1 **Pyrolysis of carboxylic acids in the** 2 **presence of iron oxides: Implications for** 3 **life detection on missions to Mars**

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9 **Abstract**

10 The search for, and characterisation of, organic matter on Mars is central to efforts
11 in identifying habitable environments and detecting evidence of life in the martian
12 surface and near surface. Iron oxides are ubiquitous in the martian regolith and
13 are known to be associated with the deposition and preservation of organic matter
14 in certain terrestrial environments, thus iron oxide-rich sediments are potential
15 targets for life detection missions. The most frequently used protocol for martian
16 organic matter characterisation (also planned for use on ExoMars) has been
17 thermal extraction for the transfer organic matter to gas chromatography-mass
18 spectrometry detectors. For the effective use of thermal extraction for martian

19 samples it is necessary to explore how potential biomarker organic molecules
20 evolve during this process in the presence of iron oxides. We have thermally
21 decomposed iron oxides simultaneously with (z)-octadec-9-enoic and *n*-
22 octadecanoic acids and analysed the products via pyrolysis-gas chromatography –
23 mass spectrometry. We found that the thermally driven dehydration, reduction and
24 recrystallization of iron oxides transformed fatty acids. Overall detectability of
25 products greatly reduced, molecular diversity decreased, unsaturated products
26 decreased and aromatisation increased. The severity of this effect increased as
27 reduction potential of the iron oxide, and inferred free radical formation,
28 increased. Of the iron oxides tested haematite showed the least transformative
29 effects, followed by magnetite, goethite, then ferrihydrite. It was possible to
30 identify the saturation state of the parent carboxylic acid at high (0.5 wt. %)
31 concentrations by the distribution of *n*-alkylbenzenes in the pyrolysis products.
32 When selecting life detection targets on Mars, localities where haematite is the
33 dominant iron oxide could be targeted preferentially, otherwise thermal analysis
34 of carboxylic acids, or similar biomarker molecules, will lead to enhanced
35 polymerisation, aromatization and breakdown that will reduce the fidelity of the
36 original biomarker, similar to changes normally observed during thermal
37 maturation.

38 **Keywords**

- 39 • Mars
- 40 • Astrobiology
- 41 • Life detection
- 42 • Carboxylic acids
- 43 • Iron oxides
- 44 • Thermal decomposition

45 **1. Introduction**

46 **1.1. The search for organic matter on Mars**

47 Organic molecules may be relatively widespread on Mars. They will at least have
48 been delivered to the planetary surface from exogenous sources such as
49 meteorites, comets, or interplanetary dust particles (Gibson, 1992; Flynn, 1996;
50 Sephton, 2012). They may also have formed from indigenous martian sources due
51 to igneous, hydrothermal and atmospheric processes (Chyba and Sagan, 1992; ten
52 Kate, 2010; Steele et al., 2012, 2018; Kohn et al., 2015). Habitable conditions are
53 believed to have existed on ancient Mars (Grotzinger et al., 2014) and may
54 transiently occur up to the present day (Jones, 2018). Potential martian
55 habitability raises the exciting possibility that organic matter has been generated
56 from the biological processes of extinct or extant life, and may, under certain
57 conditions, be preserved in near surface sediments, sedimentary rock or regolith
58 (Summons et al., 2011; Vago et al., 2017). Thus, alongside other potential

59 biosignatures such as stable isotopes, atmospheric gases, biosedimentary
60 structures and macrotextures (Summons et al., 2011), organic biomarker
61 compounds are a target for both past habitability (e.g. as sought by Mars Science
62 Laboratory) and life detection (e.g. as sought by ExoMars 2022) efforts (Des
63 Marais et al., 2008; Vago et al., 2017).

