



RESEARCH ARTICLE

10.1029/2018JE005615

Key Points:

- CO:CO₂ response during thermal decomposition of organic matter with perchlorate is a proxy for completeness of combustion
- There needs to be approximately 5 times as much organic matter than perchlorate in samples for its detection by thermal decomposition techniques
- Future life detection missions will need to look for sites that improve the organic matter:perchlorate ratio compared to the average Martian regolith

Supporting Information:

- Supporting Information S1

Correspondence to:

S. H. Royle,
s.royle@imperial.ac.uk

Citation:

Royle, S. H., Oberlin, E., Watson, J. S., Montgomery, W., Kounaves, S. P., & Sephton, M. A. (2018). Perchlorate-driven combustion of organic matter during pyrolysis-gas chromatography-mass spectrometry: Implications for organic matter detection on Earth and Mars. *Journal of Geophysical Research: Planets*, 123, 1901–1909. <https://doi.org/10.1029/2018JE005615>

Received 19 MAR 2018

Accepted 6 JUL 2018

Accepted article online 10 JUL 2018

Published online 26 JUL 2018

Perchlorate-Driven Combustion of Organic Matter During Pyrolysis-Gas Chromatography-Mass Spectrometry: Implications for Organic Matter Detection on Earth and Mars

Samuel H. Royle¹ , Elizabeth Oberlin^{2,3}, Jonathan S. Watson¹, Wren Montgomery¹ , Samuel P. Kounaves^{1,2} , and Mark A. Sephton¹

¹Impacts and Astromaterials Research Centre, Department of Earth Science and Engineering, Imperial College London, London, UK, ²Department of Chemistry, Tufts University, Medford, MA, USA, ³Now at Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

Abstract The search for life on Mars targets the detection of organic matter from extant or extinct organisms. Current protocols use thermal extraction procedures to transfer organic matter to mass spectrometer detectors. Oxidizing minerals on Mars, such as perchlorate, interfere with organic detection by thermal extraction. Thermal decomposition of perchlorate releases oxygen, which promotes combustion of organic carbon. We have assessed the minimum mass ratio of organic carbon to perchlorate required to detect organic matter by thermal extraction and mass spectrometry. Locations on Mars with organic carbon to perchlorate ratios above 4.7–9.6 should be targeted. Because habitability is enhanced by the presence of liquid water and because perchlorate is a water-soluble salt, locations on Mars with evidence of past or recent liquid water are high priority targets.

Plain Language Summary Missions to Mars look for evidence of organic molecules using thermal extraction techniques. Certain minerals on the Martian surface, such as perchlorate salts, break down during heating, releasing oxygen and causing the combustion of any organic matter, which may have been present. In this event organic carbon is lost to analysis as CO and CO₂. We used the ratio of CO: CO₂ produced as a proxy for the completeness of combustion when various ratios of organic matter and perchlorate were thermally decomposed together. This allowed us to find a minimum organic carbon: perchlorate mass ratio (~5 times) for the survival of organic molecules. Carbon monoxide can only be produced if there is an excess of carbon to oxygen, which could enable the survival of unoxidized organic molecules for their subsequent detection. Applying these findings to Mars suggests that we would not expect to be able to detect organic molecules in average Martian soil. Consequently, future life detection missions to Mars must search for areas that exceed this ratio, either by having more organic matter or less perchlorate, and locations with evidence of recent water activity or in the subsurface are most likely to fulfill both of these criteria.

1. Introduction

So far, almost all attempts to search for evidence of indigenous organic molecules on Mars have failed to detect anything other than CO, CO₂, short chain (C₁–C₄) alkyl, and single-ring aromatic organochlorine molecules (Biemann et al., 1977; Cannon et al., 2012; Freissinet et al., 2015; Glavin et al., 2013; Leshin et al., 2013; Ming et al., 2014). Only recent analysis of samples from the lower Murray mudstone, analyzed by the Mars Science Laboratory (MSL), have yielded evidence of complex organic matter (Eigenbrode et al., 2015, 2018). However, the presence of complex organic molecules should be widespread on Mars from exogenous sources via meteorites, comets, or interplanetary dust particles (Flynn, 1996; Gibson, 1992; Sephton, 2012) or formed from indigenous igneous, hydrothermal, or atmospheric processes (Chyba & Sagan, 1992; Konn et al., 2015; Steele et al., 2012; ten Kate, 2010). Additionally, there may be products of extant or extinct life, analogous to the low levels of organic compounds that have been detected in the Atacama Desert on Earth (Navarro-Gonzalez et al., 2003).

The most likely reason for the difficulty in detecting organic molecules on the Martian surface is the deleterious effects of oxidizing minerals, especially perchlorates, which oxidize organic matter during

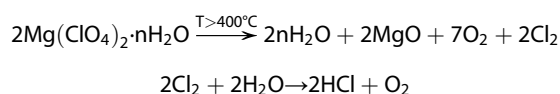
©2018. The Authors.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

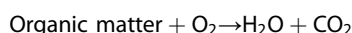
thermal extraction analyses (Blake et al., 2013; Freissinet et al., 2015; Glavin et al., 2013; Leshin et al., 2013; Lewis et al., 2015; Miller et al., 2016; Ming et al., 2014) and are present at high concentrations in hyperarid environments.

As oxidizing minerals are likely to be ubiquitous on the surface of Mars (Carrier & Kounaves, 2015; Catling et al., 2010; Clark & Kounaves, 2016), it is not possible to avoid them during in situ analysis. It may, however, be possible to identify areas with relatively low concentrations. Acceptably low levels can be determined by understanding the effects of perchlorate on organic matter during thermal decomposition analyses. Effective site selection is currently the best approach to maximize chances of detecting organic molecules, and it is therefore necessary to know the minimum organic matter to perchlorate ratio required for detection.

