Perchlorate-induced combustion of organic matter with variable molecular weights: Implications for Mars missions

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Abstract Instruments on the Viking landers and Curiosity rover analyzed samples of Mars and detected carbon dioxide and organic compounds of uncertain origin. Mineral-assisted reactions are leading to uncertainty, particularly those involving perchlorate minerals which thermally decompose to produce chlorine and oxygen which can then react with organic matter to generate organochlorine compounds and carbon dioxide. Although generally considered a problem for interpretation, the release profiles of generated gases can indicate the type of organic matter present. We have performed a set of experiments with perchlorate and organic matter of variable molecular weights. Results indicate that organic susceptibility to thermal degradation and mineral-assisted reactions is related to molecular weight. Low molecular weight organic matter reacts at lower temperatures than its high molecular weight counterparts. The natural occurrence and association of organic matter with differing molecular weights helps to discriminate between contamination (usually low molecular weight organic matter only) and indigenous carbon (commonly low and high molecular weight organic matter together). Our results can be used to provide insights into data returning from Mars.

1. Introduction

Several missions to Mars have rated the detection of extraterrestrial organic matter as a high priority. Viking I, Viking II [Biemann, 1977], and Mars Science Laboratory (MSL) [Mahaffy et al., 2012] all had thermal extraction units coupled to sensitive mass spectrometers capable of liberating organic matter from inorganic matrices followed by characterization of its structure. None of the missions have resulted in the conclusive recognition of indigenous organic compounds, although a nonterrestrial source for some analytes has been suggested [Ming et al., 2014]. At least some nonterrestrial organic matter is expected on Mars owing to the delivery of organic matter-containing comets, meteorites, and interplanetary dust particles that continuously fall to the planet surface [Benner et al., 2000].

Yet missions to Mars have detected simple carbon-bearing species. Organochlorine compounds appear to be ever-present during analysis [Biemann et al., 1977; Leshin et al., 2013; Ming et al., 2014]. One interpretation is that the carbon is simply terrestrial contamination carried to Mars with the space craft. The Viking organochlorine compounds were originally thought to represent chlorinated solvents remaining from cleaning procedures prior to flight [Biemann et al., 1977]. Another suggestion is that the organochlorine compounds are the products of a carbon source that has been transformed to its detected state by reactions with perchlorate or other oxychlorine phases [Glavin et al., 2013]. For instance, chloromethanes and chlorobenzene detected by MSL may be generated by the reaction of Martian perchlorate chloride with the terrestrial sourced derivatization agent N-methyl-N-(tert-butyl/dimethylsilyl)-trifluoroacetamide and 2,6-diphenylenoxide (Tenax) hydrocarbon trap, respectively [Glavin et al., 2013]. Perchlorates decompose to produce chlorine which can then combine with carbon to produce organochlorine compounds. Chlorine is widespread across Mars [Keller et al., 2006] and perchlorate has been detected in the polar regions by the Phoenix lander [Kounaves et al., 2010]. Chlorination reactions have been proposed to explain the organochlorine compounds in Viking [Navarro-Gonzalez et al., 2010; Steininger et al., 2012] and MSL data [Leshin et al., 2013; Ming et al., 2014]. Mars data suggest that most surface samples may have the potential for chlorination reactions with juxtaposed carbon.

The most abundant carbon-containing species observed in the Mars thermal extraction data is carbon dioxide [Leshin et al., 2013; Ming et al., 2014]. Perchlorates decompose under thermal stress to give oxygen...
Devlin and Herley, 1986] which can then combine with organic matter to produce carbon dioxide. Therefore, thermal extraction in the presence of minerals that decompose to produce oxygen can be considered a type of combustion experiment. It should be noted, however, that other sources of carbon dioxide exist for natural samples, including the thermal decarboxylation of organic matter and the thermal decomposition of carbonates, and vigilance is required during interpretation.

