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, sulphur 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 analysed 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.

Keywords

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 maximise 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 favourable 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). Each era represents a distinct planetary environment 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 prioritisation 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.

2   Method

2.1   Sample selection

To assess the utility of pyrolysis FTIR for recognising the habitability of depositional environments reflected by rock types that may be encountered on Mars we analysed a range of samples (Table 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 analysed phyllosilicate mineral-containing natural sedimentary deposits, namely Upper Jurassic Kimmeridge Clay and a recent jarositic clay.

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 favourable 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 calcium carbonate ($CaCO_3$), siderite ($FeCO_3$) and magnesium carbonate ($MgCO_3$). In addition to the carbonate standards we also analysed carbonate-containing natural sedimentary

deposits, namely the Lower Jurassic Blue Lias and the aforementioned Upper Jurassic Kimmeridge Clay.

Sulfates and other salts

Sulfate minerals on the Martian surface indicate a global shift from the equable conditions reflected by the phyllosilicates to an acidic, less hospitable environment (Bibring et al. 2006). Life on Earth can adapt to acidic conditions and some organisms are capable of occupying such extreme conditions (Zettler et al., 2003). Salts can form through the evaporation of aqueous bodies. To assess the response of sulfates and other salts to pyrolysis-FTIR we examined halite (NaCl), iron(III) sulfate ($Fe_2(SO_4)_3$) and gypsum ($CaSO_4 \cdot 2H_2O$). A natural sulfate-containing sedimentary deposit was provided by the natural jarositic clay described above.

Unaltered and altered igneous materials

There are widespread igneous products or their alteration products on Mars. When igneous rocks are subjected to water they are partly or completely altered to rocks such as serpentinite. If the igneous rocks are fine grained or glassy then palagonite is a common alteration product. Weathering without the presence of water can produce ferric oxides. To reflect igneous rocks that may be encountered on Mars we have subjected a number of rock types to pyrolysis-FTIR that cover both unaltered and altered materials. For unaltered materials we chose lherzolite and olivine sand. For hydrothermally processed igneous rocks we analysed partially serpentinised peridotite and bastite serpentinite. For weathered igneous material we utilised the JSC Mars-1 Mars analogue and palagonitic tuff.

Organic matter bearing rocks

Natural rock samples provide examples of mineral mixtures that contain enclosed organic constituents and act as good test samples for the combined inorganic and organic complexity that

may be encountered on Mars. The samples used in this study that represent organic containing matrices are the Lower Jurassic Blue Lias and the Upper Jurrassic Kimmeridge Clay.

2.2   Attenuated Total Reflectance-FTIR

Spectra of solid phase samples were obtained using a Thermo-Nicolet 5700 FT-IR spectrometer fitted with an attenuated total reflectance (ATR) Thermo Orbit accessory. Powdered forms of each mineral (previously dried in a 110 °C oven to reduce the contribution of adsorbed species) were pressed against the ATR crystal and the FTIR spectra collection method was executed. The FTIR collection method averaged 32 scans with a resolution of 4 cm^{-1} in the 4000-525 cm^{-1} infrared region; acquisition time was 39 seconds. Each analysis included a background scan obtained using the same method and conducted before the sample was loaded. Spectra were obtained and processed using the Thermo Scientific™ OMNIC™ Series software.

To identify hydrated minerals and carbonate bearing minerals as habitability indicators, the following spectral features were searched for: a strong sharp band in the 3700-3500 cm^{-1} region arising from the stretching vibration from mineral bound hydroxyl; a single broad band arising from the two stretching bands of the water molecule, apparent in the 3600-3200 cm^{-1} region for water of hydration and the 3400-3200 cm^{-1} region for adsorbed water; and the carbonate ion spectral peaks, which include a strong band usually between 1450-1400 cm^{-1} and medium strength bands at 890-800 cm^{-1} and at 760-670 cm^{-1}. Data was also inspected for peaks arising from the sulfate ion in the 1210-1040 cm^{-1} and 1030-960 cm^{-1} regions and for the presence of C-H stretches in the 3050-2650 cm^{-1} region as a test for the presence of organic matter. Quantitative analysis was not performed on the ATR-FTIR data set. Band identification was achieved by reference to published absorption band tables (Gadsden, 1975).

2.3   Pyrolysis-FTIR

Pyrolysis was achieved using a CDS Analytical Pyroprobe 5200 and the FTIR spectra were obtained using the same Thermo-Nicolet 5700 FT-IR spectrometer as described above for ATR, using a nitrogen cooled MTC/A detector. Gas phase products were accumulated in a CDS Analytical Brill Cell™ containing IR transparent ZnSe windows. A helium atmosphere was maintained inside the cell, because helium is inert and IR transparent, and a helium flow allowed the cell to be purged between experiments. The Brill Cell was held constantly at 250 °C to prevent condensation of pyrolysis products on the cell components.

Solid samples, ground to a fine powder, were loaded in small amounts (approximately 0.4 – 18 mg) into quartz tubes and held in place by a quartz wool plug at each end of the tube. Before and after pyrolysis, samples were weighed on a balance accurate to ±0.1 mg to allow mass losses to be calculated and to express pyrolysis yields as fractions of the initial sample mass. The quartz tubes and wool were cleaned by progressive rinsing with water, methanol and dichloromethane before being baked at 500 °C. Before pyrolysis, the probe was used for a final drying step by subjecting each prepared sample to 120 °C for 15 s to minimise the contribution of adsorbed species.

The spectral data was collected and processed using the Thermo Scientific™ OMNIC™ Series Software. Prior to firing the probe and collecting sample data, a background spectrum was taken for each analysis with the sample loaded in the cell. In each pyrolysis event, the desired temperature was attained at 20 °C ms^{-1} and held for 10 s before conducting FTIR data collection to allow adequate diffusion of pyrolysis products within the cell. The pyrolysis temperature was held for the duration of data collection to prevent gas products recombining with the sample residue. FTIR analyses were constructed by the combination of 32 individual spectra with resolutions of 4 cm^{-1} in the 4000-650 cm^{-1} infrared region, collected over approximately 20 s. Three spectra were collected for each

sample at each temperature step. Before each experimental session, a series of blanks were obtained by replicating the full sample analysis procedure without any sample in place.

An automatic baseline correction was performed on each spectrum before recording the intensity of absorption peaks of four gases of interest; carbon dioxide, water, sulfur dioxide and methane. Band identification was achieved by searching through the spectral data available in the NIST Webbook (http://webbook.nist.gov/chemistry/) and use of the 'IR Spectral Analysis' function provided in the Thermo Scientific™ OMNIC™ Series software. For carbon dioxide and water the areas of characteristic peaks were recorded - one located at 2349 cm^{-1} corresponding to the anti-symmetric stretch in carbon dioxide and one at 3853 cm^{-1} arising from a stretching mode of water. For methane and sulfur dioxide the absorbance intensity was recorded at characteristic frequencies (at 3016 cm^{-1} corresponding to the methane anti-symmetric stretching mode and at 1352 cm^{-1} corresponding to the sulfur dioxide anti-symmetric stretching mode).

The measured responses of all gases were processed quantitatively. Carbon dioxide and water data sets were analysed further to evaluate the added value of a quantitative approach. Mass calibration curves were constructed by direct injection of a known quantity of gas into the Brill Cell. Reference to the calibration curve allowed the masses of carbon dioxide and water yields from pyrolysis of samples to be calculated from the measured peak areas. Each value was expressed as a mass percentage of the initial sample mass.

3 Results

3.1 ATR FTIR

A representative spectrum acquired by ATR-FTIR is displayed in Figure 2a., spectra for all samples are presented in Appendices 1 to 5 and qualitative results are presented in Table 2. A sharp hydroxyl band was seen in bastite serpentinite, kaolinite, jarositic clay and the Kimmeridge Clay, with less

prominent bands being observed in montmorillonite and the Blue Lias. The broad spectral feature associated with water of hydration and adsorbed water is observed clearly in the partially serpentinised peridotite, iron(III) sulfate, jarositic clay and JSC Mars-1, and less obviously in magnesium carbonate, bastite serpentinite, montmorillonite, palagonitic tuff, Kimmeridge Clay, siderite and the Blue Lias. Only in the iron(III) sulfate sample is the band positioned at low enough frequency to identify it conclusively as adsorbed water. Whether the source of the water response is adsorbed water or water of hydration cannot be easily determined for the other samples. Presence of the carbonate ion was clearly identified in calcium carbonate, siderite, magnesium carbonate and the Blue Lias, with a weak response in the Kimmeridge Clay. Only the Kimmeridge Clay showed clearly identifiable absorption in the 3050-2650 cm^{-1} region, indicating the presence of hydrocarbons. A response in the same spectral region can be reported for the Blue Lias but with less confidence.