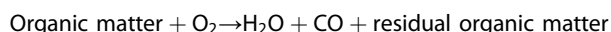
Thermal decomposition of perchlorate produces O₂:



Total combustion of organic matter produces CO₂:



Incomplete combustion of organic matter produces CO:



Only when all O₂ from the decomposition of perchlorate is consumed can any remaining carbon from organic molecules be detected. At this point CO will be produced in increasing amounts, elevating the CO/CO₂ ratio. Therefore, this ratio is a plausible proxy to find the minimum mass ratio of organic matter to perchlorate that will allow organic matter detection. In this study we investigated the gas-phase breakdown products of perchlorate and organic matter during thermal decomposition (pyrolysis) to identify this critical ratio.

2. Methods

2.1. Samples

Type IV organic matter (OM) was selected as the source of organic matter in this study. This organic matter is highly reworked and mostly composed of a network of aromatic hydrocarbons. In this way, Type IV OM bears chemical similarities to the macromolecular organic matter found in meteorites (Matthewman et al., 2013; Montgomery et al., 2016), which is expected to be a major source of organic matter in the Martian regolith (Flynn, 1996; Gibson, 1992; Sephton, 2012). The Type IV OM used was a charcoal fragment from the Wealden sands, which has a total organic carbon (TOC) content of 53.46% (Matthewman et al., 2012).

Magnesium perchlorate (Mg(ClO₄)₂) was selected as the perchlorate salt to investigate as it is one of two main perchlorate parent salts (along with calcium perchlorate) proposed to be present within the Martian regolith (Kounaves et al., 2014); other studies have also suggested the presence of iron perchlorate and sodium perchlorate to explain MSL's Evolved Gas Analysis results (Glavin et al., 2013; Ming et al., 2014; Sutter et al., 2017), although their contributions are less well constrained. Mg(ClO₄)₂·aq was obtained from Fisher Scientific UK Ltd., and previous work has shown this sample to be a mixture of the hexahydrate, tetrahydrate, and dihydrate hydration states (Royle et al., 2017).

2.2. Pyrolysis-Gas Chromatography-Mass Spectrometry

Type IV OM and Mg(ClO₄)₂ were loaded as powders in varying ratios into quartz pyrolysis tubes, supported by quartz wool. Individual samples were placed inside the platinum coil of a CDS Analytical 2000 Pyroprobe under helium carrier gas and heated at 20 °C/ms⁻¹ to 650 °C and held for 15 s. The pyrolysis unit was coupled to an Agilent Technologies 6890 gas chromatograph coupled to a 5973 mass spectrometer (GC-MS) and the interface held at 270 °C. Separation was performed on a SGE BPX5 column (25 m × 220 μm × 0.25 μm), which was selected both for its durability while running repeated highly oxidizing perchlorate samples and to allow the identification of any organic compounds surviving incomplete combustion.

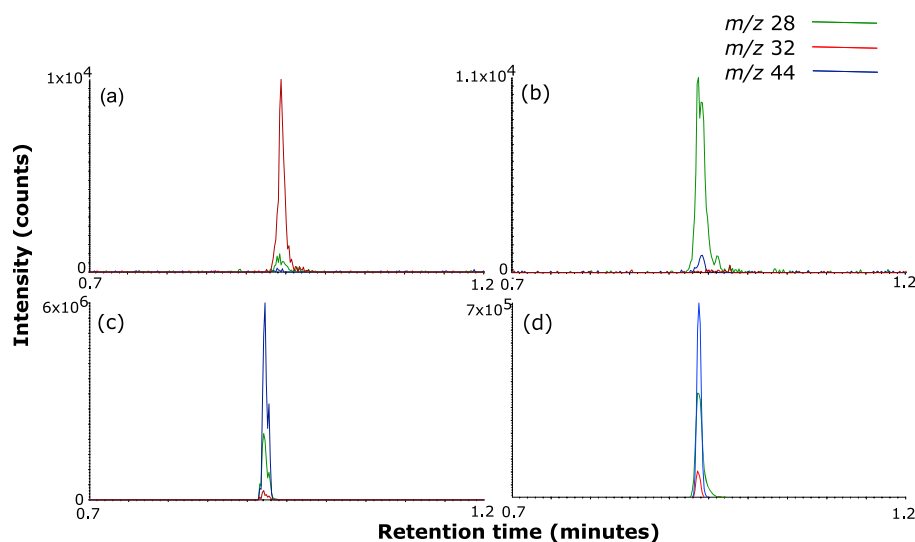


Figure 1. Partially reconstructed mass chromatograms of (a) $\text{Mg}(\text{ClO}_4)_2$; (b) Type IV organic matter; (c) subcritical ratio (6.6 times) sample of Type IV organic matter and $\text{Mg}(\text{ClO}_4)_2$; (d) supercritical ratio (20 times) sample of both Type IV organic matter and $\text{Mg}(\text{ClO}_4)_2$. The m/z responses used as proxies for the relative amounts of gases produced: m/z 28 = CO; 44 = CO_2 ; 32 = O_2 .

For gas ratio analysis the GC injector was held at 200 °C, operated in split mode (100:1), with a column flow rate of 0.9 ml/min. The GC oven was held for 2 min at 40 °C, then ramped at 15 °C/min to 150 °C where it was held for 40 s. Mass spectra were acquired over 6–250 amu. Peak identification in the chromatograms was carried out using the Agilent MSD Chemstation software package and comparison to the NIST database (<http://webbook.nist.gov/chemistry/>). The ions monitored were mass/charge (m/z) 28, 32, and 44; these reflect CO, O_2 , and CO_2 respectively. The integrated area under each peak was used as a proxy for the relative amounts of gases produced, CO_2 also produces a double ionized m/z 28 fragment, CO^+ with an intensity of 10% that of the m/z 44 base peak in the fragmentation pattern (NIST), and the contribution of this to the m/z 28 CO peak is corrected for.

For analysis of the organic matter the GC injector was held at 200 °C, operated in split mode (10:1), with a column flow rate of 1.1 ml/min. The GC oven was held for 2 min at 40 °C, then ramped at 5 °C/min to 310 °C where it was held for 10 min. Mass spectra were acquired over 50–550 amu.

