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Rapid habitability assessment of Mars samples by pyrolysis-FTIR

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ABSTRACT

Pyrolysis Fourier transform infrared spectroscopy (pyrolysis FTIR) is a potential sample selection method for Mars Sample Return missions. FTIR spectroscopy can be performed on solid and liquid samples but also on gases following preliminary thermal extraction, pyrolysis or gasification steps. The detection of hydrocarbon and non-hydrocarbon gases can reveal information on sample mineralogy and past habitability of the environment in which the sample was created. The absorption of IR radiation at specific wavenumbers by organic functional groups can indicate the presence and type of any organic matter present.

Here we assess the utility of pyrolysis-FTIR to release water, carbon dioxide, sulfur dioxide and organic matter from Mars relevant materials to enable a rapid habitability assessment of target rocks for sample return. For our assessment a range of minerals were analyzed by attenuated total reflectance FTIR. Subsequently, the mineral samples were subjected to single step pyrolysis and multi step pyrolysis and the products characterised by gas phase FTIR.

Data from both single step and multi step pyrolysis-FTIR provide the ability to identify minerals that reflect habitable environments through their water and carbon dioxide responses. Multi step pyrolysis-FTIR can be used to gain more detailed information on the sources of the liberated water and carbon dioxide owing to the characteristic decomposition temperatures of different mineral phases. Habitation can be suggested when pyrolysis-FTIR indicates the presence of organic matter within the sample. Pyrolysis-FTIR, therefore, represents an effective method to assess whether Mars Sample Return target rocks represent habitable conditions and potential records of habitation and can play an important role in sample triage operations.

1. Introduction

Mars Sample Return (MSR) missions will allow samples from the red planet to be subjected to the full range of powerful analytical techniques available back on Earth (McLennan et al., 2012) and are believed to offer higher chances of success for life detection than in situ operation (Sephton and Carter, 2015). The success of MSR will depend unavoidably on the selection of the correct samples for return. To maximize the probability of success, in situ instruments are needed to identify the most scientifically exciting samples, in particular those samples which can reveal the history of life on Mars. Constraining the past habitability reflected by Mars rocks and finding evidence for past life have been identified as the highest priority scientific objectives of MSR (McLennan et al., 2012).

When considering planetary habitability, areas of most interest are those where i) liquid water was prevalent, ii) where the building blocks of life were present and iii) where energetic conditions were favorable for life. If evidence suggests that habitable conditions persisted for long enough it is possible that life had originated and evolved. The initiation of life and its subsequent adaptation to its environments will lead to the continuous production of complex organic compounds, the remnants of which can become entombed in rocks. Thus assessing the presence of characteristic mineral phases that reflect habitability can reveal the likelihood of life existing contemporaneously with deposition of the rock. In addition, the detection of organic matter not only advocates habitability but raises the possibility of habitation.

The distribution of mineral types has led to a subdivision of Martian time into three mineralogically defined eras (Bibring et al., 2006; Fig. 1). Each era represents a distinct planetary environment

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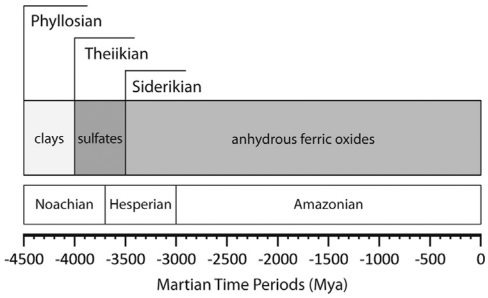

Fig. 1. The Phyllosian, Theiikian and Siderikian eras and the mineral types which define them, illustrated in chronological order. The eras defined by crater density and lava flows are included on the bottom for comparison (diagram adapted from that illustrated by Bibring et al. (2006)).

with very different associated habitabilities. The oldest era represents a period of non-acidic aqueous conditions that led to the production of widespread phyllosilicates (the Phyllosian Era), followed by an acidic aqueous environment reflected by sulfate deposits (the Theiikian Era) and finally water-free conditions that led to the generation of ferric oxides (the Siderikian Era). The changing global environmental conditions on Mars, as reflected in the rock record, indicate changing habitability with early Mars being much more conducive to life than at the present day. These widespread mineralogy-based divisions provide valuable guidance to the types of rock deposits within which Martian biosignatures may be contained.