3.2   Single step pyrolysis-FTIR

A representative spectrum acquired by single step pyrolysis-FTIR is displayed in Figure 2b and spectra for all samples are presented in Appendices 1 to 5. Carbon dioxide, water, sulfur dioxide and methane responses for single step pyrolysis-FTIR are listed in Table 3. Only the Kimmeridge Clay produced an organic response, with a clearly pronounced methane band at 3014 cm^{-1}. Carbon dioxide and water mass yields from single step pyrolysis-FTIR, represented as fractions of the initial sample mass, are recorded in Table 4.

3.3   Multi step pyrolysis-FTIR

A representative spectrum acquired by single step-FTIR is displayed in Figure 2c and spectra for all samples are presented in Appendices 1 to 5. Carbon dioxide, water, sulfur dioxide and methane responses for multi step pyrolysis-FTIR are recorded in Table 5. Again, only the Kimmeridge Clay produced identifiable organic responses, and only at 500 °C and 750 °C. A well pronounced methane

peak is visible at 3014 cm^{-1} at both temperatures, but at 500 °C there are also absorption peaks at 2966 cm^{-1}, 2933 cm^{-1} and a double peak about 2875 cm^{-1}, arising from the C-H stretching modes of aliphatic hydrocarbons. Carbon dioxide and water mass yields from multi step pyrolysis-FTIR, represented as fractions of the initial sample mass, are recorded in Table 6.

4   Discussion

4.1   ATR-FTIR

Trends can be identified in the ATR FTIR results, such as hydroxyl being a common feature of phyllosilicate materials and the carbonate ion being easily identified in the majority of the carbonate bearing materials. Water of hydration appears in altered igneous materials while it is lacking in the unaltered examples. Organic matter is usually at least an order of magnitude lower in natural abundances than the mineral matrix, making detection by ATR-FTIR relatively difficult. However, detection of organic matter in the Kimmeridge Clay was possible.

4.2   Qualitative pyrolysis-FTIR analysis

Results show that the water signal in the single step method discriminates between hydrated and non-hydrated mineral types. Single step pyrolysis also produces a strong carbon dioxide signal for all carbonate materials tested. A concurrent release of water and carbon dioxide is observed for all materials bearing organic matter. Consistent with previously published work on the thermal decomposition of sulfates (Lewis et al., 2014), gypsum is the only sulfate rich material which does not produce a sulfur dioxide signal; decomposition of calcium sulfate only becomes appreciable around temperatures of 1200 °C and above (Newman, 1941). The detection of methane for the Kimmeridge Clay sample shows that our single step pyrolysis-FTIR method has the capability to detect organic matter when present in sufficient amounts.

Detection limits for gas-phase FTIR equipment, when adjusted to parameters expected of a pyrolysis-FTIR instrument, are a few parts per million (Griffith, 1996). Gas-phase FTIR is substantially less sensitive than gas chromatography-mass spectrometer instruments, such as the Sample Analysis at Mars (SAM) instrument used on the Mars Science Laboratory (MSL) mission (Mahaffy et al., 2012), which have sensitivities at the parts per billion level. The most abundant organic compounds detected by the Mars Science Laboratory mission are chlorinated hydrocarbons which are found at levels up to several hundred parts per billion (Freissinet et al., 2015). If these data reflect indigenous organic matter, it is reasonable to suggest that when other potential classes of organic compound are considered and when the confounding effects of perchlorate induced oxidation of organic matter (Glavin et al., 2013) are discounted, that organic matter at the level of parts per million in Mars mudstones becomes a realistic expectation.

Multi step pyrolysis produces results that are in good agreement with those from single step pyrolysis. Again, all carbonate materials produce a strong carbon dioxide signal. However multi step pyrolysis provides more diagnostic information; specific carbonates break down at different temperatures, showing that multi step pyrolysis can discriminate between the various cations involved. The water responses of hydrated minerals from multi step pyrolysis also provide detailed diagnostic information about mineral types, reflecting their formation conditions. Weathered materials such as JSC Mars-1 and jarositic clay produce water at low temperatures, phyllosilicates (with the exception of montmorillonite, which releases quantities of water below our chosen detection limits) produce water at the medium temperature step, while serpentinite minerals exhibit strong medium and high temperature water signals. The sulfate rich materials that were seen to produce sulfur dioxide signals in the single step analysis are observed to produce sulfur dioxide across all temperature steps.

Although multi step pyrolysis provides more diagnostic information than single step pyrolysis it is associated with lower sensitivity. Whereas single step pyrolysis combines all pyrolysis products into

a single measurement multi step pyrolysis products are spread over several analyses. The lower sensitivity of multi step analyses is particularly evident for the Blue Lias where water is detected in the single step method but is below the level of detection when spread across the multistep analyses. During triage operations on Mars, decisions must be made to prioritise sensitivity (single step methods) over the acquisition of more diagnostic information (multi step methods).

4.3   Quantitative pyrolysis-FTIR analysis

The quantitative findings for single step pyrolysis-FTIR are in general harmony with those from qualitative analysis. Yet quantitative analysis does provide greater diagnostic potential. For example, materials from similar origins such as the Blue Lias and the Kimmeridge Clay sedimentary rocks can be separated by the relative amounts of carbon dioxide (44 ± 2 wt% and 2.5 ± 0.3 wt% respectively). The Blue Lias contains a more substantial carbonate concentration than that for the Kimmeridge Clay. However it can be the case that materials of different origins are indistinguishable through single step quantitative analysis when only considering a small number of gases, for example jarositic clay (2.4 ± 0.4 wt% carbon dioxide, 6.2 ± 1.2 wt% water) and the Kimmeridge Clay (2.5 ± 0.3 wt% carbon dioxide, 5.7 ± 1.1 wt% water). The difficulty of discriminating between samples inevitably diminishes as more gases are examined, and an attractive feature of pyrolysis-FTIR is that information on multiple gases is provided in the same analysis, but even without additional information both samples could be considered representative of habitable conditions and are suitable for collection during a sample return mission.

The quantitative findings for multi step pyrolysis-FTIR are concordant with those from qualitative analysis. It has been shown, in the qualitative analyses, that multi step pyrolysis allows discrimination between rocks of generally similar types; the diagnostic potential of pyrolysis-FTIR is further enhanced when quantitative values are available. The differences between the Blue Lias and the Kimmeridge Clay that were observed in the single step analysis are still apparent, however it is

now clear that both samples release the bulk of their carbon dioxide at the higher temperature step, indicating the presence of calcium carbonate (see Table 6). Also as previously stated, it would be difficult to identify whether a sample is jarositic clay or Kimmeridge Clay if only single step quantitative data was available for water and carbon dioxide. However, owing to the characteristic high temperature release of carbon dioxide from Kimmeridge Clay and low temperature release of water for jarositic clay, we are able to discern between the two samples by using the multi step method (see Table 6).

4.4   Habitability assessment on Mars by pyrolysis-FTIR

Our results allow us to identify trends amongst mineral types and to construct a framework of interpretation for a pyrolysis-FTIR instrument conducting sample selection on the Martian surface. An example schema for interpreting qualitative carbon dioxide and water signals in multi step pyrolysis-FTIR operation is illustrated in Figure 3. Expanding this mechanism of analysis to incorporate quantitative analysis and additional gases enhances the identification potential of pyrolysis-FTIR.