2.3. Critical Ratio Calculation

The critical ratio is the point at which more organic carbon is released during pyrolysis than can be combusted by the O_2 produced by the decomposition of perchlorate. This ratio was calculated by dividing the collected data from the gas response into two subsets. The first data subset represents the stable signal produced as a result of the complete combustion of organic matter due to the presence of perchlorate during the pyrolysis protocol, and the second data subset represents the linear increase in CO/ CO_2 (m/z 28/44) produced as a result of the incomplete combustion of organic matter. The intersection of these two data subsets represents the lowest minimum mass ratio at which organic matter can be detected in the presence of perchlorate. The data were divided by minimizing the sum of the residual error from the mean in each region.

3. Results

Significant differences were observed in the relative amounts of m/z 28, 32, and 44 responses detected during the pyrolysis of Type IV OM, $\text{Mg}(\text{ClO}_4)_2$, and mixtures of both (Figure 1).

When $\text{Mg}(\text{ClO}_4)_2$ is pyrolyzed independently (Figure 1a), the dominant product of interest is O_2 as there is no carbon source provided and any CO or CO_2 release will be due to minor organic contamination. When Type IV OM is pyrolyzed independently (Figure 1b), the dominant product is CO with only minor CO_2 release and no significant O_2 because combustion is incomplete owing to a lack of a significant O_2 source. When $\text{Mg}(\text{ClO}_4)_2$

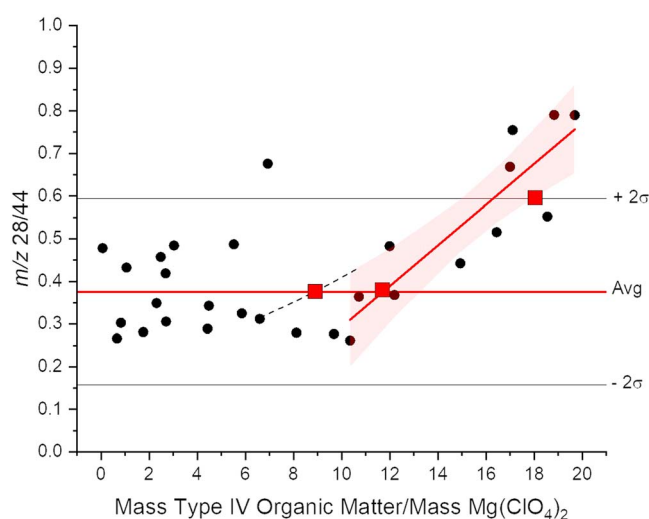


Figure 2. Ratio of Type IV organic matter: Mg perchlorate pyrolyzed against m/z 28/44 peak area, used as a proxy for the relative abundances of CO (m/z 28) and CO₂ (m/z 44). The shaded portion represents the 95% confidence interval for the linear regression line through the incomplete combustion data set. The red squares indicate the upper (18.0), lower (8.9), and predicted (11.7) minimum mass ratios for the detection of organic matter in the presence of perchlorate. The average and $\pm 2\sigma$ lines are derived from statistical calculations from the complete combustion data set. The intersection of the average of the signal from complete combustion and the regression line for the signal from incomplete combustion at 11 times Type IV/Mg perchlorate shows the *critical ratio* where not all of the carbon is fully oxidized to CO₂ due to insufficient O₂ released from the perchlorate.

and Type IV OM are pyrolyzed together (Figures 1c and 1d) the dominant product is CO₂, followed by CO and minor relative amounts of O₂. O₂ produced from the breakdown of the perchlorate is consumed by oxidation of OM and its oxidation intermediate CO. The observed multiple peaks with the same mass number are due to the coelution of the gas species with the m/z 28 double ionized CO₂ peak (due to secondary fragmentation in the mass spectrometer) interfering with the m/z 28 CO peak.

The intersection of the average signal from complete combustion and the regression line for the signal from incomplete combustion at 11.7 times Type IV/Mg perchlorate shows the *critical ratio* where not all of the carbon is fully oxidized to CO₂ due to insufficient O₂ released from perchlorate (Figure 2). Due to a large degree of noise associated with the complete combustion, a similarly large error is associated with this intersection point. The m/z 28/44 signal produced during complete combustion in the presence of perchlorate was 0.376 ± 0.218 . The error in our determined Type IV/Mg perchlorate ratio was determined by taking the intersection of the average and 2σ of the 28/44 signal produced by complete combustion, with the upper and lower limits of the 95% confidence interval of the regression line of the partial combustion data, respectively. By doing so, we determine that at a 95% confidence interval the minimum mass of Type IV OM/Mg perchlorate required to detect organic matter using thermal decomposition methodologies is between 8.9 and 18.0.

Total ion chromatograms of varying mixtures of Mg(ClO₄)₂ and Type IV OM pyrolyzed together (Figure 3) confirm that there is a necessary critical minimum mass ratio for survival and detection of organic matter. Below

the critical ratio (Figure 3d) the only molecules detected are those which can be attributed to reactions between the highly oxidizing perchlorate salt and the GC column coating (5% phenyl polysilphenylene-siloxane) as all products are also detected when Mg(ClO₄)₂ is pyrolyzed on its own (Figure 3b). Above the critical ratio (Figure 3e) the majority of the products detected when pyrolyzing Type IV OM on its own (Figure 3c) can be detected by the mass spectrometer along with the cyclosiloxanes and chlorohydrocarbons produced by the reaction of the GC column coating (and potentially carbon sourced from the Type IV OM) with the perchlorate. It was confirmed that the cyclosiloxanes and chlorohydrocarbons in the pure Mg(ClO₄)₂ analyses originated from the reaction between the GC column coating and the perchlorate by repeating the perchlorate pyrolysis through deactivated fused silica tubing (4 m $\times$ 0.15 mm, SGE) in place of the column. While ions with masses corresponding to siloxane (m/z 207), chlorobenzene (m/z 112), and carbon tetrachloride (m/z 117) were still detected in trace amounts under these conditions, the intensity of their signals were reduced by orders of magnitude.