Although the conversion of organic matter to carbon dioxide is a negative effect of mineral interaction, the process can have some benefits. Conversion of all organic compounds to carbon dioxide leads to a single, easy-to-handle analyte that can be used to reflect the organic content of a sample. Moreover, if the carbon dioxide release is prompted by a stepwise increase in temperature, discrimination of various combustible carbon components is possible [Wright and Pillinger, 1989] including organic fractions [e.g., Sephton et al., 2003]. There is a long published history of recognizing carbon-bearing components in meteorites by the use of high-resolution stepped combustion [e.g., Swart et al., 1983]. One feature that can be deduced by release temperature during stepped combustion is the molecular weight of organic matter. Low molecular weight organic matter will combust at lower temperatures than higher molecular weight counterparts. The presence, absence, and association of organic materials with different molecular weights have diagnostic potential. Molecular weight characteristics are particularly important for contamination arguments such as those concentrating on data provided by the Viking and MSL missions. Organic matter in living organisms, terrestrial fossil organic matter, and extraterrestrial organic matter is dominated by high molecular weight materials. Low molecular weight organic matter is a perpetually minor component, although highly diagnostic and frequently utilized owing to its analytical amenability [e.g., Killops and Killops, 2005]. An indigenous organic assemblage on Mars, whether from nonbiological meteoritic infall or from currently active or fossilized biology, will most likely contain both low molecular weight organic matter and high molecular weight organic matter. However, oxidative degradation will remove low molecular weight organic matter preferentially so that highly degraded indigenous organic matter may contain high molecular weight organic matter only [Matthewman et al., 2013].

Whereas indigenous organic materials are almost always characterized by a high molecular weight component, the opposite is true for contamination. In contrast to high molecular weight organic matter, low molecular weight organic matter is highly mobile and relatively easy to transport. Contamination of extraterrestrial samples most often involves easily transportable low molecular weight organic matter [e.g., Sephton et al., 2001; Watson et al., 2003]. A contaminated sample that was initially organically barren would most likely contain low molecular weight organic matter only. Exceptions to this rule do exist and include the presence of migrated low molecular weight organic matter and the preferential preservation of low molecular weight units relative to higher molecular weight counterparts during radiolysis [Pavlov et al., 2012]. Molecular weight characteristics can, therefore, be used to imply whether any organic carbon has an indigenous or contamination source.

There is, therefore, a potential method to discriminate between contamination and indigenous organic matter on Mars missions even if the organic matter is transformed to organochlorine compounds or combusted to carbon dioxide by interaction with confounding minerals. To confirm our hypothesis, we have subjected organic matter of different molecular weights to stepped heating in the presence of perchlorate. A low molecular weight fraction was prepared from an oil by precipitating an asphaltene to leave behind a maldene supernatant; maltenes typically have molecular weights <500 amu. A moderate molecular weight fraction was provided by the asphaltene fraction; asphaltenes typically have molecular weights of approximately 1000 amu. A high molecular weight fraction was generated by solvent extracting a bituminous coal to leave behind a cross-linked organic network of >10,000 amu. The temperature of release profiles of carbon dioxide from these samples provides guidance on how Mars mission data can be interpreted to discriminate between carbon sources.