During the early stages of any triage process the recognition of habitability (hydrated or precipitated mineral) or potential habitation (organic matter) could proceed with the relatively high sensitivity of single step pyrolysis-FTIR. Once rocks are identified then more detailed analysis can occur by the multi step pyrolysis-FTIR method. For habitability assessment water is produced from weathered rocks at low temperatures, from clay minerals at medium temperatures and from serpentinites at medium and high temperatures. Carbon dioxide is produced from carbonate bearing samples across a range of temperatures (but at high temperatures for all materials containing calcium carbonate). For potential past or present habitation assessment, methane is detectable at the low and medium temperature steps and more complex organic compounds are detectable at the lower temperature step.

While our lab based version of the instrument has shown how pyrolysis-FTIR can aid sample selection, its consideration for application on Mars will be dependent on meeting the required technical limitations of a robotic surface mission instrument; specifically the weight, power and volume constraints. Encouragingly, the case for pyrolysis-FTIR is supported by previous missions where thermal extraction techniques, comparable with that used here, have been incorporated successfully.

The Viking landers, the first spacecraft to successfully land on the surface of Mars, both contained ceramic ovens which performed experiments on samples from the Chryse Planitia Region of Mars by heating them up to temperatures of 500 °C, primarily in the search for organic compounds (Biemann et al., 1976). The Phoenix lander, which reached the surface of Mars in May 2008, utilised ovens as part of the Thermal and Evolved Gas Analyzer (TEGA) instrument which could heat samples up to 1000 °C (Hoffman et al., 2008). The SAM instrument on board the MSL mission employs ovens for evolved gas analysis, and can heat samples up to 1100 °C to liberate volatiles associated with mineral break-down, particularity water, carbon dioxide, sulphur dioxide (Mahaffy et al., 2012).

For the products of previous thermal extraction experiments on Mars, detection (in general) was achieved through mass spectrometer configurations. With mass spectrometry, water, carbon dioxide, sulphur dioxide and organic compounds (or the products of perchlorate oxidiation and chlorination of organic compounds) have all been detected during investigations of the Martian surface. As all these gases have vibrational modes in the infrared, FTIR could be used to replace mass spectrometry for detecting thermally evolved gases as part of future instruments. Potential strategies to improve the FTIR sensitivity to levels comparable with mass spectrometry include increasing the path length traversed through pyrolysis products in the gas cell, increasing the quantity of sample analysed, and the cumulative capture of volatiles on trapping materials from recurrent analyses followed by complete thermal desorption.

In the context of sample selection for a sample return, it is not important to perform an in-depth scientific analysis of a sample, but to survey a large number samples to identify those of greatest promise and provide high confidence in the scientific value of final candidates chosen for return to Earth. The expedience of pyrolysis-FTIR suggest that it could play a key role in sample triage on the red planet.

5   Conclusions

A pyrolysis-FTIR instrument can be used to assess the past habitability reflected by a Mars sample through the analysis of gas release. Gas release profiles of Mars samples are characteristic for certain mineral types. Important gases related to habitability that have been the target of previous space missions are detectable by FTIR, namely water, carbon dioxide and sulfur dioxide and their source materials have been shown here to have distinguishable temperature release profiles. FTIR also has a propensity for the detection of organic compounds, which could reveal potential cases of past or present habitation. The successful deployment of in situ instruments using thermal extraction technology on previous missions asserts the applicability of using pyrolysis-FTIR on Mars. Its operational attributes make it well suited for the triage phase of a Mars Sample Return mission.

Acknowledgements

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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 analogue	Pu'u Nene, Hawaii	Recent
Palagonitic tuff	Majorca, Spain	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

Table 2. Results of ATR FTIR analysis. A solid circle indicates the clear presence of spectral features linked to different mineralogical habitability indicators (hydroxyl and water of hydration for hydrated minerals, the carbonate ion for carbonate bearing materials and aliphatic hydrocarbons for organic bearing materials). A solid circle represents cases where the features were clearly identifiable while an unfilled circle represents tentative identification.

	Hydroxyl	Water of hydration/ adsorbed water	Carbonate ion	Sulfate ion	Organic compounds
Phyllosilicates					
Kaolinite	●				
Montmorillonite	○	○			
Carbonate minerals					
Calcium carbonate			●		
Siderite		○	●		
Magnesium carbonate		○	●		
Sulfates and other salts					
Halite					
Iron(III) sulfate		●		●	
Gypsum				●	
Unaltered and altered igneous materials					
Lherzolite					
Olivine sand					
Partially serpentinised peridotite	●	●			
Bastite	●	○			
JSC Mars-1 analogue		●			
Palagonitic tuff		○			
Sulfate-rich sediments					
Jarositic clay	●	●		○	
Organic, clay and carbonate-rich rocks					
Kimmeridge Clay	●	○	○	○	●
Blue Lias	○	○	●		○

Table 3. Qualitative results for the single step pyrolysis-FTIR method. A solid circle indicates a detection of high confidence, where the signal produced by that gas exceededs four standard deviations of the baseline noise. An empty circle represents a tentative detection.

	Carbon dioxide	Water	Sulfur dioxide	Methane
Phyllosilicates				
Kaolinite		○		
Montmorillonite	○	○		
Carbonate minerals				
Calcium carbonate	●			
Siderite	●	○		
Magnesium carbonate	●			
Sulfates and other salts				
Halite				
Iron(III) sulfate	○		●	
Gypsum				
Unaltered and altered igneous materials				
Lherzolite	○			
Olivine sand				
Partially serpentinised peridotite		●		
Bastite		●		
JSC Mars-1 analogue	●	●		
Palagonitic tuff		○	○	
Sulfate-rich sediments				
Jarositic clay	●	●	●	
Organic, clay and carbonate-rich rocks				
Kimmeridge Clay	●	●	○	●
Blue Lias	●	●		

Table 4. Quantitative results for the single step pyrolysis-FTIR method. Values show the mass of pyrolysis products as a percentage of the initial sample mass, with associated uncertainty. The mass of the pyrolysis products was calculated by measuring the peak area of a chosen spectral feature (characteristic of the gas) and referencing a mass calibration curve. Values in parenthesis do not exceed the calculated uncertainty, and thus can effectively be considered absent.

	Carbon dioxide	Water	Sulfur Dioxide	Methane
Phyllosilicates				
Kaolinite	[0.0 ± 1.0]	12 ± 9	[0 ± 5]	[0.0 ± 1.8]
Montmorillite	[0.7 ± 0.7]	5 ± 3	[0 ± 2]	[0.0 ± 0.9]
Carbonate minerals				
Calcium carbonate	59 ± 14	[1 ± 3]	[0 ± 3]	[-0.1 ± 1.1]
Siderite	39 ± 3	1.7 ± 1.1	[0 ± 1]	[0.0 ± 0.4]
Magnesium carbonate	19 ± 3	3 ± 2	[0.2 ± 1.7]	[0.1 ± 0.7]
Sulfates and other salts				
Halite	[0.03 ± 0.11]	[0.2 ± 0.5]	[0.0 ± 0.4]	[-0.01 ± 0.18]
Iron(III) sulfate	1.0 ± 0.7	[3 ± 3]	24 ± 6	[0.3 ± 0.9]
Gypsum	[0.4 ± 0.5]	[0 ± 2]	[0.0 ± 1.8]	[-0.1 ± 0.8]
Unaltered and altered igneous materials				
Lherzolite	0.19 ± 0.07	[0.1 ± 0.3]	[0.1 ± 0.3]	[0.00 ± 0.12]
Olivine sand	[0.07 ± 0.15]	[0.5 ± 0.7]	[0.0 ± 0.6]	[0.0 ± 0.2]
Partially serpentinised peridotite	[0.07 ± 0.18]	9.7 ± 1.3	[0.2 ± 0.7]	[0.1 ± 0.3]
Bastite	[0.10 ± 0.16]	8.5 ± 1.1	[0.1 ± 0.6]	[0.1 ± 0.3]
JSC Mars-1 analogue	3.0 ± 0.7	4.4 ± 1.9	[0.1 ± 1.4]	[0.1 ± 0.6]
Palagonitic tuff	[0.2 ± 0.2]	2.0 ± 1.0	[0.6 ± 0.8]	[0.1 ± 0.3]
Sulfate-rich sediments				
Jarositic clay	2.4 ± 0.3	6.2 ± 1.2	5.2 ± 1.0	[0.1 ± 0.3]
Organic, clay and carbonate-rich rocks				
Kimmeridge Clay	2.5 ± 0.3	5.7 ± 1.0	[0.6 ± 0.7]	2.1 ± 0.4
Blue Lias	44.4 ± 1.9	1.3 ± 0.6	[0.2 ± 0.5]	[0.07 ± 0.17]

Table 5. Qualitative results for the multi step pyrolysis-FTIR method. A solid circle indicates a detection of high confidence, where the signal produced by that gas exceeds four standard deviations of the baseline noise. An empty circle represents a detection of lower confidence.