4. Discussion

If all the organic carbon released during thermal extraction of samples is completely combusted by oxygen released from the breakdown of perchlorate (or other oxidants), then there will be no surviving organic compounds available to detect by GC-MS. Our data reveal that, in any sample analyzed by thermal extraction techniques, there must be a minimum of 8.9–18.0 times as much organic matter as perchlorate present to allow organic matter detection. This was confirmed in our experiments by the detection of organic matter present in amounts above the critical ratio value. Our data are most relevant to the degraded organic carbon in Type IV OM on Earth and by extrapolation the highly aromatic organic matter in meteorites. The TOC of the Type IV OM used in our study is 53.46%. This translates to a TOC: perchlorate critical ratio of 4.7–9.6 times. Our identification of this ratio allows for a more accurate estimation of organic matter content in highly oxidized soils through a better understanding of the method detection limit derived from the mass of perchlorate measured in the soil.

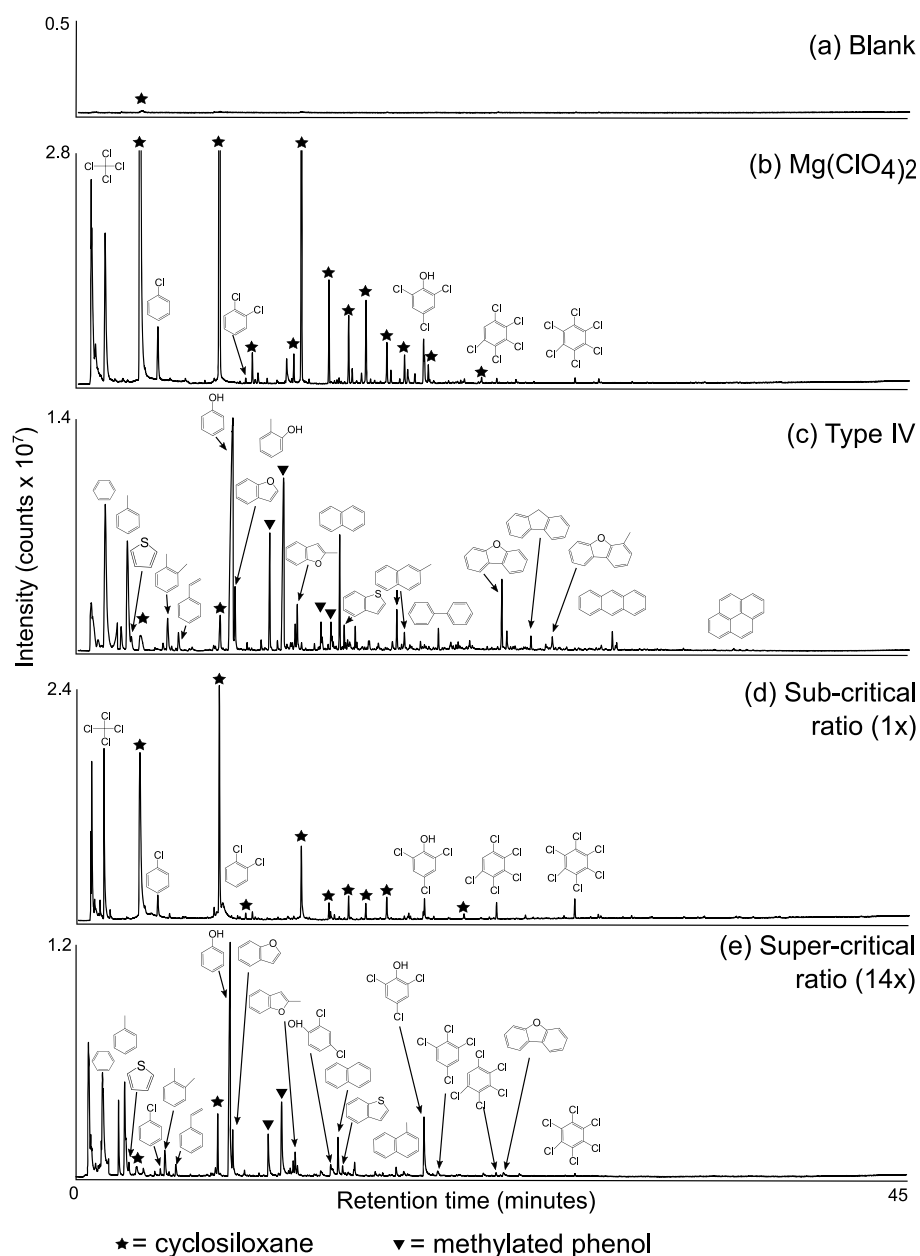


Figure 3. Pyrolysis-GC-MS total ion chromatograms of varying $\text{Mg}(\text{ClO}_4)_2$ Type IV organic matter mixtures: (a) blank; (b) $\text{Mg}(\text{ClO}_4)_2$ showing products from the reaction of this highly oxidizing salt with the GC column; cyclosiloxanes are typical products of column bleed; (c) Type IV organic matter; (d) $\text{Mg}(\text{ClO}_4)_2$ and Type IV mixture below critical ratio (1:1); all detected products may be attributed to the reaction of the perchlorate and the GC column; (e) $\text{Mg}(\text{ClO}_4)_2$ and Type IV mixture over critical ratio (1:14); surviving residual organics are observable as are chlorinated molecules from reaction of the perchlorate with the column and potentially the Type IV organic matter. The initial peak in each chromatogram represents the coelution of low molecular weight volatile phases. GC-MS = gas chromatography-mass spectrometry.

4.1. Relevance to Mars

The amount of perchlorate in the Martian regolith was measured as 0.4 to 0.6 wt% by Phoenix (Hecht et al., 2009) and 0.1–0.5 wt% by the MSL mission at the majority of sites in Gale Crater (Glavin et al., 2013; Sutter et al., 2017), although up to 1.4 wt% perchlorate was measured at the Cumberland site (Ming et al., 2014; Sutter et al., 2017). Owing to atmospheric formation and fallout of perchlorate, this value (excluding the anomalously high level of perchlorate at Cumberland) is expected to be globally consistent (Carrier & Kounaves, 2015; Catling et al., 2010). Therefore, based on this study's findings, there must be 0.5–5.6 wt %

TOC present for incomplete combustion of organic compounds and subsequent detection during thermal extraction-based measurements.

