow rate of 1.1 mL min$^{-1}$. Separation was performed on a SGE BPXS column (25 m x 0.22 mm). The GC oven was held for 5 min at 35°C and then ramped at a rate of 10°C min$^{-1}$ to 200°C where it was held for 4 min. Mass spectra were acquired in the scan range
10–150 amu. Identification of peaks in the chromatographs was carried out using the Agilent MSD Chemstation software package and comparison to the NIST database. The integrated area under each peak was used as a proxy for the amount of gas produced, normalized to the weight of the perchlorate sample preexposure; consequently, any relative differences in gas release postexposure must be the result of hydration. Replicate analysis was precluded owing to the long duration of the heating and reexposure treatment.

Data from the laboratory pyrolysis-GC-MS is assumed to be comparable to that from the SAM evolved gas analyzer (EGA). While differences in heating rate (20°C m s⁻¹ versus 35°C m s⁻¹) and environmental conditions (~1,013 and ~25 mbar He, respectively) between laboratory- and rover-based instruments (full comparison of instrument parameters shown in supporting information Table S1), and the lower resolution (100°C) of the stepped pyrolysis compared to the continuously heated EGA, could affect the distribution of pyrolysis products, there are enough similarities between the two data sets to allow effective comparison.

### 2.3. X-Ray Diffraction

Samples of Mg(ClO₄)₂·aq from each drying regime (3, 4, and 5 weeks) were also prepared for X-ray diffraction (XRD) to check hydration states and hydration state stability. Grinding of the dried samples to fine powder was accomplished using a pestle and mortar. Both grinding and loading into the sample holder were carried out in a glove bag under a nitrogen atmosphere to preserve hydration state of dried samples, while postexposure samples were prepared for analysis under ambient laboratory conditions. Samples were transported to the XRD, a 5 min period, in an airtight container under nitrogen to preserve their relevant postdrying or postexposure hydration state.

Analysis was carried out with a Panalytical X’Pert Pro MPD on finely powdered samples mounted in flat sample holders, covered in kapton foil. Cu Kα radiation (45 kV and 40 mA) and an Xcelerator position sensitive detector were used over a measurement range of 2θ from 10 to 90° in 0.017° steps, 100 s per step.

The produced data was compared and fitted to database spectra via Rietveld refinement.

### 2.4. Fourier Transform Infrared Spectroscopy

Samples of Mg(ClO₄)₂·aq from each drying regime (3, 4, 5 weeks) were prepared for Fourier Transform infrared spectroscopy (FTIR) to check hydration states and hydration state stability. Grinding of the dried samples to fine powder was accomplished using a pestle and mortar. Both grinding and loading into the sample holder were carried out in a glove bag under a nitrogen atmosphere to preserve hydration state while postexposure samples were prepared for analysis under ambient laboratory conditions.

A mixture of approximately 0.05% (weight percent) sample and dry KBr was prepared, finely ground, and compressed into a pellet for measurement in a Nicolet 6700 FTIR spectrometer with transmission accessory. Infrared spectra were collected in transmission, in the range 400–4,000 cm⁻¹. A pellet of pure KBr was used as a background. For each measurement, we collected 128 scans with a resolution of 4 cm⁻¹, which were averaged for the final data. This configuration used an IR source, a KBr beam splitter and a deuterated triglycine sulfate detector.

### 3. Results

#### 3.1. Pyrolysis-Gas Chromatography-Mass Spectrometry

Table 1 shows the stepped pyrolysis products of magnesium perchlorate. The major products were molecular oxygen, water, and hydrogen chloride (from the reaction of chlorine gas and water). These products were to be expected, as the thermal decomposition of hydrated Mg(ClO₄)₂·nH₂O progresses as:

\[
\begin{align*}
2\text{Mg(ClO}_4\text{)}_2\cdot n\text{H}_2\text{O} & \xrightarrow{T<350^\circ C} 2n\text{H}_2\text{O} + 2\text{Mg(ClO}_4\text{)}_2 \\
& \xrightarrow{T>400^\circ C} 2n\text{H}_2\text{O} + 2\text{MgO} + 7\text{O}_2 + 2\text{Cl}_2 \\
& \quad 2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{O}_2
\end{align*}
\]

(Glavin et al., 2013)

Carbon-bearing gases and organochlorine compounds were monitored but were rarely present in anything other than trace amounts and within background error. Chromatograms for all samples showing the release
files of O2 and HCl are displayed in Figure 1. O2 and HCl are displayed in isolation because of the confident assignment of their provenance as perchlorate decomposition products. Additional detected species are displayed in supporting information Figure S2.

