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Organic geochemistry of in situ thermal-based analyses on Mars: the importance and influence of minerals

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Organic Geochemistry and the Minerals of Mars

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Abstract

A high priority goal for past, present and future missions to Mars is the search for evidence of past or present life. Some of the most information-rich signals are those represented by organic biomarkers. Thermal extraction has historically been the most popular in situ analysis technique employed on Mars owing to its elegance and ability to liberate both small compounds and large macromolecular networks. The geological record of Mars contains a variety of minerals, some of which can interact with organic matter when subjected to thermal extraction. Here we discuss the organic records that may be associated with these mineral hosts and the problems encountered when mineral-organic mixtures are analysed by thermal-based methods. We also suggest potential mitigations for future experiments of a similar nature and note that these mitigating steps can be applied not only in situ on Mars but also after samples are returned to Earth as part of Mars Sample Return where more resources and time for sample preparation are available.

Introduction

A common goal of missions to Mars in the past, present and future is the search for evidence of past or present life. When seeking evidence of life some of the most information-rich signals are those represented by diagnostic organic compounds often termed biomarkers (Killops and Killops 2005). Organic biomarkers are present as low molecular weight or free compounds, but also as high molecular weight macromolecular structures representing selectively preserved biopolymers or free molecules subjected to varied polymerisation processes.

Thermal extraction has historically been the most popular in situ organic geochemical technique employed on Mars, having been present on the Viking landers (Biemann 1976), the Phoenix mission (Guinn *et al.* 2008; Hecht *et al.* 2009; Kounaves *et al.* 2009; Ming *et al.*

2009), and the MSL Curiosity rover (Grotzinger *et al.* 2012; Mahaffy *et al.* 2012). It will form a major part of the sample analysis strategy in future missions such as the Mars Organic Molecule Analyser (MOMA) instrument on the ExoMars mission (Brinckerhoff *et al.* 2013; Goetz *et al.* 2016; Goesmann *et al.* 2017). This has been in large part due to its ability to access the organic information contained within recalcitrant carbon, such as macromolecular organic matter, as well as the engineering and logistical difficulties of transporting solvents from Earth to Mars.

Certain alteration products that reflect the action of liquid water on primary mineral phases suggest the presence of habitable conditions while oxidised materials can take part in redox reactions that may help to sustain life. Yet, these minerals can cause dramatic problems for in situ analyses by thermal extraction. For instance, perchlorate has been detected in the polar regions by the Phoenix lander (Kounaves *et al.* 2010) and chlorine is widespread across Mars (Keller *et al.* 2006). Perchlorates decompose to produce chlorine which can then combine with carbon to produce organochlorine compounds (Royle *et al.* 2018) . Sulfur-rich salt deposits are widespread in the Hesperian (Bibring *et al.* 2006) and heated sulfates can promote oxidative effects (Lewis *et al.* 2015). Iron oxides and oxyhydroxides are commonly associated with the Amazonian and will thus be present on Mars. Oxidised iron can have a degradative effect when organic matter is heated (Royle *et al.* 2021a, b, 2022). Carbonates have also been detected in limited amounts on Mars and can affect the final organic architecture of compounds liberated from the mineral matrix by pyrolysis (Zafar *et al.* 2017).

There are several potential sources of organic matter on Mars. Infalling carbonaceous meteorites can contain several percent organic matter (Sephton 2014), in situ abiotic synthesis, such as the products of serpentinization that are associated with hydrogen generation, can generate subsequent hydrocarbon products (Sephton and Hazen 2013), and the remains of microbial life that may have originated or adapted to liquid water-containing environments existing while the rocks were being altered.

Knowledge of organic preservation in Mars analogues on Earth (see review by Hays *et al.* 2017) provides guidance on what may be observed in samples of Mars if the organic remains of life were once present (Figure 1). Analytical experience also suggests methods that may be employed to maximise our ability to detect and characterise any organic matter discovered by future in situ analysis missions.

Some Minerals of Mars and their potential organic records

Sulfates

On Mars, sulfates primarily exist in the form of evaporite salts derived from the weathering of olivine-rich basalts (Tosca *et al.* 2005); these include gypsum/anhydrite, jarosite, and epsomite/kieserite, which are Ca-, Fe-, and Mg-sulfates in different hydration states, respectively (e.g., Squyres *et al.* 2004a; Gendrin *et al.* 2005; Gaillard *et al.* 2013; Vaniman *et al.*, 2014; Vaniman *et al.* 2018). Even from the earliest stages of Mars exploration, sulfate minerals were believed to be of astrobiological importance, primarily because organic compounds could be protected from the oxidizing conditions at the Martian surface when trapped within intracrystalline inclusions (Sumner 2004). Sulfates were seen as particularly ideal minerals because of the extremely slow rates of SO_4^{2-} reduction (Ohmoto and Lasaga 1982), which would allow carbonaceous material to be preserved over geological timescales.

The potential of sulfate minerals as a host for organic biomarkers has since been investigated in great detail; as predicted, the preservation potential of sulfates can be attributed primarily to the incorporation of organic compounds within its mineral matrix. Sulfates have been recognized in weathered basaltic rocks on Earth (Ruiz-Galende *et al.* 2020). Organic compounds trapped inside fluid inclusions within magnesium sulfate have been found to be preserved for over 40 Ma (Bowden and Parnell 2007; François *et al.* 2016). Terrestrial gypsum deposits have been found to host permineralised Permian microfossils (Schopf 2012), while other researchers have observed potentially viable microorganisms and biotic organic materials trapped within the fluid inclusions of gypsum salts or at the surfaces of gypsum crystals (Rouchy and Monty 2000; Benison and Karmanocky III 2014). Molecular lipid biomarkers have also been found to be preserved in sulfate-rich environments such as acid saline lakes (Benison and Karmanocky III 2014; Johnson *et al.* 2020), acidic sulfur streams (Tan *et al.* 2018), and marginal marine basins (Natalicchio *et al.* 2021).

Iron

Iron oxides and oxyhydroxides are common weathering products of igneous materials (Ruiz-Galende *et al.* 2020) and were formerly considered to have poor preservation potential on Mars compared to silica- or clay-rich environments (Sumner, 2004; Klein, 2005), primarily because organic compounds can be oxidised to simpler compounds by the action of free radicals due to Fenton reactions (Pignatello et al., 2006). In addition, photo-Fenton reactions that occur due to the interactions between hematite, perchlorate, and high-energy and/or cosmic radiation can also destroy organic materials (Wadsworth and Cockell 2017). However, these preconceptions have been challenged by recent research.