The organic matter content of the Martian regolith is highly uncertain. Organic compounds such as alkylbenzenes, naphthalene and higher polycyclic aromatic hydrocarbons (PAHs), insoluble organic matter, amino acids, and carboxylic acids will have been delivered to Mars by meteorites and other exogenous sources (Benner et al., 2000; Flynn, 1996; ten Kate, 2010). Steininger et al. (2012) estimated that the Martian surface could contain up to 60-ppm organic carbon from meteoritic sources, although other estimates are as high as 0.2–2.9% (Flynn & McKay, 1990). PAHs may, however, oxidize (in the presence of ultraviolet radiation) to metastable benzenecarboxylic acids which may have accumulated up to 500 ppm in the top meter of the Martian regolith (Benner et al., 2000). Hence, there is a wide range of estimates of TOC in the average regolith, with only the most optimistic being above the 0.5–5.6 wt% organic carbon that this study suggests is necessary for its detection.

With this in mind, future missions to detect organic matter on Mars must aim for sites that exceed this average value. Efforts must concentrate on localities where mechanisms may have altered the organic carbon: perchlorate ratio to above the critical ratio, that is, where organic matter will be concentrated or perchlorate will have been reduced. Areas with evidence of recent surface or near-surface water flow may concentrate organic compounds downslope in fluvial/lacustrine sediments while perchlorate will be leached away as occurs on Earth due to its high solubility. If triggered by wet (Chevrier & Rivera-Valentin, 2012; McEwen et al., 2011) rather than dry (Dundas & McEwen, 2015) flow, locations downslope of recurring slope lineae could be attractive targets in the search for organic matter. However, there are planetary protection issues to consider if we want to explore these, and other, potential *Special Regions* as they are also the most likely regions to support life (Committee on Preventing the Forward Contamination of Mars, 2006; Kminek & Rummel, 2015; Rummel et al., 2014).

It also must be considered that surface and near-surface organic molecules may have been heavily degraded by ionizing radiation from solar X-ray, extreme ultraviolet (EUV), galactic and solar cosmic rays due to Mars's thin and variable atmosphere (Sagan & Pollack, 1974), and lack of a protective global magnetic field for at least 3.5 billion years (Acuña et al., 1998; Carr & Head, 2010). While X-ray and EUV will be blocked by just a few mm of sediment (Cockell & Raven, 2004), galactic cosmic rays can penetrate down to 1–2 m below the surface to destroy organic compounds (Pavlov et al., 2012), drastically decreasing the expected abundance of organic matter in long-exposed strata. It has been calculated that the preservation of ancient complex organic molecules in the shallow subsurface is unlikely for outcrops with an exposure age over 300 Myr (Pavlov et al., 2012). Thus, organic matter may be more abundant in deeper or more freshly exposed (e.g., recent impact sites) materials.

At depth, it is also possible that perchlorate concentrations will be reduced. Perchlorate and other oxychlorines are produced in the atmosphere and on the ultraviolet-exposed surface (Carrier & Kounaves, 2015; Catling et al., 2010). Reworking of the sediments by cryoturbation, meteoric impact gardening, and aqueous processes may redistribute oxychlorines to depth (Carrier & Kounaves, 2015) in decreasing abundance, assuming that constant surface production, a mixing rate less than the production rate, and no barriers to transport (such as impermeable layers) exist.

Decreasing levels of organic matter degradation by cosmic radiation combined with potentially lower levels of oxychlorines at depth should benefit the organic carbon: perchlorate ratio. Therefore, ExoMars 2020's ability to drill down to 2 m for sample collection (Barnes et al., 2006; Vago et al., 2015) should greatly increase the potential for organic matter detection by thermal extraction methods. However, since it is likely that perchlorate has been produced through long periods of Martian history, perchlorate is likely to be present in the subsurface even at depth. Our determination of the organic matter: perchlorate ratio necessary for detection of organic molecules by thermal extraction will allow for better interpretation of results and more effective sample selection during the Mars 2020 mission.

In light of our newly defined ratio, it is also worth reconsidering existing MSL data. The detection of low levels of chlorobenzenes and C₂-C₄ dichloroalkanes in the Sheepbed Mudstone (Freissinet et al., 2015) suggests that organic matter is present around the critical ratio in these sediments. Chlorine competes with oxygen, and chlorination prevents oxidative breakdown (Steininger et al., 2012), so it should be expected that organic molecules detected from sediments around the critical ratio will be chlorinated. The recently confirmed detection of more complex, nonchlorinated organic molecules in the lower Murray mudstones

(Eigenbrode et al., 2018) suggests, however, that organic matter is present above the critical ratio in these sediments. Organic compounds concentrate in sediments in lacustrine depositional environments on Earth similar to those proposed for the formation of these mudstones and perchlorate content of these Martian sediments could be expected to be low owing to the aqueous environment in which they were deposited. It has been suggested that the survival of organic molecules in the Murray mudstone may have been higher (than in the Sheepbed) allowing its detection (Eigenbrode et al., 2018). However, it is also possible, based on the findings of the current study, that the organic matter contents of the two units are similar and that it is the decreased level of perchlorate in the lower Murray mudstone that has facilitated the detection of more complex, nonchlorinated, organic molecules. The lower Murray mudstone samples, which yielded the complex organic matter detection (Eigenbrode et al., 2018), have around 10 times less perchlorate than the Sheepbed mudstone samples which only yielded simple organochlorines (Freissinet et al., 2015; Sutter et al., 2017).