2. Experimental

2.1. Samples

Post flight experiments aimed at understanding the perchlorate responses of the 2008 Phoenix Lander suggest that the perchlorate detected on Mars is a 60:40 mixture of Ca and Mg salts [Kounaves et al., 2014].
Irrespective of the type of perchlorate present, differentials in degradation temperatures of organic materials with distinct molecular weights are expected to remain reasonably similar. In our experiments we chose to use magnesium perchlorate (Mg(ClO₄)₂) which was obtained from Fisher Scientific and mixed with three organic matter types that represent distinct molecular weight ranges. Although initially anhydrous, the hygroscopic nature of magnesium perchlorate suggests that it would become hydrated (Mg(ClO₄)₂·nH₂O) once exposed to the atmosphere. For the low and moderate molecular weight organic matter a heavy oil was obtained from Osmington Mills, Dorset, United Kingdom. The oil was sourced from the Lower Jurassic Blue Lias marine shales which contain type II kerogen before migration and exposure at the surface where partial degradation took place. Moderate molecular weight asphaltenes were precipitated from the sample using an excess of n-hexane with a 12 h settling time; further separation was achieved by centrifugation. The precipitation process was repeated three times in total. Following each precipitation step the supernatants were collected and combined to produce a low molecular weight maltene fraction. For the high molecular weight organic matter, a bituminous coal was obtained from the 7 ft seam in Taff Merthyr South Wales, VR% 1.87 C% 92.4. The high molecular weight organic network portion of the coal was isolated by repeated (3X) extraction with a mixture of organic solvents (93:7 dichloromethane:methanol). Magnesium perchlorate was mixed with the samples in a 1:1 ratio. Given the uncertainty surrounding indigenous organic carbon contents in Martian samples, producing a representative perchlorate/organic matter ratio for our analyses presents some difficulties. However, perchlorate is present at 0.6% on Mars [Hecht et al., 2009] and carbon in clay rich rocks on Earth and in some carbonaceous meteorites is often found in amounts of around 0.6%. For the purposes of this study we assume the remaining mineral matrix is inactive. Consequently, a 1:1 perchlorate/organic matter ratio appears a reasonable and practical starting point. Exact stoichiometry is not essential because the objective of the study is to identify combustion or reaction products and their temperature of release. In all cases the magnesium perchlorate was added to the pyrolysis tube as a powder. Both the maltenes and asphaltenes were dissolved in dichloromethane, syringed on to the perchlorate powder, and allowed to dry. Each sample was allowed to dry for 72 h and no residual dichloromethane was detectable. For the coal the powdered sample was gradually added to the tube until there was a 1:1 ratio of perchlorate to coal. Given that the samples are either completely (maltenes and asphaltenes) or almost completely (coal) organic in composition, contrasting results should reflect only the effects of chemical structure, most specifically average molecular weight.

2.2. Pyrolysis-Gas Chromatography-Mass Spectrometry

Powdered samples were introduced to quartz pyrolysis tubes and held in place by quartz wool. The pyrolysis tubes were placed inside the platinum coil of a Chemical Data Systems 5200 pyroprobe under helium and heated at a rate of 20°C m s⁻¹ to the target temperature where it was held for 15 s. Individual samples were run at 100°C steps between 200°C to 800°C. 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 150°C. The GC injector was held at 200°C and operated in split mode (35:1) with a column flow rate of 2 ml min⁻¹. Separation was performed on a J&W GS-Q PLOT column (30 m x 0.32 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. Data are presented in a semiquantitative fashion by normalizing peak area against perchlorate mass (in milligrams). The responses of the different gases in the mass spectrometer are not suitable for absolute quantification owing to the variation in ionization efficiency between the different species.

3. Results and Discussion

3.1. Pure Perchlorate Decomposition Products

To recognize the contribution of reactions of organic matter and confounding minerals it is important to first isolate the products of mineral decomposition alone. Table 1 and Figure 1a reveal the stepped pyrolysis products of pure magnesium perchlorate. Molecular oxygen begins to appear at 500°C, peaks at 600°C and continues to be produced at temperatures up to 800°C in declining amounts. Hydrochloric acid follows exactly the same profile indicating that both gases are generated by the decomposition of magnesium perchlorate. Chlorine gas from perchlorate decomposition can combine directly with water to produce...
Carbon-bearing gases are not major products with carbon dioxide only appearing at 700°C and 800°C and carbon monoxide at 800°C. The most likely source of these high temperature of release oxidized carbon gases is a carbonate impurity. Organochlorine compounds (e.g., chloromethane, dichloromethane, and phosgene) were searched for but make no contribution to the decomposition products.