64 The majority of attempts to detect martian organic molecules have, however, only
65 found simple organochlorine molecules (Biemann et al., 1977; Leshin et al., 2013;
66 Glavin et al., 2013; Ming et al., 2014; Freissinet et al., 2015). So far, the lack of
67 complex organic compound detection has been partly attributed to the deleterious
68 effects of oxidizing (and chlorinating) minerals on the martian surface where
69 perchlorates and potentially sulphates cause the oxidation of organic matter during
70 thermal extraction experiments (Blake et al., 2013; Leshin et al., 2013; Glavin et
71 al., 2013; Ming et al., 2014; Freissinet et al., 2015; Lewis et al., 2015; Miller et
72 al., 2016). The organochlorine molecules are, therefore suggested to be the
73 reaction products of more complex martian organic molecules, such as polycyclic
74 aromatic hydrocarbons or organic acids, being transformed in the presence of
75 oxidising minerals. Recent detections of non-chlorinated organic molecules on
76 Mars have identified relatively simple species such as alkanes, thiophene,
77 alkylbenzenes and naphthalene (Eigenbrode et al., 2018; Freissinet et al., 2019).
78 The aromatic compounds have been attributed to be the pyrolysis products of a
79 macromolecular source (Eigenbrode et al., 2018), while it has been suggested that

80 the alkanes may be from the decarboxylation of carboxylic acids (Freissinet et al.,
81 2019); suggesting that a variety of sources and types of organic matter do exist on
82 Mars.

83 The crust of Mars has abundant iron (Taylor and McLennan, 2009) and its oxides
84 are ubiquitous on the martian surface. The nanophase, hydrated iron oxide species
85 ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) is believed to be widespread on the martian surface as
86 a major component of the iron-rich amorphous soil component (Dehouck et al.,
87 2017), along with the more crystalline oxyhydroxide goethite ($\text{FeO}(\text{OH})$) and the
88 iron (II, III) and iron (III) oxides magnetite (Fe_3O_4) and haematite (Fe_2O_3). These
89 iron species have been detected in martian meteorites (Steele et al., 2007; Muttik
90 et al., 2014); by infrared spectroscopy (Evans and Adams, 1980; Bell et al., 1993);
91 by the Mössbauer spectrometers on both the Mars Exploration Rovers (MER)
92 (Klingelhöfer et al., 2005; Morris et al., 2006a, 2006b) and by X-ray diffraction
93 (XRD) by the Chemistry and Mineralogy (CheMin) instrument on board the Mars
94 Science Laboratory (MSL) *Curiosity* rover (Bish et al., 2013; Blake et al., 2013;
95 Treiman et al., 2016).

96 Iron oxides can preserve biosignatures through a variety of mechanisms. These
97 include the entombment of bacteria by iron oxide crystals (Ferris et al., 1989;
98 Peng et al., 2013), the formation of textural biosignatures by iron oxide
99 encrustation (Potter-McIntyre et al., 2014; Williams et al., 2015, 2017), the

100 formation of organo-metallic complexes (Lalonde et al., 2012), and the
101 preservation of organic molecular biosignatures via adsorption onto the surface of
102 iron oxides and oxyhydroxides (Parenteau et al., 2014; Tan et al., 2018). The end
103 results of these preservative mechanisms can be clearly seen in a variety of
104 aqueous environments on Earth. Almost a quarter of organic carbon in
105 sedimentary deposits has been found to be directly bound to reactive iron phases
106 with this association promoting its preservation over geological timescales; this is
107 known as the ‘rusty sink’ effect (Lalonde et al., 2012). Many of these terrestrial,
108 iron-rich settings are analogous to environments present on ancient Mars (Allen et
109 al., 2000, 2004; Schelble et al., 2004; Fernández-Remolar et al., 2005); hence,
110 iron-oxide rich sediments are potential targets for future life-detection missions.