Owing to differences in the thermal decomposition techniques employed by this study and by Sample Analysis on Mars (SAM) on Mars there are limits to the conclusions drawn by this study. The flash pyrolysis technique employed here rapidly ($20\text{ }^{\circ}\text{C}/\text{ms}^{-1}$) heats the sample to the target temperature ($650\text{ }^{\circ}\text{C}$), whereas the ramp technique employed by SAM on Mars gradually ($35\text{ }^{\circ}\text{C}/\text{min}$) heats the sample allowing the separation of species that decompose over wide temperature ranges.

Variations in release temperature of oxygen from perchlorates can vary owing to cation content (Glavin et al., 2013), differing hydration states (Royle et al., 2017), and the presence of catalysts (Bruck et al., 2014), with variable oxygen release from around $200\text{--}800\text{ }^{\circ}\text{C}$ depending on these factors. Likewise organic assemblages vary in their resistance to thermal decomposition. For biological organic matter on Earth, during heating in the absence of oxygen, labile organic matter breaks down between 200 and $380\text{ }^{\circ}\text{C}$, recalcitrant organic matter $380\text{--}475\text{ }^{\circ}\text{C}$ and refractory organic matter $475\text{--}650\text{ }^{\circ}\text{C}$ (Guo et al., 2016). For nonbiological organic matter in meteorites, a range of decomposition temperatures are observed that can be related to variations in chemical structure (Sephton et al., 2003).

Flash heating, as opposed to temperature ramped pyrolysis, is advantageous as it ensures the coincidence of maximal perchlorate and organic matter thermal decomposition and therefore our results represent the worst-case scenario with the greatest potential for reaction between the oxidative and reductive phases.

The labile organic compounds with the lowest temperatures of decomposition, if present, could well be detected without the interference of perchlorate oxidation as could organic molecules trapped in sulfate minerals (François et al., 2016; Lewis et al., 2015) that are not released until after perchlorate breakdown is complete. If these fractions exist in the Martian shallow subsurface then they appear to be a window of opportunity for future missions.

Our experiments are thus most relevant to perchlorate salts with magnesium as a counter ion, a constant perchlorate hydration state and the presence of isolated components. Different cations in the perchlorate salt (Glavin et al., 2013), varying hydration states (Royle et al., 2017), and the presence of catalysts (Bruck et al., 2014) have all been found to be important in affecting perchlorate decomposition and oxygen release. Other oxidizing minerals such as chlorates, sulfates, nitrates, phosphates, and oxides in the Martian regolith may also play a role in the oxidation of organic matter. The influence of oxidizing minerals appear to limit effective organic detection on Mars, and further studies should extend our quantitative assessment to provide additional guidance for future missions.

5. Conclusions

Our data confirm the oxidizing potential of perchlorate salts on organic matter during thermal decomposition analysis experiments. It is concluded that there needs to be a minimum of 4.7 times more organic carbon than perchlorate in analyzed samples for the survival of organic molecules for detection by GC-MS; although for a statistically significant detection this rises to 9.6 times. It is further suggested that previous py-GC-MS analyses of low organic matter/high perchlorate samples can be reinterpreted to include a more accurate estimation of the organic matter content based on a combination of the py-GC-MS results, and the concentration of perchlorate in the samples. Other oxidants present in the samples, such as sulfates, nitrates, and phosphates, may also have effects to lesser extents and future work should explore this further.

At the estimated concentrations of perchlorate and organic matter on the Martian surface, we do not expect detection of organic molecules in the average Martian regolith. Therefore, we need to look for sites that improve this ratio, either where organic matter may have been concentrated or where perchlorate may have been reduced, such as areas with evidence for recent water activity. These areas are typically designated as Special Regions, which hold the greatest possibility of harboring life, and will inevitably introduce planetary protection considerations.

Acknowledgments

We thank two anonymous reviewers whose thoughtful suggestions significantly improved the manuscript. This work was supported by Science and Technology Funding Council/UK Space Agency grant ST/N000560/1. Data used for calculations are available in the supporting information.