Iron has been found to play a direct role in the preservation of organic material. Specifically, there are two primary mechanisms by which iron can be bound to organic matter: 1) the sorption of organic matter to the surface of iron oxides, and 2) the formation of organo-metallic complexes (Lalonde *et al.* 2012). Sorptive processes were already known to play a role in the preservation of dissolved organic matter by protecting them from microbial decay (Kaiser and Guggenberger 2000), and it was shown that sorption slowed remineralisation rates by up to five orders of magnitude (Keil *et al.* 1994). Ferric hydroxides were also shown to increase the resistance of carbon substrates to degradation by sorption processes (Jones and Edwards 1998), especially in amorphous iron compounds such as ferrihydrite.

The complexation of iron and organic matter during coprecipitation and deposition has also been the subject of scrutiny. It has been shown that purely sorptive processes cannot account for the ratio of organic carbon to iron in several soil samples, suggesting an additional complexation process (Wagai and Mayer 2007). Iron in soils was shown to have a protective effect on citric acid against biodegradation, and this resistance to degradation increased with increasing metallic complexation (Boudot *et al.* 1989; Lalonde *et al.* 2012); a mechanism whereby iron co-precipitates and/or chelates with organic carbon in sediments, forming a 'rusty sink' which sequesters the organic carbon with stable iron phases for long-term storage, has been proposed. It has been found that 21.5 ± 8.6% of organic carbon in surface marine sediments is preserved as a result of interactions with iron phases (Lalonde *et al.* 2012).

An indirect observation related to the preservation of organic molecules by iron phases has been recently obtained when analysing the simultaneous iron and associated organic carbon release during dissolution of permafrost thaw (Patzner et al., 2020). Permafrost environments have been described on Mars (Smith and McKay, 2005), being possible sinks for organic matter preserved for millions of years.

The preservation of organic biomarkers in various iron deposits has also been investigated. Lipid biomarkers have been recorded as surviving the initial stages of diagenesis in iron-bearing hot spring deposits (Parenteau *et al.* 2014) and iron-rich acidic streams (Tan *et al.* 2018), while fatty acid methyl-esters (FAME) have been reported in hydrous ferric oxides in sulfur-rich systems (Williams *et al.* 2016). Several iron-rich hot spring environments are also associated with the deposition of silica, a strong preservative agent of preservation of organic molecules and microstructures (Farmer and Des Marais 1999). Further investigation showed that iron oxides in hot springs could preserve up to 15% TOC despite the initial processes of diagenesis (Parenteau *et al.* 2014). Peptides have also been found in the extracts of ferruginous sediments in the Rio Tinto system (Colín-García *et al.* 2011).

Carbonates

Despite the widely accepted idea that Mars once possessed an atmosphere rich in carbon dioxide (Carr 1999; Bibring *et al.* 2006), there is a relative lack of carbonate deposits at the surface of the planet (Bridges *et al.* 2001; Ehlmann *et al.* 2008; Horgan *et al.* 2020). Most of the sedimentary carbonates identified on Mars are Mg-carbonates, such as those at Columbia Hills, Gusev Crater (Morris *et al.* 2010), and at Jezero Crater (Ehlmann *et al.* 2008; Goudge *et al.* 2017; Horgan *et al.* 2020). There may, however, be additional carbonates buried in the subsurface that have not yet been detected (Michalski and Niles 2010; Wray *et al.* 2016).

Owing to the lack of large-scale carbonate deposits on Mars, the preservative potential of carbonates has not been the subject of significant study. In addition, fluid circulation, hydrochemical alteration, and recrystallization are common in carbonate environments, and can alter and/or destroy organic and isotopic biosignatures (McMahon *et al.* 2018). Nevertheless, carbonates are known to adsorb acidic organic compounds into intracrystalline spaces (Carter and Mitterer 1978; Sykes *et al.* 1995). In addition, hydrothermal carbonates appear to have relatively similar preservation potential as hydrothermal silica – lipid biomarkers have been retrieved from travertine in carbonate hot spring environments (Zhang *et al.* 2004; Jorge-Villar *et al.* 2007) or detected in stromatolitic chert, ~1.9 Ga Gunflint Formation (Aramendia *et al.*, 2019), while other studies have shown that biogenic carbon isotope fractionations may have been shown to be retained in carbonates even after remineralisation (Léveillé *et al.* 2007). Carbonates are also conducive to the preservation of structural biomarkers. Sideritic concretionary Lagerstätte on Earth are capable of excellent preservation, with the remains of even labile organisms such as jellyfish being entombed in carbonate concretions (McCoy 2014). Biofilms have been observed in carbonate hot springs (Potter-McIntyre *et al.* 2017), and biological communities can also create their own carbonate deposits such as stromatolites and other microbialites (Riding 1991; Kamber and Webb 2001).

Rather than for their effects on the preservation of organic matter, carbonates are better known as a source of reduced carbon. Indeed, the thermal decomposition of siderite has been proposed as a source of meteoritic organic matter (McCollom 2003). The dissolution of siderite under hydrothermal conditions has been found to result in the precipitation of magnetite and condensed carbon, which could potentially be further transformed by the Fischer–Tropsch-type (FTT) reactions (Milesi *et al.* 2015). In terms of the transformation of organic matter, carbonates have been known to catalyse the ketonisation of fatty acids during pyrolysis, which occurs at temperatures between 330 and 360°C (Curtis *et al.* 1947).

What problems can we expect on future in situ space missions?

Perchlorates

Perchlorates (ClO_4^-) were originally discovered by the Phoenix Lander in 2008, when the Wet Chemistry Laboratory (WCL; (Kounaves et al. 2009) observed concentrations of ~0.6 wt % of a 3:2 mix of calcium-magnesium perchlorate in the regolith (Hecht *et al.* 2009; Kounaves *et al.* 2010). Similar levels of perchlorate were detected at the Rocknest deposit in Gale Crater by the SAM instrument on the MSL Curiosity rover (Glavin *et al.* 2013; Leshin *et al.* 2013), as well as in some Martian meteorites (Kounaves *et al.* 2014). Perchlorates have also recently been identified within voids in igneous rocks from Jezero crater floor (Farley *et al.* 2022). Their presence across samples from different localities and of different geological ages indicate that perchlorates occur on a global scale over sediments (Archer *et al.* 2013) and pores in basaltic rocks (Farley et *al.*, 2022) at the Martian surface, and there is evidence to suggest that their deposition was occurring as early as the Hesperian (Carrier and Kounaves 2015; Farley *et al.* 2016).

The ionizing radiation incident on the surface of Mars gives rise to a highly oxidizing environment that results in the production of perchlorates on Cl-bearing mineral surfaces (Catling *et al.* 2010; Carrier and Kounaves 2015). These perchlorates can subsequently oxidise any organic matter present on these surfaces (Hecht *et al.* 2009; Glavin *et al.* 2013). The combination of a highly oxidizing radiation environment and the presence of perchlorates at the Martian surface suggest that only refractory or well-protected organic molecules may survive over geological timescales (Hecht *et al.* 2009; Kounaves *et al.* 2014; Pavlov *et al.* 2022).