In general, increasing time spent in the drying oven leads to a shift in O2 release from 500°C to 600°C and a narrowing of the initially broad peak between weeks 0 and 5. Week 4 shows an intermediate state with two distinct end-members present in a bimodal distribution. It can also be seen that, generally, the O2 release peak rebroadens with exposure time (i.e., increasing hydration). While less consistent, the HCl release shows a similar pattern to O2; going from a lower temperature 500 °C broad release in the undried sample, narrowing in the 3 week sample, through a bimodal stage for the 4 week sample, and then finally a higher-temperature narrow and unimodal release at 700°C for the 5 week sample. The HCl peak also generally rebroadens, becoming less distinct with exposure time, although this trend pattern is not as clear as it is for O2.

Superimposition of the O2 data for the various drying times analyzed directly from the oven (Figure 2a) and the 3 week drying time with increasing exposure times (Figure 2b) show the clear trends noted above.

Table 1
Temperature of Release of Various Gas Species During Stepped Pyrolysis of Mg(ClO4)2 · nH2O

| m/z | Species | Range (peak) (°C) | Comment |
|-----|---------|-------------------|---------|
| 18  | O2      | 400–1000 (500–600) | Major decomposition product for all samples |
| 32  | H2O     | 200–500 (200–400) 800–1000 | Major decomposition product for all samples |
| 36  | HCl     | 500–1000 (500–600) | Major decomposition product for all samples |
| 44  | CO2     | 400 (trace) 800–1000 | Observed for two samples, evidence of minor organic contamination |
| 70  | Cl2     | 500–700           | Observed for five samples, decomposition product |
| 117 | CCl4    | 600–700           | Observed for one sample, evidence of minor organic contamination |

Note: Both CCl2O and SO2 were monitored as evidence of organic contamination, but neither was detected in any of the samples.

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Superimposition of the O2 data for the various drying times analyzed directly from the oven (Figure 2a) and the 3 week drying time with increasing exposure times (Figure 2b) show the clear trends noted above.

Figure 1. O2 and HCl release curves for all Mg(ClO4)2·nH2O samples. "Undried" is a sample that was analyzed directly from storage, without being subjected to oven drying. For all other samples the time spent in the drying oven and time reexposed to the (laboratory) atmosphere to allow hydration is shown. X axis is temperature in °C. Black wt % numbers refer to the amount of water absorbed from the atmosphere during reexposure, while gray italics refer to XRD data. Asterisk denotes that absorbed water wt % for sample 4:72 is unknown as the vial was damaged during reweighing.
3.2. XRD

The XRD results shown in Figure 3 and summarized in Figure 4 (full data including Rietveld parameters in supporting information Figures S3–S9) confirm the presence of different hydration states of \( \text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O} \) after various drying and reexposure treatments. It can be seen that the sample analyzed straight from the bottle is a mixed assemblage of the three hydration states (hexahydrate, tetrahydrate, and dihydrate), but with increased drying time the concentration of hexahydrate decreases as tetrahydrate increases. Peaks also become sharper, showing increasing crystallite size and/or better crystallinity over time, although the samples are already well crystalline from week 3. With exposure to the laboratory ambient conditions (allowing hydration) the samples are transformed to hexahydrate, with the most dried samples changing most rapidly, presumably reflecting their relatively enhanced hydrophilic capacity.