### 3.2. Perchlorate and Organic Matter Reaction Products

Compounds not observed when the pure mineral decomposes (Figure 1a) but seen when perchlorate and organic matter are heated (Figures 1b–1d) can be assumed to be the result of inorganic-organic reactions. The perchlorate and organic matter data clearly indicate that magnesium perchlorate decomposes to produce oxygen which combines with adjacent organic matter to produce carbon dioxide and its reaction intermediate carbon monoxide. Although relatively small amounts of carbon dioxide and carbon monoxide

#### Table 1. Temperature of Release Characteristics for Three Different Average Molecular Weight Organic Materials Heated in a Stepwise Fashion With Magnesium Perchlorate

| Perchlorate | Low Molecular Weight OM | Medium Molecular Weight OM | High Molecular Weight OM |
|------------|-------------------------|----------------------------|--------------------------|
| Range (Peak) (°C) | Range (Peak) (°C) | Range (Peak) (°C) | Range (Peak) (°C) |
| H₂O 200–500 & 800 (200–400) | 200–400 and 700–800 (200–500) | 200–400 and 700–800 (200–400) | 200–500 and 800 (200–500) |
| O₂ 400–800 (500–600) | 200–600 (400–600) | 300–800 (300–500) | 400–500 and 800 (500–700) |
| CO 800 (800) | 400–500 and 700–800 (400) | 400–800 (400–500) | 400–800 (400–500) |
| CO₂ 400–800 (400–500) | 300–800 (400–500) | 400–800 (400–600) | 400–800 (500–700) |
| HCl 500–800 (600) | 400–600 (400–600) | 300–600 (300–600) | 400–800 (600–700) |
| CCl₄ 400 (400) | 1000 (1000) | 500 (500) | 400–500 (500) |
| CCl₂O 400 (400) | 500 (500) | 500 (500) | 500 (500) |

### Figure 1. Volatile products from (a) the thermal decomposition of magnesium perchlorate and products from the same mineral mixed in a 1:1 ratio of (b) low molecular weight organic matter (maltenes fraction from an oil), (c) medium molecular weight organic matter (asphaltene fraction from an oil), and (d) high molecular weight organic matter (a solvent extracted coal). Data are presented in a semiquantitative fashion by normalizing peak area against perchlorate mass (in milligrams).
can be produced from the mineral at high temperatures, low temperature, and correlatable carbon monoxide and carbon dioxide are useful indicators of the presence of organic matter. Chlorine-containing carbon compounds among the decomposition products are also indicators of the presence of organic matter. Both phosgene and carbon tetrachloride are absent when organic matter is not mixed with the thermally decomposing perchlorate. Chlorination of hydrocarbons can occur by the radical substitution of hydrogen. In the context of perchlorate decomposition in the presence of organic matter, the perchlorate decomposes to give chlorine gas. Heat can induce the formation of chlorine radicals through homolytic cleavage. The chlorine radicals then either (i) abstract hydrogen from the hydrocarbon to leave behind organic radicals that can react with spare chlorine radicals or (ii) combine with thermally generated organic radicals directly to form organochlorine compounds. The presence of phosgene might be expected when it is noted that this gas can be synthesized by combining carbon monoxide and chlorine in the presence of a carbon catalyst [Schneider and Diller, 2000]. Interestingly, excepting phosgene, only the fully chlorine-substituted C₁ compound was detected, perhaps indicating the efficiency of the laboratory chlorination reaction with pure materials.

3.3. Indicators of Molecular Weight
Carbon dioxide release profile appears to reflect the average molecular weight of the organic matter present. Low molecular weight organic matter produces a sharp and relatively low-temperature peak centered at 400°C. Medium molecular weight organic matter produces a broad medium-temperature peak centered between 400°C and 500°C. High molecular weight organic matter produces a broad relatively higher-temperature peak centered at 500°C. The location of the peaks reflects the susceptibility of the different organic matter types to combustion.