Perchlorates also complicate organic matter detection by thermal extraction techniques as they decompose into chlorine and oxygen at temperatures between 300 and 600°C (Shimokawabe *et al.* 1977), and may chlorinate and/or oxidise any otherwise pristine organic matter present in the sample (Hecht *et al.* 2009; Ming *et al.* 2009; Navarro-González *et al.* 2010; Steininger *et al.* 2012; Sephton *et al.* 2014). Perchlorate induced degradation of martian organic matter is supported by the detection of chlorinated organic molecules at the surface of Mars by thermal extraction techniques (Glavin *et al.* 2013; Freissinet *et al.* 2015), and may also be responsible for the lack of organic matter detected by the Viking Landers (Biemann and Bada, 2011; Navarro-González et al., 2010). Thermal extraction experiments involving $Mg(ClO_4)_2$ reveal an additional complication because perchlorate was observed to react with the gas chromatography column coating to generate chlorinated organic compounds such as chlorinated benzenes (Royle et al. 2018). The ubiquity of perchlorates across the Martian surface has prompted the development of various methods to account for these salts, including laser desorption-mass spectrometry, which will be part of the MOMA instrument on the ESA ExoMars mission (Goesmann *et al.* 2017; Li *et al.* 2017).

Sulfates

Minerals containing sulfates (SO_4^{2-}) are predominantly found in Hesperian soils in the form of iron sulfates, such as jarosite, and magnesium sulfates, such as kieserite (Squyres *et al.* 2004b; Gendrin *et al.* 2005; Griffes *et al.* 2007; Milliken *et al.* 2010) and more recently as calcium sulfates, such as gypsum, basanite and anhydrite (Vaniman *et al.*, 2018). However, sulfates also comprise 5.82 wt % of the globally mixed Martian dust that is constantly redistributed by dust storms (Gellert *et al.* 2004), and have been detected in several samples encountered at Gusev Crater (Arvidson *et al.* 2004), Gale Crater (Leshin *et al.* 2013), and now Jezero Crater (Farley *et al.* 2022).

Sulfate minerals can potentially aid the preservation of organic matter by trapping organics within fluid inclusions or by entombing these compounds within their crystal lattices (Aubrey *et al.* 2006; Bowden and Parnell 2007; François *et al.* 2016). However, like perchlorates, sulfates pose a problem for thermal detection techniques due to the generation of sulfur dioxide and oxygen; in particular, jarosite decomposition occurs between 450 and 550°C (Lewis et al., 2015). Evidence of the obfuscating nature of sulfates during the detection of organic matter has been observed in the concurrent release of sulfur dioxide and carbon dioxide between 500 and 550°C in the pyrolysis of Gale Crater samples (Leshin *et al.* 2013). The carbon dioxide peak observed is likely a result of the combustion of organic matter due to the release of oxygen as the sulfates decomposed.

Iron Oxides

Hematite (Fe_2O_3) and magnetite (Fe_3O_4) are the most common iron oxides found on the surface of Mars, and have been observed both in situ and from orbit (Fraeman *et al.* 2013; Rampe *et al.* 2020). While these iron oxides are not as abundant as previously thought, these minerals are still present in almost every sample analyzed on Mars (Bish *et al.* 2014; Vaniman *et al.* 2014; Treiman *et al.* 2016; Rampe *et al.* 2017, 2020; Farley *et al.*, 2022). Iron minerals have also been closely linked to sulfur, with acidic, iron- and sulfate-rich outcrops observed at the Burns Formation at Meridiani Planum (Klingelhöfer *et al.* 2004; Squyres *et al.* 2004b), and Pahrump Hills at Gale Crater (Cavanagh *et al.* 2015).

Other iron species observed in the Martian regolith include goethite (FeOOH), which was identified by the MER Spirit rover at Gusev Crater (Klingelhöfer *et al.* 2005), and akageneite [β-FeO(OH,Cl)], which was found to be present in several localities during Curiosity's traverse through Gale Crater (Rampe et al., 2020; Treiman et al., 2016; Vaniman et al., 2014). Additional reduced ferrous deposits were also observed at Mawrth Vallis (Bishop et al., 2013; Horgan et al., 2014). Ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$), an amorphous, nano-crystalline iron oxide, is stable on at the surface of Mars and is a prominent component of Martian soils, at times comprising up to 50 wt% of mudstones analysed at Yellowknife Bay (Dehouck *et al.* 2017). Ferrihydrite has also been observed at Gusev Crater and Meridiani Planum (Morris *et al.* 2006), as well as in McLaughlin Crater (Michalski *et al.* 2019).

Research has shown that iron oxides and oxyhydroxides are much more amenable to pyrolysis techniques than sulfates and perchlorates as they release less atomic oxygen as the other two mineral types (Lewis *et al.* 2018). However, iron oxides can nonetheless catalyse transformative reactions on mineral surfaces (Watson and Sephton 2015; Tan *et al.* 2021a), which can transform more diagnostic organic compounds (such as C_{16}- and C_{18}-fatty acids) into compounds such as polyaromatic hydrocarbons, whose origins are more ambiguous. In addition, free radicals produced during the reduction of iron oxides in the presence of organic matter (Pignatello *et al.* 2006; Grzybowski *et al.* 2013; Bouarab *et al.* 2014; Watson and Sephton 2015) can promote bond cleavage, contributing to the deleterious oxidation of organic matter (Foustoukos and Stern 2012; Shuai *et al.* 2019; Tan *et al.* 2021a).

Carbonates

Carbonates represent a rock type often implicated in organic preservation (Farmer and Des Marais, 1999), yet certain analytical procedures can induce carbonate-assisted molecular transformations that reduce the diagnostic power of any organic structures detected. A study that combined adsorption isotherms with pyrolysis-gas chromatography-mass spectrometry revealed that monolayers of fatty acids reacted in an analogous fashion to fatty acid salts and symmetrical mid-chain ketones were formed (Zafar *et al.* 2017). It follows that the amount of fatty acids adsorbed to the surface of carbonates rather than free in the host rocks will be reflected in an increase in the relative abundance of ketones relative to hydrocarbons in the pyrolysate. Future in situ pyrolysis-gas chromatography-mass spectrometry data can therefore be used to reveal past diagenetic process in Mars sediments.

Preparations for organic detection on future in situ space missions

Organic/oxidant ratios

One potential means of detecting organic matter despite the oxidizing nature of its mineral host would be to target samples with sufficient organic-oxidant ratios. If there is sufficient organic carbon hosted within the sample, then organic compounds can still be detected using thermal extraction techniques despite the release of oxygen during pyrolysis.