	Carbon dioxide			Water			Sulfur dioxide			Methane		
	500 °C	750 °C	1000 °C	500 °C	750 °C	1000 °C	500 °C	750 °C	1000 °C	500 °C	750 °C	1000 °C
Phyllosilicates												
Kaolinite					●							
Montmorillite												
Carbonate minerals												
Calcium carbonate			●									
Siderite	●	●		●								
Magnesium carbonate	●			○								
Sulfates and other salts												
Halite												
Iron(III) sulfate				●			○	●	●			
Gypsum												
Unaltered and altered igneous materials												
Lherzolite												
Olivine sand												
Partially serpentinised peridotite				○	●	●						
Bastite					●	●						
JSC Mars-1 analogue	●	●	○	●	●							
Palagonitic tuff		○		○					○			
Sulfate-rich sediments												
Jarositic clay	●	●		●	○		●	●	○			
Organic, clay and carbonate-rich rocks												
Kimmeridge Clay	●	●	●	●	●	○		●	○	●	●	
Blue Lias	●	●	●									

Table 6. Quantitative results for the multi step pyrolysis-FTIR method. Values show the mass of pyrolysis products as a percentage of the initial sample mass, with associated uncertainty. The mass of the pyrolysis products was calculated by measuring the peak area of a chosen spectral feature (characteristic of the gas) and referencing a mass calibration curve. Values in parenthesis do not exceed the calculated uncertainty, and thus can effectively be considered absent.