111 Searches for life, and abiotic organic molecules, on Mars have so far been almost
112 exclusively carried out by thermal extraction experiments, by the Viking Landers
113 (Klein et al., 1976; Biemann et al., 1977), the Phoenix mission (Hecht et al., 2009;
114 Cull et al., 2010; Kounaves et al., 2014) and the Sample Analysis at Mars
115 instrument suite on the Mars Science Laboratory (Mahaffy et al., 2012; Blake et
116 al., 2013; Leshin et al., 2013; Glavin et al., 2013; Ming et al., 2014; Freissinet et
117 al., 2015; Miller et al., 2016), and this technique will also be applied to samples
118 from up to 2 m below the martian surface on the forthcoming ExoMars mission
119 (Barnes et al., 2006).

120 Despite their potential for preserving co-deposited martian organic matter, iron
121 oxides are known to promote the oxidative breakdown of organic molecules on
122 heating (Minicò et al., 2000), and are likely to have an effect on the detectability
123 of any organic molecules present in an iron oxide-rich sediment analysed by
124 thermal decomposition techniques. We need to know, therefore, if and how Mars-
125 relevant iron oxides catalyse the breakdown of organic biosignature molecules
126 during thermal decomposition and how this may lead to false negative life
127 detections.

128 1.2. **Carboxylic acids as biosignatures**

129 In this study we have focussed on carboxylic (fatty) acids as unlike most other
130 biomolecules, they are relatively chemically recalcitrant even under harsh
131 environmental conditions and so may persist over geological timescales
132 (Summons et al., 2008) and it has been suggested that alkanes detected at Mars
133 may be the degradation products of carboxylic acids (Freissinet et al., 2019).
134 Carboxylic acids are useful biosignatures with their alkyl chain length and
135 saturation state suggestive of their source. In the context of this paper, we define a
136 short alkyl chain as $\leq C_5$ (SCFA), medium as $C_6 - C_{12}$ (MCFA), long as $C_{13} - C_{21}$
137 (LCFA), very long $\geq C_{22}$ (VLCFA).

138 Abiotic processes yield primarily shorter length molecules and decreasing
139 amounts of carboxylic-acids of longer chain lengths in an Anderson-Schulz-Flory

140 (AFS) type distribution, typical of polymerization processes, where an alkyl chain
141 grows probabilistically by bonding with additional methylene (CH₂) groups verses
142 chain terminating moieties (McCollom and Seewald, 2007; Smith et al., 2013).
143 This discriminates against longer chain lengths to create a unimodal distribution
144 and gives no preference to neither odd nor even carbon numbers (Summons et al.,
145 2008) as may be observed in experimental Fisher Troph Type (FTT) reactions
146 (Mißbach et al., 2018) and abiotic settings such as meteorites (Cronin and
147 Pizzarello, 1990; Sephton, 2002). Any deviations from this probability
148 distribution, usually in the form of increased MCFA or LCFA, are indicative of
149 formation processes that preferentially select for longer chain lengths. In addition,
150 these formation processes must dominate over random addition reactions to be
151 expressed in carboxylic acid profiles.

152 Biotically sourced carboxylic acids are the decomposition products of lipids,
153 phospholipids and triglycerides, which are critical components of biological cells
154 (Kates, 1964). Biologically controlled processes select for carboxylic acids of
155 longer chain lengths as they have stronger intermolecular attractions and thus
156 form stronger structures (Rawicz et al., 2000). In terrestrial biosignatures,
157 carboxylic acids with a distribution around C₁₆-C₁₇ are indicative of a microbial
158 source, C₁₈-C₂₂ of algae and >C₂₃ of higher plants (Cranwell, 1974; Tissot and
159 Welte, 1978; Perry et al., 1979; Bianchi, 1995). Biotic carboxylic acids also show
160 a strong even-over-odd preference in their carbon number due to their extension

161 via the addition of two methylene (C_2H_4 or CH_2-CH_2) units (Hartgers et al., 2000;
162 Summons et al., 2008; Georgiou and Deamer, 2014).