A study monitored the CO/CO_2 ratio generated from the pyrolysis of kerogen in the presence of perchlorate (Royle *et al.* 2018), and found that the organic carbon : ClO_4^- ratio required for the detection of organic compounds was 11 : 1. Considering that the amount of perchlorate detected in the Martian regolith is approximately 0.1–0.6 wt% (Hecht *et al.* 2009; Carrier and Kounaves 2015; Sutter *et al.* 2017), approximately 5.6 wt% of organic matter must be present within the sample for any organic compounds to be detected by thermal methods (Royle *et al.* 2018). While the study only considered interactions between organic carbon and perchlorates, pyrolysis studies in sulfate-rich acid streams and circumneutral iron-rich bogs have shown that this concept can be applied to other environments with oxidizing minerals (Lewis *et al.* 2015; Tan *et al.* 2018, 2021a).

Hence, one potential solution to the issue of oxidizing materials is to target sampling sites where the abundance of organic carbon is expected to exceed this threshold. We can improve our chances of finding samples with high organic content by considering the mechanisms that either concentrate organic matter or reduce the abundance of oxidizing minerals. Biological communities often congregate in areas with high water activities, allowing for the natural concentration of organic matter in the form of microbial mats (Tan *et al.* 2018). Evidence of recent near-surface fluid flow, such as recurring slope lineae or seasonal brines, could also concentrate organic matter downslope of these flows (Royle *et al.* 2018). Aqueous activity may also result in the leaching of perchlorates, reducing the critical ratio necessary for the detection of organics (Royle *et al.* 2018; Montgomery *et al.* 2019).

Alternatively, targeting samples at depths below the penetration ranges of Ultraviolet (UV) radiation, Galactic Cosmic Radiation (GCR), and Solar Cosmic Radiation (SCR) would maximise the amount of pristine organic carbon present within the sample (Pavlov *et al.* 2012, 2022; Hassler *et al.* 2014). Using depth as a method for avoiding radiation-induced organic degradation is a strategy employed by the ExoMars mission (Dartnell et al. 2007). Perchlorates are also likely to be found at lower abundances at depth, primarily because the formation of perchlorates is a surface process involving the interaction between chloride-bearing minerals and UV irradiation (Carrier and Kounaves 2015). Moreover, the detected calcium- and magnesium-perchlorates are relatively soluble compounds and can be formed when dissolved perchlorates flow to the inner parts of the soils, reducing their mobility. Although there are processes such as impact gardening and cryoturbation that could rework the topsoil and thus redistribute perchlorates into the subsurface (Hartmann *et al.* 2001; Levy *et al.* 2010), targeting rocks at depth would reduce the proportion of oxidizing minerals in the sample.

Mineral Histories

Another way of avoiding problems associated with oxidizing minerals is by understanding the complex geochemical evolution of mineralogy within an environment and targeting the minerals that are most amenable to thermal extraction techniques while still retaining the fidelity and integrity of the organic record in those environments.

For example, terrestrial acidic, iron-rich sulfur stream environments are analogues of potentially habitable environments that existed on the Hesperian Mars. Jarosites precipitating from these waters may have incorporated organic material, either by the adsorption of organic compounds or thier encapsulating them within fluid inclusions (François *et al.* 2016). This process would have been encouraged because any putative Martian life would have thrived in areas of higher water activity, in close proximity to jarosite precipitation (Tan *et al.* 2018). Despite being associated with a high abundance of organic matter, jarosite is a poor target for pyrolysis experiments (Lewis *et al.* 2015).

In contrast to jarosite, goethite and hematite are far more amenable to pyrolysis techniques (Lewis *et al.* 2018). Jarosite is very often associated with goethite in areas with pH > 3 or when water activities are high; this goethite is either coprecipitated with jarosite (Zolotov and Shock 2005) or is produced during the transformation of jarosite (Bigham *et al.* 1996; Bigham and Nordstrom 2000). Hematite can also be formed from the low-temperature oxidation of jarosite (Tosca *et al.* 2008; McLennan 2012), or from the dehydration of goethite (Cornell and Schwertmann 2003). Analyses of goethite samples from a terrestrial acidic sulfur stream has shown that organic records are retained within these minerals despite their transformation from jarosite (Lewis *et al.* 2018; Tan *et al.* 2018). Hence, goethites and hematites associated with jarosite are excellent targets for pyrolysis experiments.

The above is one example of how mineral histories can be used to generate a framework that guides researchers to mineralogical targets that finely balance the integrity of the organic record and their amenability to analytical techniques available on current missions to Mars. If similar frameworks can be developed for other geological environments on Mars, this will dramatically improve the chances of detecting organic compounds during *in situ* analyses.

Gas Release Profiles

The oxidative degradation of organic matter represents a dramatic reduction of information, yet that does not mean that all chemical information is lost. The temperature-release profiles of gases can indicate the type of organic matter present (Sephton *et al.* 2014). The susceptibility of organic matter to thermal degradation and mineral-assisted reactions is related to molecular weight. Low molecular weight organic matter reacts or combusts at lower temperatures, whereas organic material of high molecular weights requires higher temperatures for their conversion to gas. Earth-based knowledge would also help to discriminate between migrated materials introduced by water (usually low molecular weight organic matter only) and in situ materials (commonly low and high molecular weight organic matter together).

Beyond ExoMars: Future mitigations for organic detection in problematic mineral matrices

Leaching

Future missions to Mars may employ more sophisticated preparation steps that avoid the issues associated with thermal extraction in the presence of perchlorates as described above. Several pre-processing steps may be conducted to unlock organic information held within Martian samples. It is suspected that perchlorate species are responsible for the non-detection of organic matter on the Viking missions (Navarro-González et al. 2010), as well as the detection of chlorinated organic matter on Mars (Freissinet et al. 2015). However, the deleterious effects of these minerals can be avoided if they are removed prior to sample analysis without compromising the integrity of the organic payload

Samples have been studied from the Atacama Desert (Montgomery *et al.* 2019), a site that is considered to be an excellent analogue for Hesperian and Amazonian Mars due to its high aridity and salinity and low abundance of organic matter (e.g., Fairén *et al.* 2010). They showed that when using an optimal sample extraction duration and suitable water-to-rock ratios, simple aqueous leaching can remove almost all potentially destructive ions, such as perchlorates, nitrates, and phosphates, from the sample. The removal of water-soluble perchlorate salts by aqueous leaching allowed the sample to reach the critical threshold described by previous authors (Royle *et al.* 2018), enabling the detection of diagnostic organic matter via Py-GC-MS. These simple pre-processing steps, while impossible to conduct on Mars, are routine experiments in terrestrial laboratories that can greatly improve the chance of detecting diagnostic organic matter at a low opportunity cost.

Acid/Alkali Treatment

Like perchlorates, it is clear that iron and sulfate minerals can obfuscate the detection of organic compounds, either by the release of atomic oxygen during pyrolysis experiments (Lewis *et al.* 2015, 2018), the oxidation of organics adsorbed onto oxidizing mineral surfaces (Watson and Sephton 2015; Tan *et al.* 2021a), or the production of hydroxyl radicals during the reduction of minerals in the presence of organic matter (Pignatello *et al.* 2006; Watson and Sephton 2015; Tan *et al.* 2021a). Similarly, these problems can be addressed by removing such minerals from the samples entirely; this can be done by treating the samples with a strong alkali, followed by a strong acid, a process which does not affect the organic repository of the samples and has been used to facilitate detection of macromolecules hosted within the minerals present within an acid, iron-rich sulfur stream (Tan *et al.* 2021a). Removal of oxidizing minerals from the samples by the aforementioned alkali/acid treatment revealed the presence of diagnostic organic information, such as the presence of bacterial hopanes, that was otherwise lost during pyrolysis.