|	Carbon dioxide			Water			Sulfur dioxide			Methane		
	500 °C	750 °C	1000 °C	500 °C	750 °C	1000 °C	500 °C	750 °C	1000 °C	500 °C	750 °C	1000 °C
Phyllosilicates												
Kaolinite	[0.2 ± 0.3]	[0.0 ± 0.3]	[-0.2 ± 0.5]	[1 ± 2]	10 ± 5	[2 ± 3]	[0.2 ± 1.3]	[-0.1 ± 0.8]	[0 ± 2]	[0.1 ± 0.3]	[0.3 ± 0.5]	[0.7 ± 1.0]
Montmorillite	[0.2 ± 0.3]	[0.2 ± 0.5]	[0.1 ± 0.7]	[2 ± 3]	[3 ± 4]	[2 ± 4]	[0.2 ± 1.7]	[-0.1 ± 1.0]	[0 ± 3]	[0.2 ± 0.5]	[0.3 ± 0.6]	[0.9 ± 1.4]
Carbonate minerals												
Calcium carbonate	[0.0 ± 0.3]	[0.5 ± 0.6]	50 ± 13	[0 ± 2]	[1 ± 4]	[0 ± 3]	[0.9 ± 1.8]	[0.9 ± 1.1]	[1 ± 3]	[-0.1 ± 0.4]	[0.0 ± 0.6]	[0.4 ± 1.3]
Siderite	21.9 ± 1.6	8.1 ± 0.8	[0.0 ± 0.2]	1.9 ± 0.8	[0.2 ± 1.0]	[0.3 ± 0.9]	[0.0 ± 0.5]	[0.0 ± 0.3]	[0.0 ± 0.8]	[0.06 ± 0.12]	[0.1 ± 0.2]	0.3 ± 0.3
Magnesium carbonate	16 ± 4	[0.2 ± 0.4]	[-0.1 ± 0.6]	4 ± 3	[1 ± 3]	[0 ± 3]	[0.6 ± 1.5]	[0.1 ± 0.9]	[0 ± 3]	[0.1 ± 0.4]	[0.2 ± 0.5]	[0.6 ± 1.1]
Sulfates and other salts												
Halite	[0.02 ± 0.03]	[0.01 ± 0.04]	[-0.02 ± 0.06]	[0.1 ± 0.2]	[0.2 ± 0.3]	[0.1 ± 0.3]	[0.01 ± 0.14]	[0.00 ± 0.09]	[0.0 ± 0.3]	[0.02 ± 0.04]	[0.03 ± 0.05]	[0.08 ± 0.10]
Iron(III) sulfate	[0.1 ± 0.2]	[0.2 ± 0.3]	[0.0 ± 0.5]	8 ± 3	[1 ± 2]	[0 ± 2]	[1.1 ± 1.3]	2.1 ± 1.0	23 ± 4	[0.1 ± 0.3]	[-0.1 ± 0.4]	[0.4 ± 0.9]
Gypsum	[0.0 ± 0.3]	[0.2 ± 0.4]	[-0.1 ± 0.6]	[1 ± 2]	[1 ± 3]	[1 ± 3]	[0.7 ± 1.5]	[0.6 ± 0.9]	[1 ± 3]	[0.0 ± 0.4]	[0.02 ± 0.52]	[0.4 ± 1.1]
Unaltered and altered igneous materials												
Lherzolite	[0.05 ± 0.10]	0.20 ± 0.15	[0.0 ± 0.2]	[0.0 ± 0.7]	[0.1 ± 1.1]	[0.4 ± 1.0]	[0.0 ± 0.5]	[0.2 ± 0.3]	[0.5 ± 0.9]	[-0.02 ± 0.13]	[-0.05 ± 0.18]	[0.1 ± 0.4]