3.3. FTIR

The FTIR spectra of the samples in the 1,550–1,700 cm\(^{-1}\) range (Figure 5) show two prominent peaks, the larger peak occurring without variation at 1,631 cm\(^{-1}\) and the smaller peak at 1,608 cm\(^{-1}\). The 1,631 cm\(^{-1}\) peak is present in all samples. The smaller peak (1,608 cm\(^{-1}\)) is (weakly) present in samples containing more than 50% tetrahydrate (0 weeks, 3 weeks, 4 weeks, 5 weeks, and 3 weeks in oven +72 h exposure), suggesting that the 1,608 cm\(^{-1}\) peak is related to the tetrahydrate phase. Bishop et al. (2014) assigned a peak at 1,650 cm\(^{-1}\) to \( \text{H}_2\text{O} \) bending vibrations in hydrated \( \text{Mg(ClO}_4\text{)}_2 \) (specific hydration state not given); this is likely the same peak as our 1,631 cm\(^{-1}\) peak. The difference in peak wave-length maximum may be due to the differing measurement techniques used (i.e., transmission versus reflection) or to the variation in this peak’s position due to hydration state as mentioned by Bishop et al. (2014). Miller and Wilkins (1952) reported a single peak at 1,625 cm\(^{-1}\) in anhydrous \( \text{Mg(ClO}_4\text{)}_2 \), which we did not observe in any of our samples, consistent with their hydration state as determined by XRD.

4. Discussion

4.1. Changes in \( \text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O} \) Hydration State

The three modes of \( \text{O}_2 \) release observed (broad peak at 500°C, bimodal peaks, and narrow, unimodal peak at 600°C) suggest that \( \text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O} \) changes its hydration state while desiccating in the drying oven. The undried and week 3 samples represent a more hydrated state, the week 5 samples represent a more dehydrated state, and the bimodality of the responses for the week 4 samples represent an intermediate situation where both these hydrated and dehydrated states are present.

The XRD and FTIR data show the behavior of \( \text{Mg(ClO}_4\text{)}_2 \) to be more complex than expected, mainly because the hydration state changes with desiccation time. However, the initial state of the \( \text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O} \) appears to be a metastable assemblage of the dihydrate, tetrahydrate, and hexahydrate forms, rather than the pure hexahydrate which would be expected based on the previously published (Robertson & Bish, 2011) stability field (Figure 6). The broad peak of oxygen release from the undried (0 weeks) sample is therefore the result of
the three states decomposing over a range of temperatures. The hydration and dehydration of salts has been shown by previous studies to be a slow process (Gough et al., 2011; Vaniman & Chipera, 2006). Phase transitions of salts to a more ordered (less hydrated) state requires nucleation and is, therefore, kinetically hindered (Gough et al., 2014). The highly dry microenvironment, “buffered” by the bulk of hydrophilic material in the storage jar, may have allowed this metastable assemblage to gradually form over the >20 years the jar had been stored in the laboratory (Figure 6).

With drying and heating, the highly unstable dihydrate recrystallized to the more stable hydrous forms so that only hexahydrate and tetrahydrate remained. This narrowed the peak for the 3 week sample and created the bimodal distribution in the 4 week sample. The minor differences in the XRD and FTIR data and the large differences in the Py-GC-MS data between these two samples is likely the result of heterogeneity within the samples used for the different analysis, and thus, it suggests that the 3 week sample analyzed for O₂ release.

**Figure 3.** XRD patterns of Mg(ClO₄)₂·nH₂O after various drying and exposure regimes; the 4 week data are not shown as very similar to 5 weeks (full data including Rietveld parameters in supporting information Figures S3–S9, color version online). Changing percentage concentrations of the various hydration states present are noted and summarized in the inset bar chart.

**Figure 4.** XRD-defined proportions of Mg(ClO₄)₂ hydration states (w = weeks dried, h = hours exposed).
was predominantly hexahydrate while the portion used for XRD was predominantly tetrahydrate.

By week 5 almost all of the hexahydrate had dehydrated and recrystallized to tetrahydrate, the most stable form under the drying conditions (Figure 6). In addition to hydration state changes, the XRD data also reveal that the crystallinity and/or crystal size increases slightly with time in the oven causing sharpening of the XRD peaks in samples between weeks 3 and 5. This may have had a secondary (posthydration state change) effect on the temperature of decomposition because increasing crystal size and decreasing crystal defects will decrease the surface area on which reactions can initiate, leaving the sample more resistant to decomposition (Anderson & Horlock, 1962; Prout & Tompkins, 1944). However, owing to the small changes observed in the XRD patterns, surface area effects are likely to have been minor. Changes in thermal decomposition temperatures related to crystal surface area is nonetheless another factor to take into account in determining perchlorate parent salt identity.