Furthermore, the effects of the removal of iron and sulfate minerals were even more obvious in samples that had been artificially matured by hydrous pyrolysis (Tan *et al.* 2021a), suggesting that the obfuscating effect of oxidizing minerals was exacerbated following burial and diagenesis. Comfortingly, these experiments also showed that diagnostic organic compounds such as hopanes could still be preserved in oxidizing environments, even after thermal maturation. This work suggests that the detection of organic materials of unambiguously biological origin could be possible should oxidizing minerals be removed from samples returned from Mars.

Conclusions

The search for evidence of past or present life on Mars often involves information-rich signals such as organic biomarkers. Thermal extraction has historically been the most popular in situ analysis technique employed on Mars but minerals that are sometimes associated with habitable conditions can interact with organic matter when subjected to such heat-based methods. Hence, it is analytically ironic that habitable conditions can aid entombment but sometimes hinder longer-term preservation and certain types of analysis. Fortunately, extensive study of Mars analogue sites on Earth have provided, and will continue to provide, some guidance on how valuable samples can be prepared and analyzed so that their organic contents are recognized and understood. Optimism is warranted because of several potential mitigating options that minimise or avoid completely the impact of thermally-induced organic-mineral modifications. These mitigating steps can be applied not only in situ on Mars but also after samples are returned to Earth as part of Mars Sample Return where more resources and time for sample preparation is available.

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Data Access Statement

All data generated or analysed during this study are included in this published article (and its supplementary information files or cited work).

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Figure 1. Images of Mars analogues that contain minerals useful to help analysts and planners understand the organic challenges presented by in situ analysis on the Red Planet. A) Acidic sulfur- and iron-rich stream in Dorset, UK, produced by the aqueous dissolution of sandstone-hosted pyrite, supporting acidophilic microbes and precipitating jarosite and goethite. B) Sediments in the Yungay region of Atacama containing gypsum (calcium sulfate dihydrate) polygons and heterogeneous vertical soil profiles of perchlorate (Image credit: S. Kounaves). C) Antarctic Dry Valleys containing homogeneous vertical soil profiles of perchlorate (Image credit: S. Kounaves). D) Circumneutral iron seeps in Berkshire, UK that are rich in dissolved Fe(II) and ferrihydrite flocs produced by anaerobic leaching of sandstone-hosted glauconite.

Figure 2. Ratio of organic matter/Mg perchlorate against peak areas of CO (m/z 28) and CO_2 (m/z 44) generated during pyrolysis. Shaded area: 95% confidence interval for the linear regression line through the incomplete combustion dataset; red squares: upper (18.0), lower (8.9) and predicted (11.7) minimum mass ratios for the detection of organic matter. Intersection of the signal from complete combustion and the regression line for the signal from incomplete combustion occurs at 11x Organic Matter/Mg Perchlorate and shows the 'critical ratio' where perchlorate-released O_2 begins to fail to oxidise organic matter. (Figure from Royle et al. 2018).

Figure 3. Diagram describing the potential geochemical evolution of a Martian sulfur stream. A) A potential habitat for extremophilic organisms in a sulfur-rich stream. B) The precipitation of jarosite results in the incorporation and concentration of organic matter in this habitable environment. C) Subsequent goethite and hematite transformation could potentially be favoured if the stream waters become less acidic or the water activity increases. D) At the present day, both jarosite and goethite/hematite would contain organic records; however, goethite/hematite would be far more amenable to pyrolysis-GC-MS analysis than jarosite. (Figure from Lewis et al. 2018).

Figure 4. Gases released 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, c) medium molecular weight organic matter and d) high molecular weight organic matter. This comparison illustrates the correlation between molecular weight and perchlorate assisted combustion temperature. (Figure from Sephton *et al.* 2014).

Figure 5. Differences in Total Ion Current (TIC)/Extracted Ion Current (EIC) signals between unleached and leached samples. The leached samples exhibited considerably stronger organic signals than the unleached samples. In addition, organic signals that were diagnostic of biology, such as C_{15} alkanes, were detected in the leached samples. This emphasises the importance of pre-processing during the analysis of the limited number of samples that will be returned from Mars. (Figure from Montgomery *et al.* 2019).

Figure 6. Differences in TIC signals collected from unleached and leached artificially matured samples collected from an acid-rich sulfur stream. The leached samples had considerably stronger organic signals than the unleached samples. In addition, highly diagnostic signals such as bacterial hopanes were detected in the leached samples. (Figure from Tan *et al.* 2021b).