Olivine sand	[0.02 ± 0.05]	[0.06 ± 0.08]	[-0.03 ± 0.13]	[0.0 ± 0.4]	[0.3 ± 0.6]	[0.3 ± 0.6]	[0.0 ± 0.3]	[-0.01 ± 0.18]	[0.0 ± 0.5]	[0.04 ± 0.07]	[0.1 ± 0.1]	[0.2 ± 0.2]
Partially serpentinised peridotite	[0.06 ± 0.08]	0.12 ± 0.11	[-0.01 ± 0.18]	0.9 ± 0.6	5.5 ± 1.2	3.6 ± 1.0	[0.0 ± 0.4]	[0.1 ± 0.3]	[0.3 ± 0.7]	[-0.01 ± 0.10]	[0.00 ± 0.15]	[0.1 ± 0.3]
Bastite	[0.06 ± 0.13]	[0.2 ± 0.2]	[0.0 ± 0.3]	[0.8 ± 1.1]	4.5 ± 1.9	3.8 ± 1.8	[0.1 ± 0.7]	[0.3 ± 0.5]	[0.5 ± 1.3]	[-0.01 ± 0.18]	[0.0 ± 0.3]	[0.1 ± 0.5]
JSC Mars-1 analogue	1.07 ± 0.16	1.7 ± 0.2	0.4 ± 0.2	3.6 ± 0.9	2.6 ± 1.1	[0.6 ± 0.9]	[0.2 ± 0.5]	[0.2 ± 0.3]	[0.2 ± 0.8]	[0.01 ± 0.11]	[0.02 ± 0.16]	[0.1 ± 0.3]
Palagonitic tuff	[0.07 ± 0.11]	0.21 ± 0.16	[0.0 ± 0.2]	1.8 ± 0.9	[1.0 ± 1.2]	[0.4 ± 1.1]	[0.0 ± 0.5]	[0.3 ± 0.3]	[0.7 ± 1.0]	[0.08 ± 0.14]	0.4 ± 0.2	[0.3 ± 0.4]
Sulfate-rich sediments												
Jarositic clay	0.9 ± 0.2	0.9 ± 0.3	[0.0 ± 0.3]	4.2 ± 1.4	3.3 ± 1.8	[0.5 ± 1.4]	1.0 ± 0.7	2.9 ± 0.6	[0.9 ± 1.3]	[-0.02 ± 0.17]	[0.1 ± 0.3]	[0.3 ± 0.5]
Organic, clay and carbonate-rich rocks												
Kimmeridge Clay	0.66 ± 0.11	1.21 ± 0.17	2.3 ± 0.3	2.0 ± 0.7	3.9 ± 1.0	1.2 ± 0.8	[0.2 ± 0.4]	0.4 ± 0.3	[0.5 ± 0.7]	[0.09 ± 0.10]	0.63 ± 0.15	[0.1 ± 0.3]
Blue Lias	0.27 ± 0.08	3.3 ± 0.3	41 ± 2	[0.5 ± 0.5]	0.9 ± 0.8	1.7 ± 0.8	[0.2 ± 0.4]	[0.0 ± 0.2]	[0.3 ± 0.6]	[-0.01 ± 0.09]	[0.07 ± 0.12]	[0.1 ± 0.3]
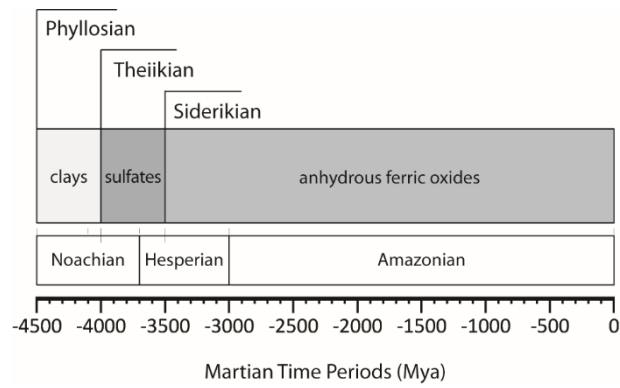
Figure 1. The Phyllosian, Theiikian and Siderikian eras and the mineral types which define them, illustrated in chronological order. The eras defined by crater density and lava flows are included on the bottom for comparison (diagram adapted from that illustrated by Bibring et al. (2006)).