The profiles of temperature of release for chlorinated organic compounds also appear to reflect the molecular weight of any organic matter present. For carbon tetrachloride low molecular weight organic matter and medium molecular weight organic matter both generate peaks that start at 400°C and 300°C, respectively, and then last until 600°C. High molecular weight organic matter produces a broad long-lasting peak that starts at 400°C and persists until 800°C but which has a major release between 600°C and 700°C. Organic matter type appears to have an effect on phosgene release temperature with low molecular weight organic matter producing a sharp low-temperature peak (400°C), medium molecular weight organic matter generating a sharp higher-temperature peak (500°C) and high molecular weight organic matter producing a broad higher-temperature peak (400°C to 500°C). The location of the peaks may reflect the simultaneous production of organic and chlorine radicals, and therefore, the varying temperature of thermal dissociation of the different molecular weight organic matter types.

3.4. Use of Molecular Weight Information
The new data demonstrate a method of both obtaining a suggestion of organic carbon and an indication of the type of material present. The stepped combustion of organic matter-containing samples has a lengthy track record of discriminating contamination from indigenous carbonaceous components, albeit using other oxidation methods [Swart et al., 1983]. In the case of perchlorate sourced oxygen, the coevolution of chlorinated hydrocarbons alongside the usual oxidized carbon combustion products, provides as additional indicator of thermally-sensitive organic material.

The expected molecular weight fractions on Mars can be used to support assertions of indigeneity for any detected carbon (Figure 2). The detection of exclusively low molecular weight organic fractions requires consideration that terrestrially sourced contamination has been delivered by the space craft and the interrogation of instrument blanks and controls must follow. If contamination is thought improbable then some noncontamination explanations may be available. Hydrocarbon seeps representing fluid
communication with the subsurface cannot be ignored as a possibility for providing low molecular weight organic compounds to the near surface or surface of Mars. Additionally, models suggest that organic susceptibility to radiation in the shallow subsurface is dependent on organic compound size with higher molecular weight units degrading faster than their lower molecular weight counterparts [Pavlov et al., 2012] providing the possibility of a selective accumulation of small organic units in the irradiated near surface or surface. The presence of exclusively high molecular weight organic matter would indicate a heavily processed sample in which organic matter has been partially oxidized or thermally metamorphosed and would warrant further investigation. The recognition of both low and high molecular weight organic fractions would suggest the presence of a rich organic inventory, derived from either Martian biological or nonbiological processes or from meteoritic infall, and untroubled by excessive degradation.

3.5. Molecular Weight Arguments and MSL Data

Insight generated by the new perchlorate and organic molecular weight data can be tested against existing data from Mars to assess its utility. Although the two GC-MS systems were operated under different conditions (Table S2 in the supporting information), the data from our study and that from MSL share enough common features to allow an effective comparison.

3.5.1. Water and Oxygen

MSL data from the Rocknest aeolian deposit and Sheepbed mudstone reveal low-temperature water that declines with increasing temperature and suggest multiple sources including adsorbed water, structural water in salts, water in phyllosilicate interlayers, structural water in iron oxyhydroxides, and occluded water in glass or minerals [Leshin et al., 2013; Ming et al., 2014]. It is suggested that water from Sheepbed mudstone may also derive from the decomposition of organic matter [Ming et al., 2014].

It is interesting that in our data the pure perchlorate mineral generates a similar temperature of release profile for water to that for the published MSL data. The introduction of organic matter of various types, including coal which contains some minerals, provides no major variation in the water temperature of release profile, and therefore, no modification is required of our interpretation that the low-temperature water is overwhelmingly derived from that adsorbed onto the perchlorate mineral. Perchlorate itself can account for low-temperature water.

3.5.2. Oxides of Carbon

The new organic molecular weight data can be used to consider published carbon dioxide data for Mars samples. Carbon dioxide release correlates with the generation of hydrochloric acid for the Sheepbed mudstone samples [Ming et al., 2014] and led to the suggestion that the acid dissolution of carbonates may produce carbon dioxide. Our data also show a correlation between hydrochloric acid release and carbon dioxide but in carbonate-free samples and so the correlation may not be highly diagnostic.