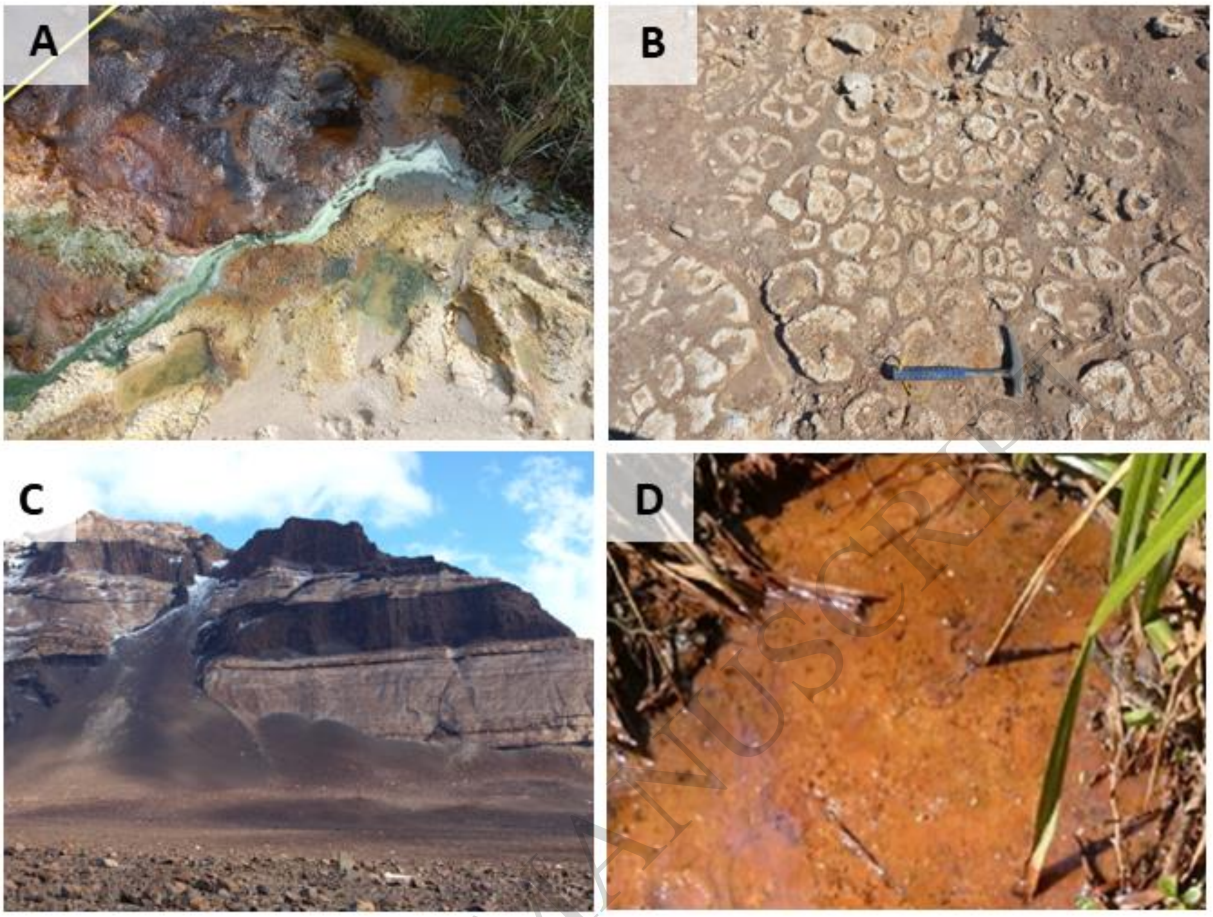

Figure 1

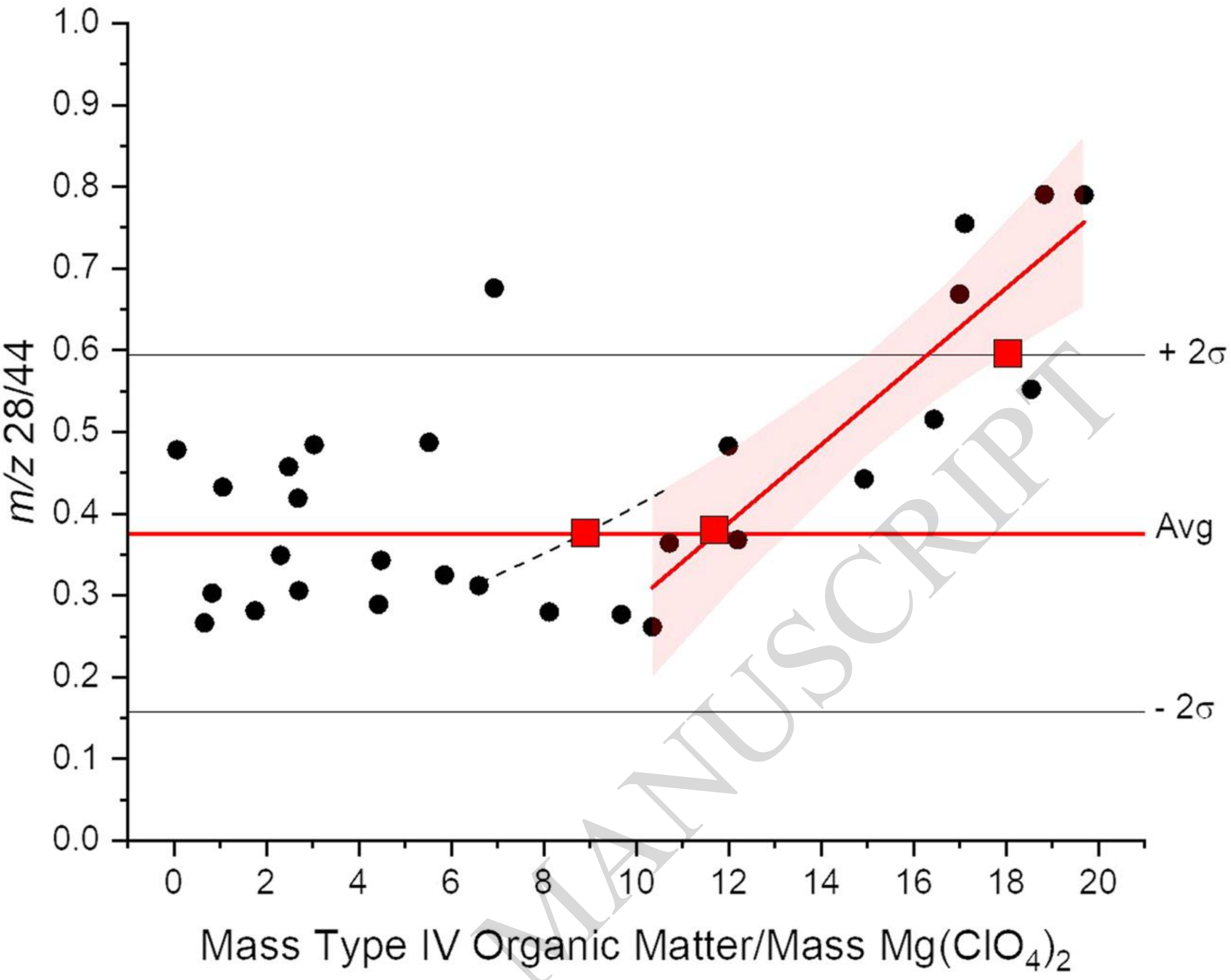
m/z 28/44
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
12
14
16
18
20
Mass Type IV Organic Matter/Mass $Mg(ClO_4)_2$
+ 2σ
Avg
- 2σ