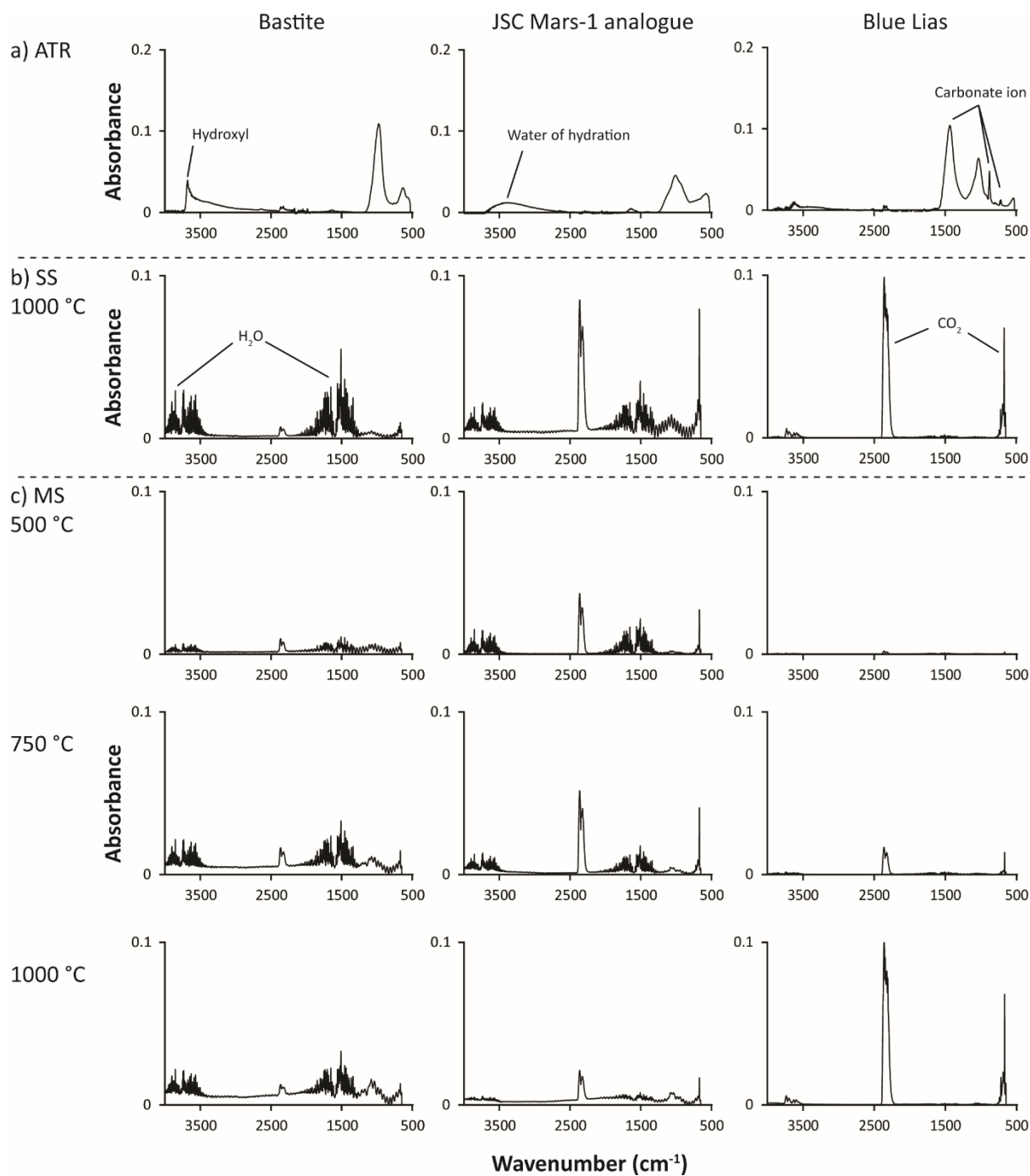
Figure 2. A comparison of different Fourier transform infrared spectroscopy (FTIR) analytical techniques, by showing the relevant spectra of three different materials used in the survey; bastite, JSC Mars-1 analogue and the Blue Lias. The responses in the pyrolysis methods have been scaled to they show relative responses for when materials are all of the same mass. a) Attenuated total reflectance (ATR) FTIR. Spectral features which represent habitability indicators are labelled. b) Example spectra resulting from single step pyrolysis-FTIR of the samples at 1000 °C. The positions of spectral features characteristic to two gases of interest, carbon dioxide and water, are labelled. c) Multi step pyrolysis-FTIR.
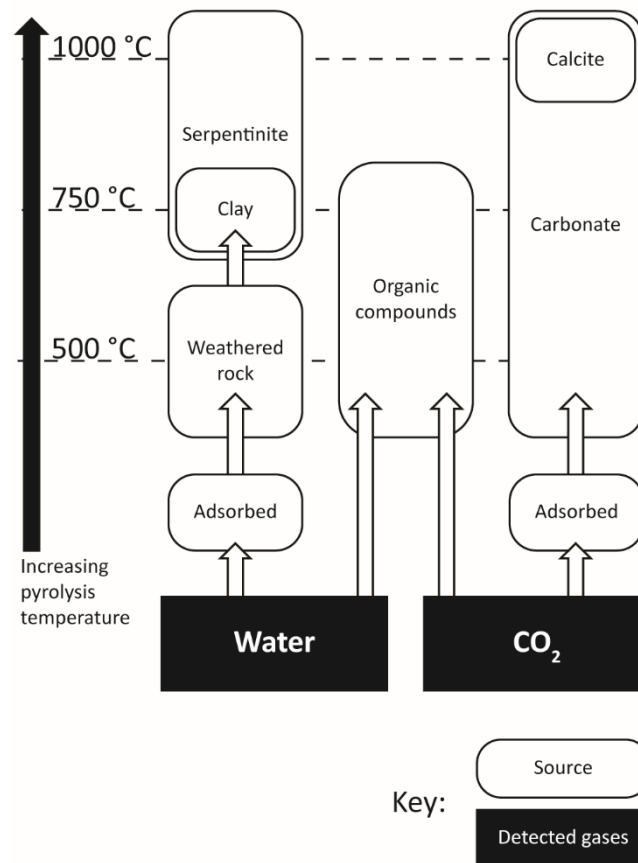
Figure 3. The temperatures at which gases are produced in pyrolysis-FTIR can be indicative of their source; trends observed in our survey for different mineral types allows us to construct an example framework of interpretation for multi step pyrolysis-FTIR signals, illustrated here. During a pyrolysis-FTIR analysis program of ascending temperature steps, should any temperature step produce a gas (or combination of gases), a schema like this can be referenced to allow speculation on the source (given that adsorbed gases have been expunged at some lower temperature). The diagnostic capability of such an instrument allows a precursory determination of the scientific value of a sample, and this capability only increases as such a framework for interpretation is expanded to include additional gases, temperature steps and quantitative measurements.