References

- Acuña, M. H., Connerney, J. E. P., Wasilewski, P., Lin, R. P., Anderson, K. A., Carlson, C. W., et al. (1998). Magnetic field and plasma observations at Mars: Initial results of the Mars Global Surveyor mission. *Science*, 279(5357), 1676–1680.
- Barnes, D., Battistelli, E., Bertrand, R., Butera, F., Chatila, R., del Bianco, A., et al. (2006). The ExoMars rover and Pasteur payload Phase A study: An approach to experimental astrobiology. *International Journal of Astrobiology*, 5(03), 221. <https://doi.org/10.1017/S1473550406003090>
- Benner, S. A., Devine, K. G., Matveeva, L. N., & Powell, D. H. (2000). The missing organic molecules on Mars. *Proceedings of the National Academy of Sciences of the United States of America*, 97(6), 2425–2430. <https://doi.org/10.1073/pnas.040539497>
- Biemann, K., Oro, J., Toulmin, P. III, Orgel, L. E., Nier, A. O., Anderson, D. M., et al. (1977). The search for organic substances and inorganic volatile compounds in the surface of Mars. *Journal of Geophysical Research*, 82(28), 4641–4658. <https://doi.org/10.1029/J5082i028p04641>
- Blake, D. F., Morris, R. V., Kocurek, G., Morrison, S. M., Downs, R. T., Bish, D., et al. (2013). Curiosity at Gale crater, Mars: Characterization and analysis of the Rocknest sand shadow. *Science*, 341(6153), 1239505. <https://doi.org/10.1126/science.1239505>
- Bruck, A. M., Sutter, B., Ming, D. W., & Mahaffy, P. (2014). Thermal decomposition of calcium perchlorate/iron-mineral mixtures: Implications of the evolved oxygen from the Rocknest Eolian deposit in Gale Crater, Mars, in 45th Lunar and Planetary Science Conference, Houston, United States.
- Cannon, K. M., Sutter, B., Ming, D. W., Boynton, W. V., & Quinn, R. (2012). Perchlorate induced low temperature carbonate decomposition in the Mars Phoenix Thermal and Evolved Gas Analyzer (TEGA). *Geophysical Research Letters*, 39, L13203. <https://doi.org/10.1029/2012GL051952>
- Carr, M. H., & Head, J. W. (2010). Geologic history of Mars. *Earth and Planetary Science Letters*, 294(3–4), 185–203. <https://doi.org/10.1016/J.EPSL.2009.06.042>
- Carrier, B. L., & Kounaves, S. P. (2015). The origins of perchlorate in the Martian soil. *Geophysical Research Letters*, 42, 3739–3745. <https://doi.org/10.1002/2015GL064290>
- Catling, D. C., Claire, M. W., Zahnle, K. J., Quinn, R. C., Clark, B. C., Hecht, M. H., & Kounaves, S. (2010). Atmospheric origins of perchlorate on Mars and in the Atacama. *Journal of Geophysical Research*, 115, E00E11. <https://doi.org/10.1029/2009JE003425>
- Chevrier, V. F., & Rivera-Valentin, E. G. (2012). Formation of recurring slope lineae by liquid brines on present-day Mars. *Geophysical Research Letters*, 39, L21202. <https://doi.org/10.1029/2012GL054119>
- Chyba, C., & Sagan, C. (1992). Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: An inventory for the origins of life. *Nature*, 355(6356), 125–132. <https://doi.org/10.1038/355125a0>
- Clark, B. C., & Kounaves, S. P. (2016). Evidence for the distribution of perchlorates on Mars. *International Journal of Astrobiology*, 15(04), 311–318. <https://doi.org/10.1017/S1473550415000385>
- Cockell, C. S., & Raven, J. A. (2004). Zones of photosynthetic potential on Mars and the early Earth. *Icarus*, 169(2), 300–310. <https://doi.org/10.1016/J.ICARUS.2003.12.024>
- Committee on Preventing the Forward Contamination of Mars (2006). *Preventing the forward contamination of Mars*. Washington, DC: National Academies Press.
- Dundas, C. M., & McEwen, A. S. (2015). Slope activity in Gale crater, Mars. *Icarus*, 254, 213–218. <https://doi.org/10.1016/j.icarus.2015.04.002>
- Eigenbrode, J. L., Steele, A., Summons, R. E., Sutter, B., McAdam, A., Franz, H. B., et al. (2015). Evidence of refractory organic matter preserved in the mudstones of Yellowknife Bay and the Murray Formations, in American Geophysical Union, Fall Meeting, p. P31F–08.
- Eigenbrode, J. L., Summons, R. E., Steele, A., Freissinet, C., Millan, M., Navarro-González, R., et al. (2018). Organic matter preserved in 3-billion-year-old mudstones at Gale crater, Mars. *Science*, 360(6393), 1096–1101. <https://doi.org/10.1126/science.aas9185>
- Flynn, G. J. (1996). The delivery of organic matter from asteroids and comets to the early surface of Mars. *Earth, Moon, and Planets*, 72(1–3), 469–474. <https://doi.org/10.1007/BF00117551>
- Flynn, G. J., & McKay, D. S. (1990). An assessment of the meteoritic contribution to the Martian soil. *Journal of Geophysical Research*, 95(B9), 14497. <https://doi.org/10.1029/JB095iB09p14497>
- François, P., Szopa, C., Buch, A., Coll, P., McAdam, A. C., Mahaffy, P. R., et al. (2016). Magnesium sulfate as a key mineral for the detection of organic molecules on Mars using pyrolysis. *Journal of Geophysical Research: Planets*, 121, 61–74. <https://doi.org/10.1002/2015JE004884>
- Freissinet, C., Glavin, D. P., Mahaffy, P. R., Miller, K. E., Eigenbrode, J. L., Summons, R. E., et al. (2015). Organic molecules in the Sheepbed mudstone, Gale crater, Mars. *Journal of Geophysical Research: Planets*, 120, 495–514. <https://doi.org/10.1002/2014JE004737>
- Gibson, E. K. (1992). Volatiles in interplanetary dust particles: A review. *Journal of Geophysical Research*, 97(E3), 3865–3875. <https://doi.org/10.1029/92JE00033>
- Glavin, D. P., Freissinet, C., Miller, K. E., Eigenbrode, J. L., Brunner, A. E., Buch, A., et al. (2013). Evidence for perchlorates and the origin of chlorinated hydrocarbons detected by SAM at the Rocknest aeolian deposit in Gale crater. *Journal of Geophysical Research: Planets*, 118, 1955–1973. <https://doi.org/10.1002/jgre.20144>
- Guo, F., Wu, F., Mu, Y., Hu, Y., Zhao, X., Meng, W., et al. (2016). Characterization of organic matter of plants from lakes by thermal analysis in a N₂ atmosphere. *Scientific Reports*, 6(1), 22877. <https://doi.org/10.1038/srep22877>
- Hecht, M. H., Kounaves, S. P., Quinn, R. C., West, S. J., Young, S. M. M., Ming, D. W., et al. (2009). Detection of perchlorate and the soluble chemistry of Martian soil at the Phoenix lander site. *Science*, 325(5936), 64–67. <https://doi.org/10.1126/science.1172466>
- Kminek, G., & Rummel, J. D. (2015). COSPAR's planetary protection policy. *Space Research Today*, 193, 7–18.
- Konn, C., Charlou, J. L., Holm, N. G., & Mousis, O. (2015). The production of methane, hydrogen, and organic compounds in ultramafic-hosted hydrothermal vents of the Mid-Atlantic Ridge. *Astrobiology*, 15(5), 381–399. <https://doi.org/10.1089/ast.2014.1198>
- Kounaves, S. P., Chaniotakis, N. A., Chevrier, V. F., Carrier, B. L., Folds, K. E., Hansen, V. M., et al. (2014). Identification of the perchlorate parent salts at the Phoenix Mars landing site and possible implications. *Icarus*, 232, 226–231. <https://doi.org/10.1016/j.icarus.2014.01.016>
- Leshin, L. A., Mahaffy, P. R., Webster, C. R., Cabane, M., Coll, P., Conrad, P. G., et al. (2013). Volatile, isotope, and organic analysis of martian fines with the Mars Curiosity rover. *Science*, 341(6153), 1238937. <https://doi.org/10.1126/science.1238937>