Figure 2

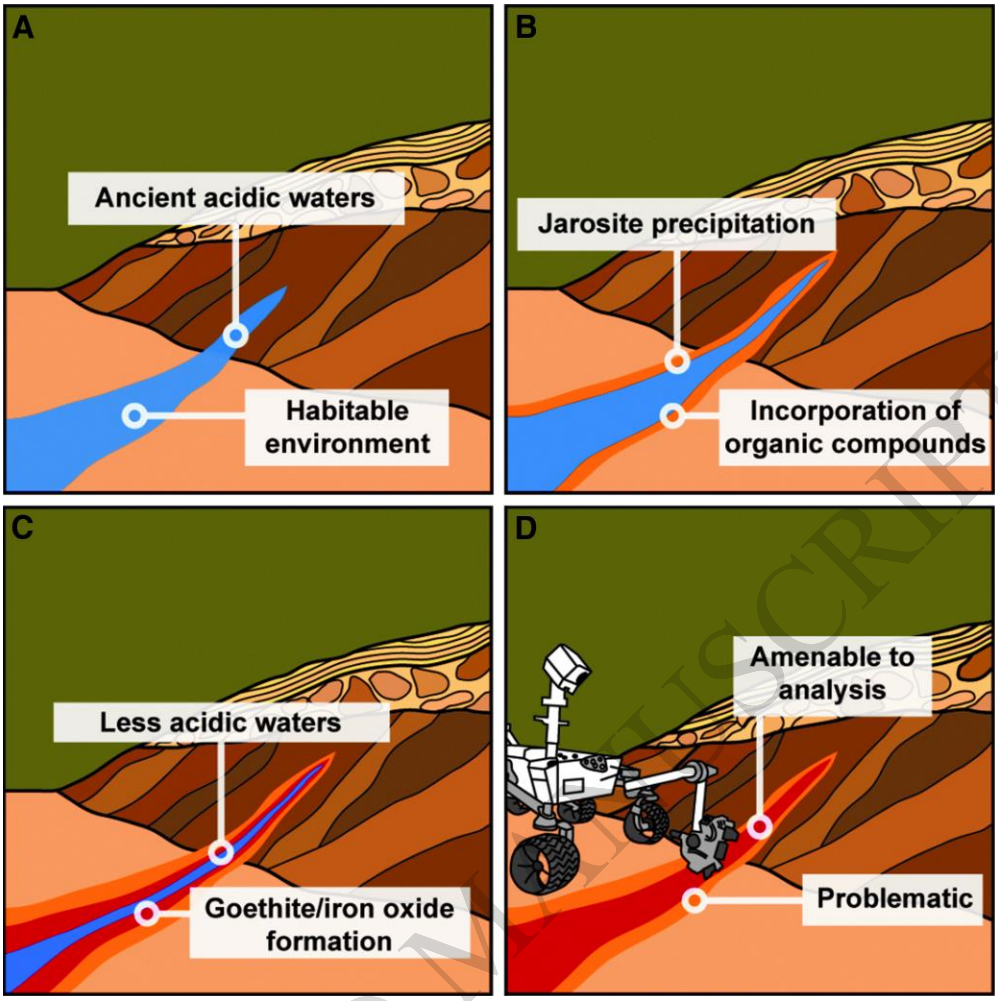
A
Ancient acidic waters
Habitable environment
B
Jarosite precipitation
Incorporation of organic compounds
C
Less acidic waters
Goethite/iron oxide formation
D
Amenable to analysis
Problematic

Figure 3

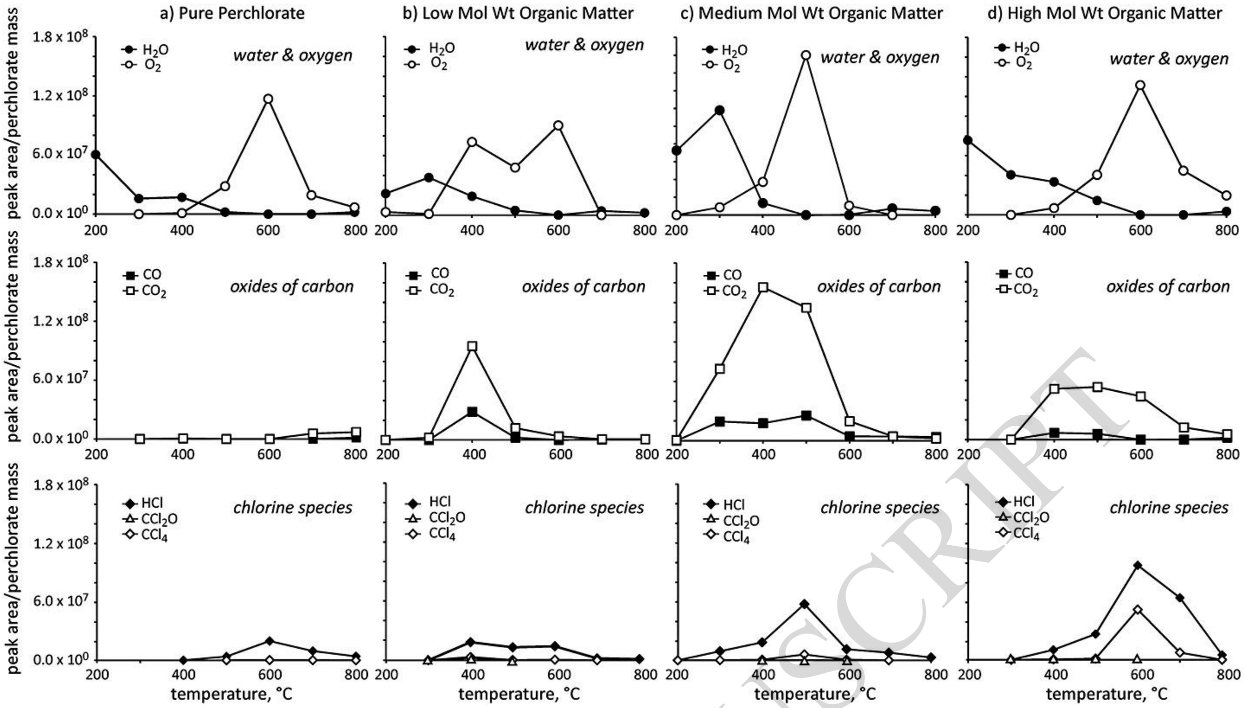
a) Pure Perchlorate
b) Low Mol Wt Organic Matter
c) Medium Mol Wt Organic Matter
d) High Mol Wt Organic Matter
peak area/perchlorate mass
1.8 x 10⁸
1.2 x 10⁸
6.0 x 10⁷
0.0 x 10⁰
water & oxygen
H₂O
O₂
oxides of carbon
CO
CO₂
chlorine species
HCl
CCl₂O
CCl₄
200
400
600
800
temperature, °C