Carbon dioxide peak release temperatures in Rocknest aeolian materials [Leshin et al., 2013] and the Sheepbed mudstone [Ming et al., 2014] differ by over 100°C, and were interpreted as the higher-temperature peak representing carbonate decrepitation and the lower-temperature peak reflecting organic matter combustion. Yet we have shown that the molecular weight of organic matter can also generate differences in peak release temperatures.

If organic matter were the only source a sharp and relatively low temperature of release of carbon dioxide at 250°C in the Sheepbed mudstone would suggest low molecular weight organic matter while a broad carbon dioxide release centered around 350°C for the Rocknest sample could suggest medium molecular weight organic matter. Yet uncertainty exists and correlations of carbon dioxide with other volatiles, notably chlorinated organic compounds are required before organic matter can be considered as a probable source of the MSL carbon dioxide.

3.5.3. Organochlorine Compounds

The organic matter and perchlorate experiments reveal that the correlation of organochlorine compounds with other volatiles is potentially diagnostic. Data from the Rocknest aeolian sample indicate a release of organochlorine compounds with a maximum at 250°C [Leshin et al., 2013]. The lack of a correlation of peak release temperature for carbon dioxide and organochlorine compounds in the Rocknest sample is dissimilar to our perchlorate and organic matter experiments. Hence, the temperature of release features would favor a nonorganic source of the carbon dioxide in the Rocknest sample.
Data for the Sheepbed mudstone samples reveal concurrent evolution of oxygen and organochlorine compounds and interpret this as an indication of the presence of perchlorates and possibly organic matter [Ming et al., 2014]. All of our experiments with perchlorate and organic matter display correlatable oxygen and organochlorine compounds and so support the assertion that organic matter is present.

Results from the Sheepbed mudstone indicate a carbon dioxide release centered around 250°C. Organochlorine compounds appear with a maximum also at 250°C. The correlation of carbon dioxide and organochlorine compounds in the Sheepbed mudstone [Ming et al., 2014] appears similar to our perchlorate and organic experiments and therefore favor the presence of organic matter as a source of both volatile species.

3.5.4. Oxygen

Oxygen is released earlier in the Sheepbed mudstone [Ming et al., 2014] compared to the Rocknest aeolian sample [Leshin et al., 2013]. The cause of the low-temperature release is uncertain. The only occurrence of anomalously low-temperature oxygen release, i.e., lower than the pure mineral, in our experiments is when perchlorate is mixed with low molecular weight organic matter. The presence of organic matter is supported for the Sheepbed mudstone and the carbon dioxide and organochlorine compounds correlate with low molecular weight organic matter.

3.5.5. Synthesis

Insights from the stepped heating of perchlorate and organic matter of variable molecular weights suggest that existing Mars data from the MSL Rocknest aeolian deposit contains a carbon dioxide source that is inorganic while the Sheepbed mudstone sample contains a carbon dioxide source that is organic. The temperature of release profiles for carbon dioxide and organochlorine compounds in the Sheepbed mudstone suggest low molecular weight organic matter which would be consistent with a contamination source, although migrated or radiolytically processed indigenous organic matter would also be possibilities.

4. Conclusions

Perchlorate-induced combustion interferes with organic analysis on Mars. Yet the effects can be interpreted positively to reveal the nature of organic matter present. Stepped heating reveals profiles of carbon dioxide and chlorinated organic compound release with temperature that indicate both the occurrence of organic matter and its molecular weight. Molecular weight information is valuable because it can be used to help discriminate between contamination and indigenous carbon. Low molecular weight material suggests only contamination while high molecular weight material is probably indigenous carbon; a combination of low and high molecular weight organic matter is also likely to be indigenous. Interpretations of MSL data and future missions can be aided by approaches that use molecular weight-based arguments for perchlorate-induced combustion products.
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