4.2. Relevance to Martian Data

We have shown that $O_2$ release from $\text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O}$ differs depending on the hydration state. Previous studies (Glavin et al., 2013; Leshin et al., 2013) have used the temperature of $O_2$ release during evolved gas analysis from Martian regolith analyzed by the Sample Analysis at Mars (SAM) instrument suite on the MSL to infer the cation present in the perchlorate salt. This led to a conclusion that calcium perchlorate ($\text{Ca(ClO}_4\text{)}_2$) is the most likely candidate for the main $O_2$ release at Rocknest (Glavin et al., 2013). There are no published experiments where perchlorate salts analyzed under SAM-like conditions unequivocally matched the release temperatures observed on Mars. Calcium perchlorate was suggested as the parent salt owing to a degree of overlap with the data. Figure 7 shows a comparison of the $O_2$ release temperatures from our differing hydration states of $\text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O}$ and those measured by SAM on Mars (Glavin et al., 2013; Ming et al., 2014).

When the previously published results are compared to those from our study (Figure 7), it can be seen that there is almost as much variability in decomposition temperature between the analyzed hydration states of $\text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O}$ as there is between the different cations of perchlorate salts. The lower (500°C) peak $O_2$ release for the more hydrated samples (Figure 7a) corresponds to the peak release temperature for $\text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O}$ reported previously (Glavin et al., 2013). It should be noted that this interpretation takes the lower resolution of stepped pyrolysis compared to evolved gas analysis into consideration. However, the most dehydrated (almost 100% tetrahydrate) sample (5 weeks, Figure 7a) is a closer match to the published data for sodium perchlorate ($\text{Na(ClO}_4\text{)}_2$) (Figure 7c (Glavin et al., 2013)) with the intermediate group (4 week dried samples, Figure 7a) appearing as a mixture of the two perchlorates. It is evident that a mixture of hydration states of perchlorate salts may produce multimodal $O_2$ release curves during pyrolysis similar to those observed for a mixture of perchlorate salts.

In contrast to the above results, data obtained using thermogravimetric and controlled temperature and humidity XRD experiments have suggested that the hexahydrate is the stable form of $\text{Mg(ClO}_4\text{)}_2 \cdot n\text{H}_2\text{O}$ on Mars (Robertson & Bish, 2011). However, it is plausible that various hydration states of perchlorate salts and

**Figure 5.** Infrared spectra of $\text{Mg(Cl}_4\text{O}_2\text{)}$ perchlorate in the region 1,550–1,700 cm$^{-1}$. Solid lines indicate samples which were measured directly out of the oven, while dashed lines indicate samples which have been exposed to atmosphere for a minimum of 72 h (3, 4, and 5 weeks; "0 week" sample is estimated to have been exposed for 20 years). Full spectra (400–4,000 cm$^{-1}$) are available in the supporting information.

**Figure 6.** The $\text{Mg(Cl}_4\text{O}_4\text{)}_2 \cdot n\text{H}_2\text{O}$ hydration state stability diagram, after Robertson and Bish (2011). RH with respect to liquid water. Arrows show potential conditions analyzed samples subjected to, solid arrows represent dried samples, and dashed arrow represents potential microenvironment inside the $\text{Mg(Cl}_4\text{O}_4\text{)}_2 \cdot n\text{H}_2\text{O}$ jar. Laboratory conditions will have been around 20–25°C and 50–60% RH; oven heating exposed samples to 110°C and low RH.
mixtures of those hydration states could be present under Martian conditions. The Phoenix lander measured site surface relative humidity (RH), with respect to ice, varying from 100% in the early morning and late evening to well under 0.01% during most of the day and year (Zent et al., 2010, 2016), and thus at Mars temperatures, and lower latitudes, Mg(ClO$_4$)$_2$ · nH$_2$O is potentially stable as a mixture of hexahydrate, tetrahydrate, and dihydrate most of the time. Owing to the slow reaction kinetics of the hydration and dehydration of salts (Gough et al., 2011, 2014; Vaniman & Chipera, 2006), it is likely that metastable forms of perchlorate salts continue to be present for long periods (as we have observed with the undried sample), especially where they may come into contact with subsurface water-ice as this allows much faster rehydration and deliquescence than atmospheric water vapor (Fischer et al., 2014).