Figure 4

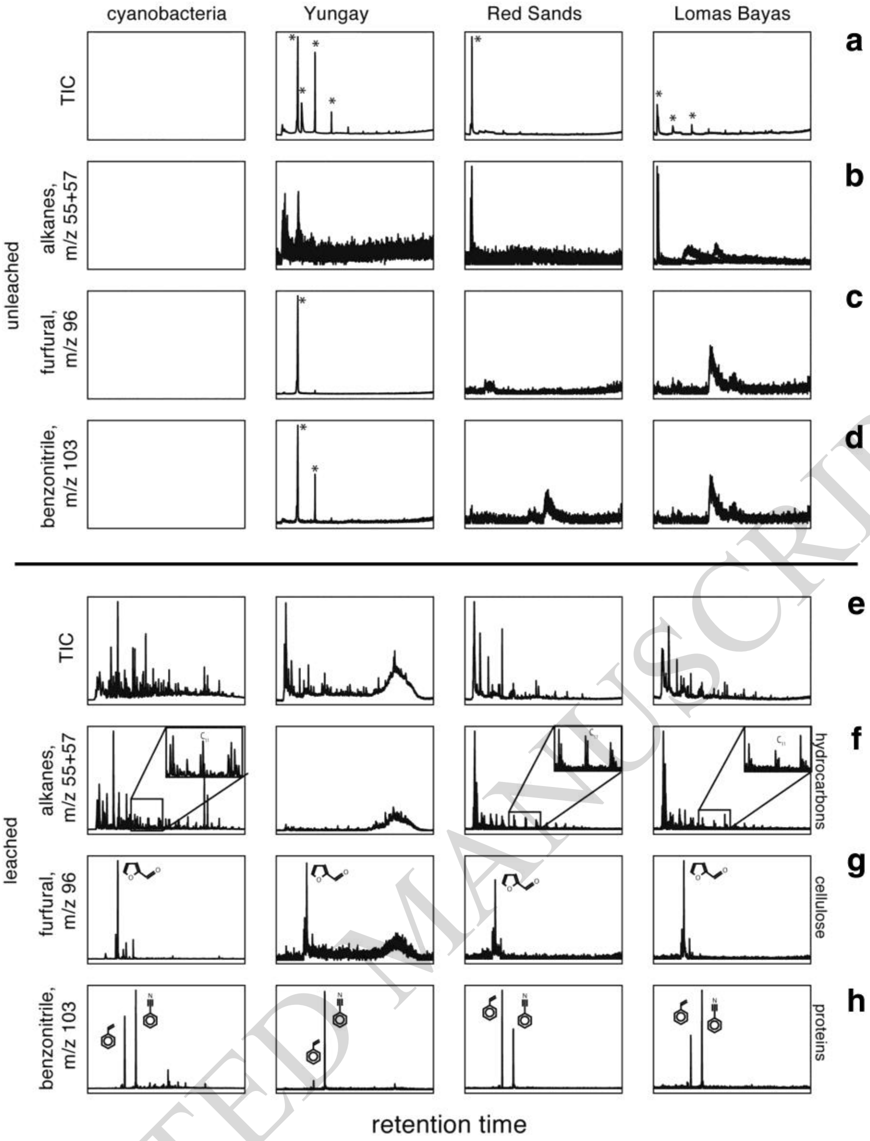
cyanobacteria
Yungay
Red Sands
Lomas Bayas
a
b
c
d
e
f
g
h
unleached
leached
TIC
alkanes, m/z 55+57
furfural, m/z 96
benzonitrile, m/z 103
TIC
alkanes, m/z 55+57
furfural, m/z 96
benzonitrile, m/z 103
hydrocarbons
cellulose
proteins
retention time

Figure 5

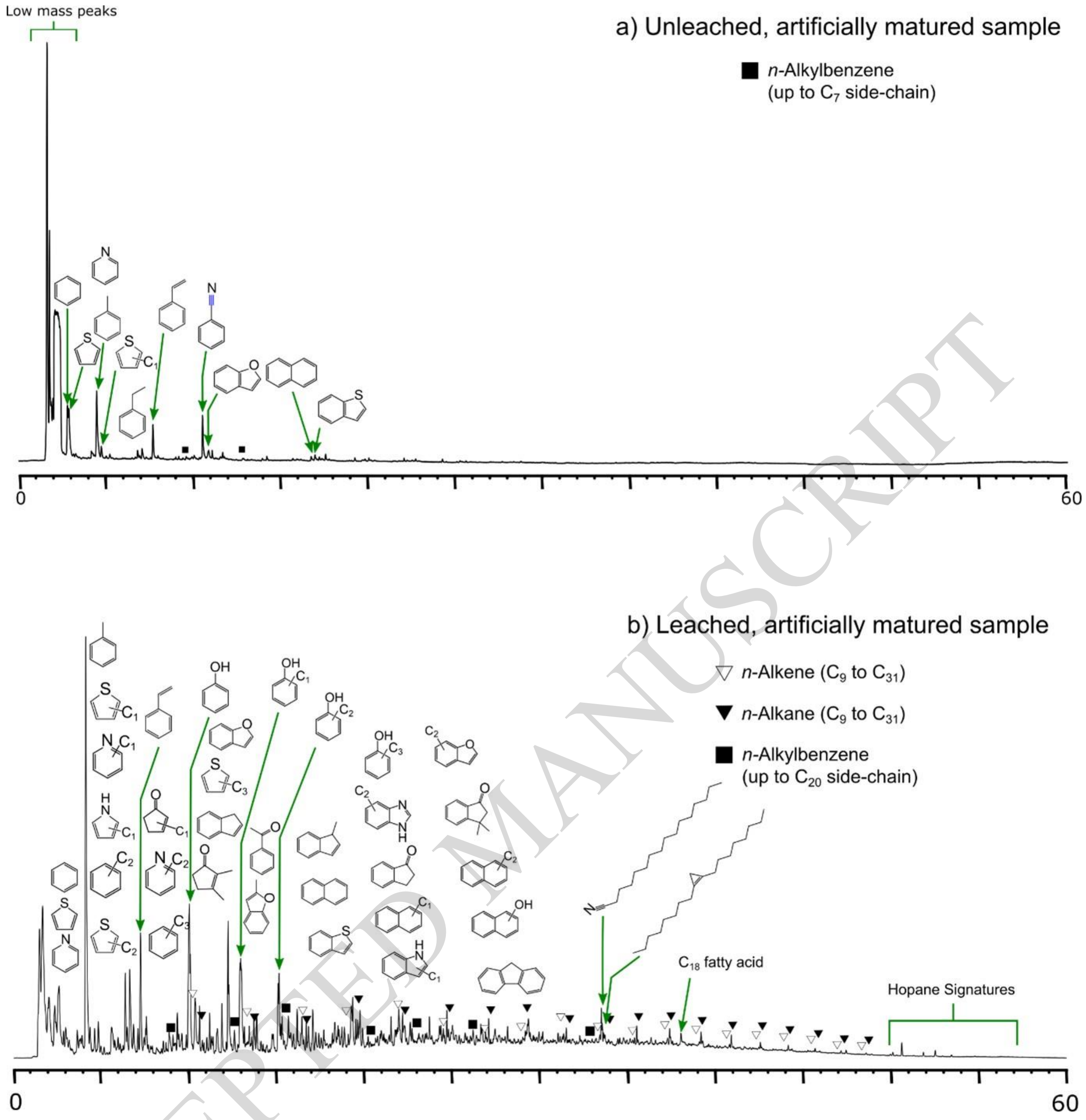
Low mass peaks
a) Unleached, artificially matured sample
■ n-Alkylbenzene (up to C7 side-chain)
N
S
C1
O
0
60
b) Leached, artificially matured sample
▽ n-Alkene (C9 to C31)
▼ n-Alkane (C9 to C31)
■ n-Alkylbenzene (up to C20 side-chain)
OH
C1
C2
C3
H
N
C18 fatty acid
Hopane Signatures
0
60

Figure 6