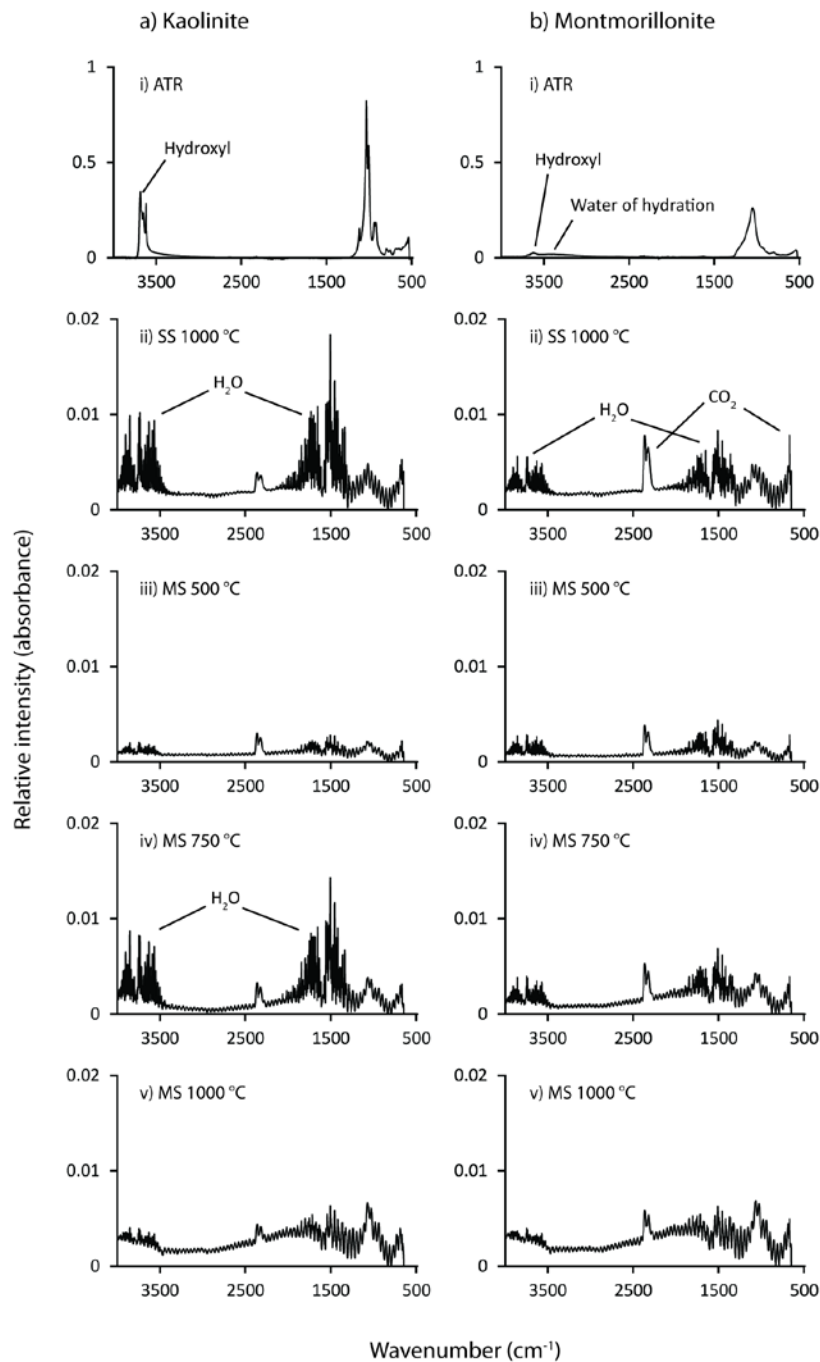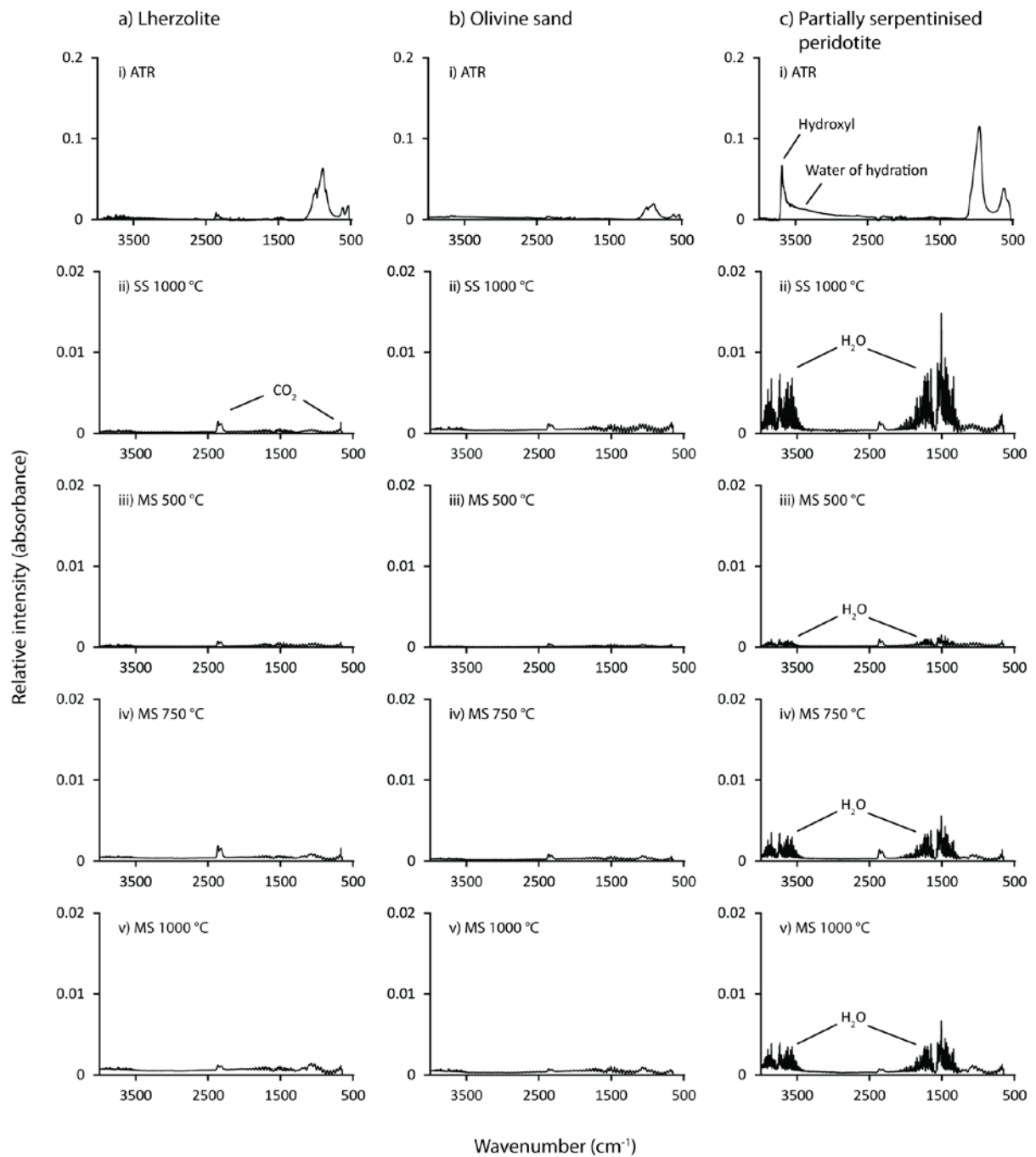
Appendix 1 – Pyrolysis-FTIR spectra for the phyllosilicates surveyed. ATR = attenuated total reflectance, SS = single step pyrolysis-FTIR, MS = multi step pyrolysis-FTIR.
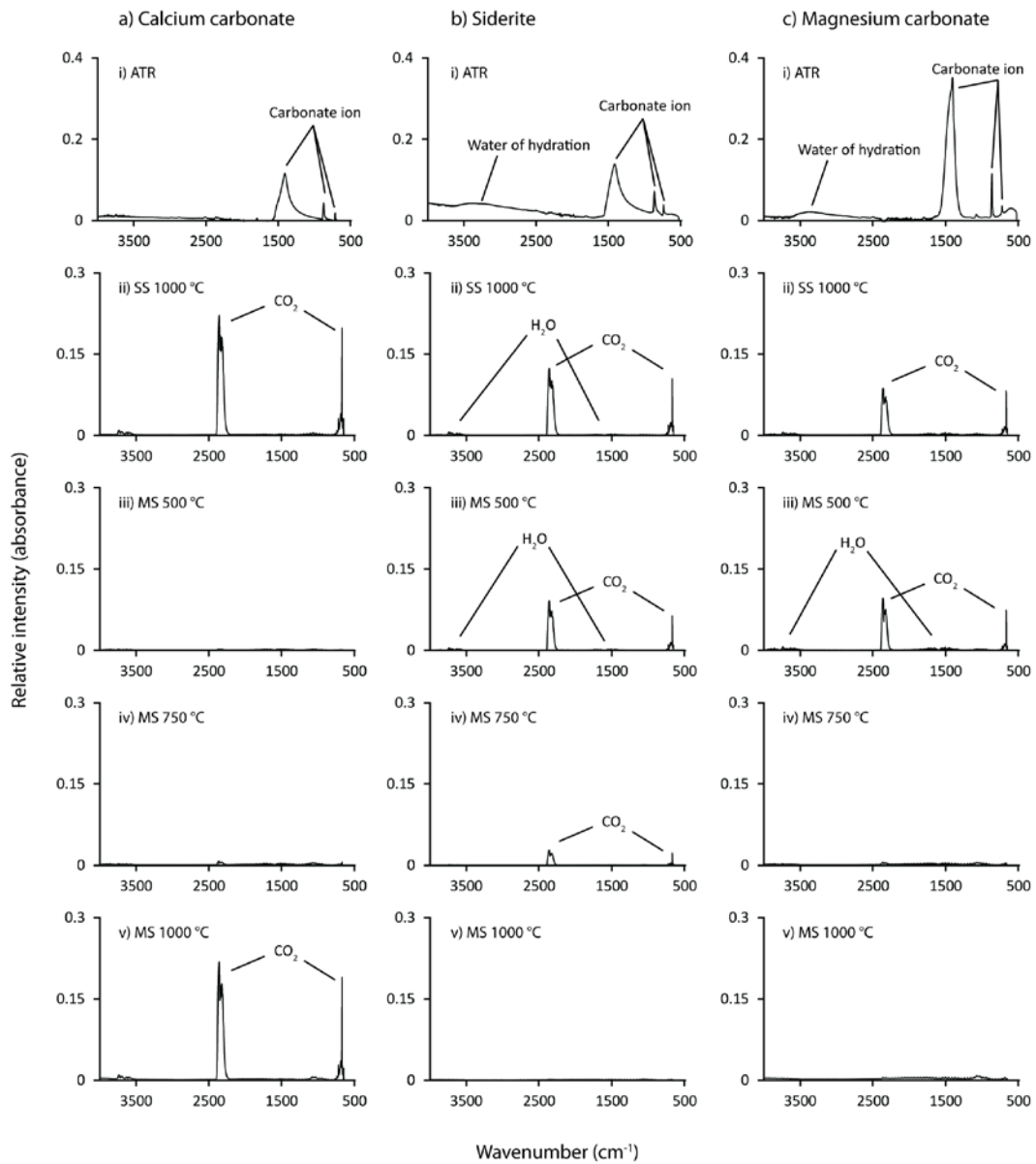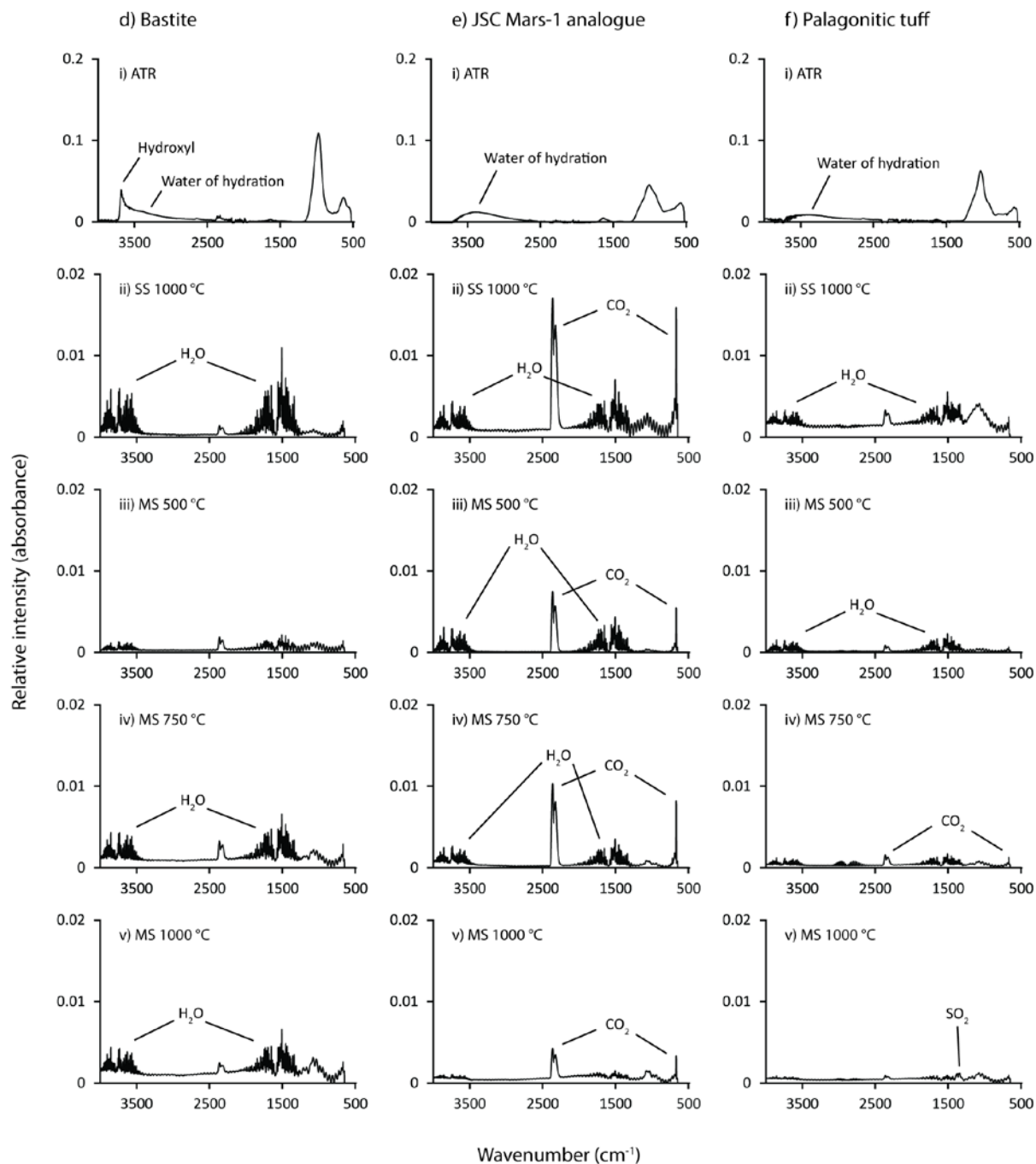
Appendix 2 - Pyrolysis-FTIR spectra for the carbonate minerals surveyed. ATR = attenuated total reflectance, SS = single step pyrolysis-FTIR, MS = multi step pyrolysis-FTIR.
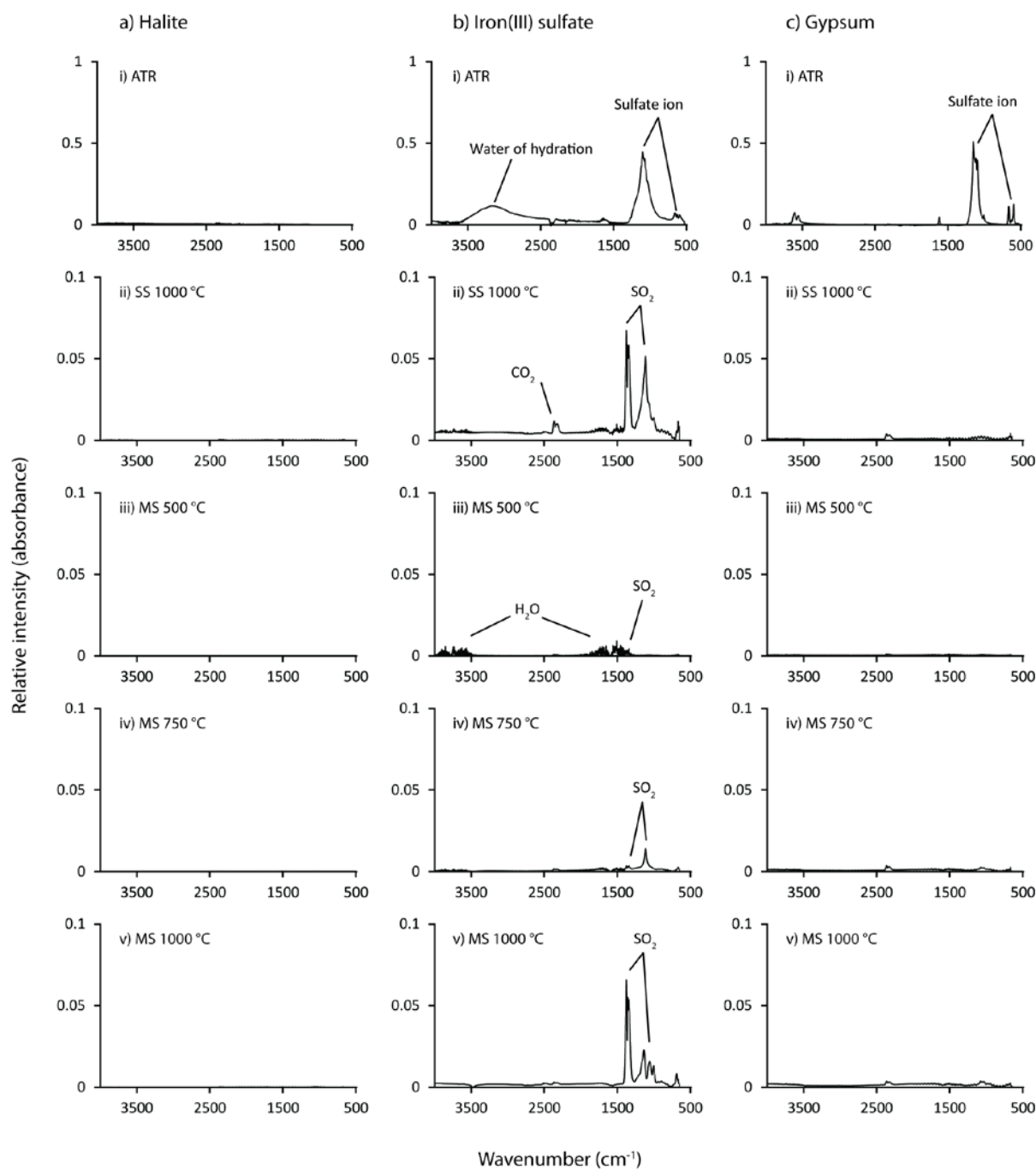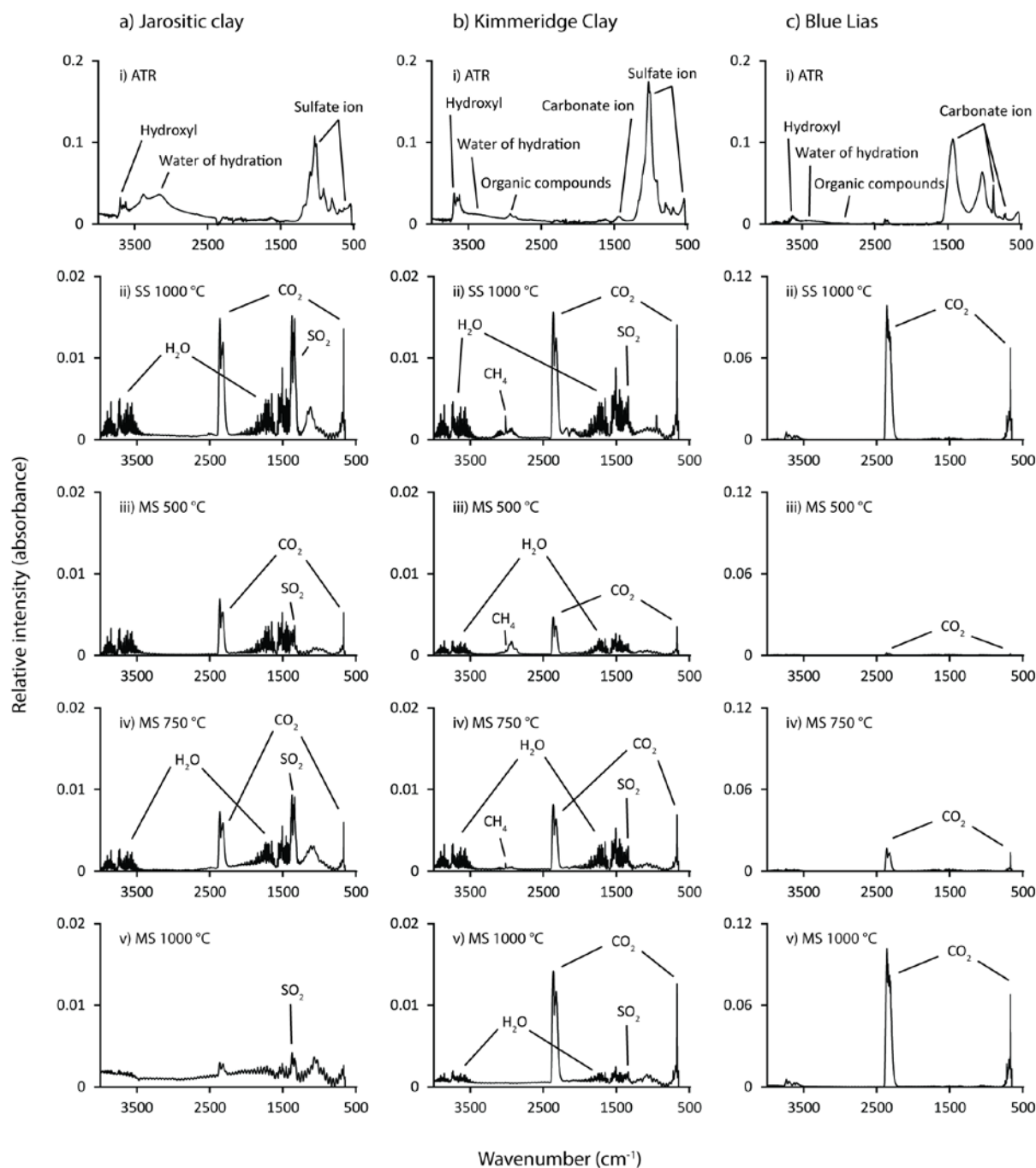
Appendix 3 - Pyrolysis-FTIR spectra for the sulfates and other salts. ATR = attenuated total reflectance, SS = single step pyrolysis-FTIR, MS = multi step pyrolysis-FTIR.

Appendix 4 - Pyrolysis-FTIR spectra for the unaltered and altered igneous materials surveyed. ATR = attenuated total reflectance, SS = single step pyrolysis-FTIR, MS = multi step pyrolysis-FTIR.

Appendix 4 (cont.)- Pyrolysis-FTIR spectra for the unaltered and altered igneous materials surveyed. ATR = attenuated total reflectance, SS = single step pyrolysis-FTIR, MS = multi step pyrolysis-FTIR.

Appendix 5 - Pyrolysis-FTIR spectra for the jarositic clay, and the organic, clay and carbonate rich rocks. ATR = attenuated total reflectance, SS = single step pyrolysis-FTIR, MS = multi step pyrolysis-FTIR.