Organic biosignatures from the habitable environments on early Mars need to be effectively preserved so they can be detected (Summons et al., 2011). The various Martian rock types have different propensities to preserve organic matter. Fortunately, those rock types that indicate habitable conditions such as phyllosilicate-rich rocks and sulfate deposits are also very good at preserving organic matter. For instance phyllosilicate-rich rocks are co-deposited with organic matter and have high surface areas that allow organic adsorption (Hedges, 1977). Sulfates can host organic matter by promoting organic salt formation (Aubrey et al., 2006) and once organic matter is incorporated the low porosities and permeabilities will exclude agents of degradation, such as oxidants, and therefore assist preservation. By contrast, oxide rich rocks reflect oxidizing conditions which are generally incompatible with organic preservation.

Mars presents an overwhelming number of potential samples for return to Earth and some prioritization is essential. Triage protocols, directed by detailed multidisciplinary scientific deliberations (McLennan et al., 2012; Summons et al., 2011) help to determine which samples are of highest priority. Triage methods must provide operational simplicity, wide applicability and should generate information-dense data sets. One technique that may satisfy all these triage requirements is pyrolysis-Fourier transform infrared spectroscopy (FTIR) (Sephton et al., 2013). In this study we explore the capability of pyrolysis-FTIR for in situ habitability assessment. Different modes of pyrolysis, namely single step and multi step, are compared. A simple approach was adopted for processing the resulting spectra; only a restricted set of spectral features were considered for determining habitability as reduced complexity is beneficial when rapid processing of samples is desired. Quantitative data sets were produced to assess their potential added analytical value. The data and interpretations provide guidance on the assessment of mineral decomposition products and their use in determining past habitability, biosignature preservation potential and even biosignature content for MSR target rocks.

Table 1
Details of samples for the pyrolysis-FTIR study.

	Source	Age
Phyllosilicates		
Kaolinite	Sigma-Aldrich	Not applicable
Montmorillonite	Sigma-Aldrich	Not applicable
Carbonate minerals		
Calcium carbonate	Sigma-Aldrich	Not applicable
Siderite	Sigma-Aldrich	Not applicable
Magnesium carbonate	Sigma-Aldrich	Not applicable
Sulfates and other salts		
Halite	Sigma-Aldrich	Not applicable
Iron(III) sulfate	Sigma-Aldrich	Not applicable
Gypsum	Sigma-Aldrich	Not applicable
Unaltered and altered igneous materials		
Lherzolite	Ol Doinyo Lengai, Tanzania	Undefined
Olivine sand	Industrial source	Not applicable
Partially serpentinised peridotite	Kennack Sands, Cornwall, UK	Early-mid devonian
Bastite	Kynance Cove, Cornwall, UK	Early-mid devonian
JSC Mars-1 analog	Pu'u Nene, Hawaii	Recent
Palagonitic tuff	Madeira, Portugal	Recent
Sulfate-rich sediments		
Jarositic clay	Brownsea Island, Dorset, UK	Eocene
Organic, clay and carbonate-rich rocks		
Kimmeridge Clay	Kimmeridge Bay, Dorset, UK	Upper Jurassic
Blue Lias	Lyme Regis, Dorset, UK	Lower Jurassic

2. Method

2.1. Sample selection

To assess the utility of pyrolysis FTIR for recognizing the habitability of depositional environments reflected by rock types that may be encountered on Mars we analyzed a range of samples (Table 1).

2.1.1. Phyllosilicates

Phyllosilicates define the Phyllosian Era and generally form through the weathering of silicate bearing rocks. Thus detection of phyllosilicates on Mars indicates an area which experienced a period of abundant liquid water (Bibring et al., 2006). To assess the response of phyllosilicates and phyllosilicate-rich rocks to pyrolysis-FTIR we examined the standards montmorillonite and kaolinite. In addition to the phyllosilicate mineral standards we also analyzed phyllosilicate mineral-containing natural sedimentary deposits, namely Upper Jurassic Kimmeridge Clay and a recent jarositic clay.

2.1.2. Carbonate minerals

Carbonate minerals also provide a record of water presence and chemistry. Carbonates mostly form in regions which are pH neutral to slightly alkaline and aqueous; both favorable conditions for life. Some carbonate precipitation is strongly linked with microbial activity, and it has even been argued that carbonates found in unexpected regions on Mars could be explained by microbial activity (Fernández-Remolar et al., 2012). To assess the response of carbonates to pyrolysis-FTIR we examined