- Lewis, J. M. T., Watson, J. S., Najorka, J., Luong, D., & Sephton, M. A. (2015). Sulfate minerals: A problem for the detection of organic compounds on Mars? *Astrobiology*, 15(3), 247–258. <https://doi.org/10.1089/ast.2014.1160>
- Matthewman, R., Cotton, L. J., Martins, Z., & Sephton, M. A. (2012). Organic geochemistry of late Jurassic paleosols (Dirt Beds) of Dorset, UK. *Marine and Petroleum Geology*, 37(1), 41–52. <https://doi.org/10.1016/J.MARPETGEO.2012.05.009>
- Matthewman, R., Martins, Z., & Sephton, M. A. (2013). Type IV kerogens as analogues for organic macromolecular materials in aqueously altered carbonaceous chondrites. *Astrobiology*, 13(4), 324–333. <https://doi.org/10.1089/ast.2012.0820>
- McEwen, A. S., Ojha, L., Dundas, C. M., Mattson, S. S., Byrne, S., Wray, J. J., et al. (2011). Seasonal flows on warm Martian slopes. *Science*, 333(6043), 740–743. <https://doi.org/10.1126/science.1204816>
- Miller, K. E., Eigenbrode, J. L., Freissinet, C., Glavin, D. P., Kotrc, B., Francois, P., & Summons, R. E. (2016). Potential precursor compounds for chlorohydrocarbons detected in Gale crater, Mars, by the SAM instrument suite on the Curiosity rover. *Journal of Geophysical Research: Planets*, 121, 296–308. <https://doi.org/10.1002/2015JE004939>
- Ming, D. W., Archer, P. D., Glavin, D. P., Eigenbrode, J. L., Franz, H. B., Sutter, B., et al. (2014). Volatile and organic compositions of sedimentary rocks in Yellowknife Bay, Gale crater, Mars. *Science*, 343(6169), 1245267. <https://doi.org/10.1126/science.1245267>
- Montgomery, W., Bromiley, G. D., & Sephton, M. A. (2016). The nature of organic records in impact excavated rocks on Mars. *Scientific Reports*, 6(1), 30,947. <https://doi.org/10.1038/srep30947>
- Navarro-Gonzalez, R., Rainey, F. A., Molina, P., Bagaley, D. R., Hollen, B. J., de la Rosa, J., et al. (2003). Mars-like soils in the Atacama Desert, Chile, and the dry limit of microbial life. *Science*, 302(5647), 1018–1021. <https://doi.org/10.1126/science.1089143>
- Pavlov, A. A., Vasilyev, G., Ostryakov, V. M., Pavlov, A. K., & Mahaffy, P. (2012). Degradation of the organic molecules in the shallow subsurface of Mars due to irradiation by cosmic rays. *Geophysical Research Letters*, 39, L13202. <https://doi.org/10.1029/2012GL052166>
- Royle, S. H., Montgomery, W., Kounaves, S. P., & Sephton, M. A. (2017). Effect of hydration state of Martian perchlorate salts on their decomposition temperatures during thermal extraction. *Journal of Geophysical Research: Planets*, 122, 2793–2802. <https://doi.org/10.1002/2017JE005381>
- Rummel, J. D., Beaty, D. W., Jones, M. A., Bakermans, C., Barlow, N. G., Boston, P. J., et al. (2014). A new analysis of Mars “special regions”: Findings of the second MEPAG special regions science analysis group (SR-SAG2). *Astrobiology*, 14(11), 887–968. <https://doi.org/10.1089/ast.2014.1227>
- Sagan, C., & Pollack, J. B. (1974). Differential transmission of sunlight on Mars: Biological implications. *Icarus*, 21(4), 490–495. [https://doi.org/10.1016/0019-1035\(74\)90151-1](https://doi.org/10.1016/0019-1035(74)90151-1)
- Sephton, M. A. (2012). Pyrolysis and mass spectrometry studies of meteoritic organic matter. *Mass Spectrometry Reviews*, 31(5), 560–569. <https://doi.org/10.1002/mas.20354>
- Sephton, M. A., Verchovsky, A. B., Bland, P. A., Gilmour, I., Grady, M. M., & Wright, I. P. (2003). Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, 67(11), 2093–2108. [https://doi.org/10.1016/S0016-7037\(02\)01320-0](https://doi.org/10.1016/S0016-7037(02)01320-0)
- Steele, A., McCubbin, F. M., Fries, M., Kater, L., Boctor, N. Z., Fogel, M. L., et al. (2012). A reduced organic carbon component in Martian basalts. *Science*, 337(6091), 212–215. <https://doi.org/10.1126/science.1220715>
- Steininger, H., Goesmann, F., & Goetz, W. (2012). Influence of magnesium perchlorate on the pyrolysis of organic compounds in Mars analogue soils. *Planetary and Space Science*, 71(1), 9–17. <https://doi.org/10.1016/j.pss.2012.06.015>
- Sutter, B., McAdam, A. C., Mahaffy, P. R., Ming, D. W., Edgett, K. S., Rampe, E. B., et al. (2017). Evolved gas analyses of sedimentary rocks and eolian sediment in Gale crater, Mars: Results of the Curiosity rover’s sample analysis at Mars instrument from Yellowknife Bay to the Namib Dune. *Journal of Geophysical Research: Planets*, 122, 2574–2609. <https://doi.org/10.1002/2016JE005225>
- ten Kate, I. L. (2010). Organics on Mars? *Astrobiology*, 10(6), 589–603. <https://doi.org/10.1089/ast.2010.0498>
- Vago, J., Witasse, O., Svedhem, H., Baglioni, P., Haldemann, A., Gianfiglio, G., et al. (2015). ESA ExoMars program: The next step in exploring Mars. *Solar System Research*, 49(7), 518–528. <https://doi.org/10.1134/S0038094615070199>