It is possible, therefore, that there are mixed perchlorate hydration states in the John Klein and Cumberland samples analyzed by SAM from the Sheepbed mudstone (Ming et al., 2014). In Figure 7, it can be seen that the John Klein and Cumberland samples have distinctly different O$_2$ release profiles, both of which are much lower than that for the Rocknest sample. John Klein has a bimodal distribution, releasing at 150–500°C with peaks around 210°C and 380°C, while Cumberland releases at 230–420°C, peaking at 320°C. Although the O$_2$ release profiles for John Klein and Cumberland do not match exactly those of common perchlorate salts the best matches are thought to be with Fe-perchlorates (Ming et al., 2014). However, the responses from the John Klein and Cumberland samples appear similar (at lower temperatures) with the intermediate and final hydration states analyzed in this study, inferring that the MSL data may reflect sites where various hydration states of the same perchlorate salt are present.

There is, however, no obvious relationship between the daily range of relative humidity at the locality when the samples were drilled (or scooped as is the case for Rocknest) and the temperature or form of peak O$_2$ release. This is clear when the evolved gas analysis data for all drill sites released so far (Sutter et al., 2016) is compared to concurrent climate conditions as measured by the Rover Environmental Monitoring Station (Table 2).

The lack of a direct relationship between the relative humidity and the O$_2$ release indicates that the different sites reflect conditions on longer timescales than the daily humidity and temperature cycle. Yet samples collected in the Martian Winter and Spring (e.g., Windjana and Rocknest) have generally lower release temperatures than Mid-Summer and Early Autumn samples (e.g., Telegraph Peak and Buckskin) suggesting that peak O$_2$ release, and therefore, hydration state may be related to the climatic conditions of the proceeding few months. The slow response to changing conditions is to be expected as our results show that perchlorate salts take a long time to equilibrate to local conditions and remain in a metastable state for weeks. It is also notable that the samples with multimodal O$_2$ release are from the late Spring and late Autumn and may therefore represent mixed transitional states between the more wet Winter and more dry Summer hydration states.

It is plausible that the amount of time a collected sample spends in MSL’s sample handling system (CHIMRA (Jandura, 2010)) may influence the hydration state of perchlorate minerals present. Samples may sit in storage for some time, under a controlled 20°C environment, which could allow enough time for changes in hydration state to occur so that evolved gas analysis data may not reflect the original hydration state of the sample. The effect of this could be minimized by immediate analysis of collected samples.
The presence of iron minerals (which have been identified in the Martian regolith (Bish et al., 2013)) has also been shown to affect the thermal decomposition of perchlorate salts, acting as catalysts, and reducing the temperature of peak $O_2$ release (Bruck et al., 2014; Sutter et al., 2015). The effect on altering the temperature of decomposition when perchlorates and iron minerals are mixed in solution is of similar magnitude to the effect we find by changing the hydration state (Sutter et al., 2015). The presence of other minerals is therefore another factor which may complicate the identification of oxychlorine species and must be taken into consideration.

5. Conclusions

Perchlorate salts are an important component of Martian surface materials and severely interfere during organic compound analyses that employ thermal extraction protocols. Understanding the decomposition behavior of perchlorate salts with temperature is a commonly used method for identification of the parent salt. Drying experiments using $Mg(ClO_4)_2\cdot nH_2O$ indicate that the thermal decomposition temperature of different hydration states produce distinct and discrete responses. Any effects on the thermal decomposition related to crystallinity/crystal size are suggested to be secondary to this and minor in this study, although this is an area where there is clearly scope for future research. Future interpretations of thermal decomposition profiles of perchlorate containing samples should consider the hydration state of these important Martian salts. An important implication of our results is that the variation in thermal decomposition temperature, owing to hydration state, may provide a mechanism by which the different windows of decomposition for perchlorates and organic components of interest can be optimized.

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