163 Unsaturated LCFA may indicate the presence of recent (extant) life (O’Leary,
164 1962; Volkman et al., 1989; Alfaro et al., 2006) but they are highly labile,
165 undergoing reactions at the sites of their double carbon bonds (through microbial
166 degradation, autoxidation with the atmosphere or other diagenetic processes) to
167 quickly hydrogenate to saturated LCFA which are more stable over geological
168 timescales (Parker and Leo, 1965; Matsuda and Koyama, 1977; Van Vleet and
169 Quinn, 1979; Haddad et al., 1992). Chain length distribution patterns, however,
170 are more resistant to alteration (Duda et al., 2018). Figure 1 shows saturated and
171 unsaturated forms of C_{18} LCFA.

172 Further to these distribution patterns, abundances of specific carboxylic acids may
173 be indicative of the metabolites of certain taxa (O’Reilly et al., 2017). For
174 example, C_{18} polyunsaturated fatty acids are diagnostic of cyanobacteria (Allen et
175 al., 2010; Willers et al., 2015; Sánchez-García et al., 2020), while methyl-
176 branched unsaturated fatty acids may be indicative of sulfate reducers (Londry et
177 al., 2004).

178 1.3. Pyrolysis of carboxylic acids

179 Under normal pyrolysis conditions, the breakdown of saturated carboxylic acids
180 proceeds through a sequence of reactions starting with decarbonylation (Figure

181 1(ai)) at low temperatures (the loss of a carbon and oxygen) or decarboxylation
182 (Figure 1(bii)) at higher temperatures (the loss of the carboxyl group to form CO₂
183 and the addition of a proton to the remaining alkene/alkane) and proceeding with
184 cleavage of hydrocarbon bonds by β -scission (Hartgers et al., 1995). With
185 unsaturated carboxylic acids, deoxygenation (via either decarbonylation or
186 decarboxylation depending on temperature) occurs simultaneously with β -scission
187 which takes place preferentially at the sites of double carbon bonds (Figure 1(bi)
188 and 1(bii)). The process results in a series of *n*-alk-1-enes and *n*-alkanes and
189 carboxylic acids, with the carboxylic acids and any surviving internal alkenes
190 becoming progressively depleted due to further breakdown as temperatures and
191 reaction times increase (Asomaning et al., 2014a, 2014b).

192 The presence and position of the double bond influences the pyrolysis behaviour
193 of unsaturated carboxylic acids as the lower bond dissociation energy of the C=C
194 bond (compared to C-H and C-O) means that initiation of the pyrolysis reaction
195 involves homolytic cleavage around the C=C bond. This means that, for example
196 as shown in Figure 1(bi) and 1(bii), (z)-octadec-9-enoic acid will preferentially
197 crack to form a *n*-non-1-ene and non-8-enoic acid, and further break down to a *n*-
198 non-1-ene and *n*-octa-1,7-diene depending on temperature. A saturated carboxylic
199 acid would eventually form a series of alkanes and terminal dienes/alk-1-enes
200 with no preferential chain length (Hartgers et al., 1995). This preferential
201 breakdown means that, in theory, by examining the pyrolytic products and their

202 distribution, it should be possible to determine the carbon chain length of the
203 parent carboxylic acid, its saturation state and the positions of the double carbon
204 bonds.

205 1.4. **Pyrolysis of carboxylic acids on iron oxides**

206 Mineral substrates can affect both the distribution and yield of pyrolysis products
207 (Davis and Stanley, 1982; Espitalié et al., 1984; Karabakan and Yürüm, 1998;
208 Faure et al., 2006b, 2006a; Fréty et al., 2014; Zafar et al., 2017). Thus, when
209 pyrolyzing carboxylic acids adsorbed onto iron oxides, deviation from the
210 theoretical products may provide information on the extent to which the substrate
211 is influencing the breakdown products. This information can then be used to
212 determine what organic species detected on Mars could be evidence of these
213 interactions taking place during thermal decomposition analyses.

214 In this study, the saturated *n*-octadecanoic acid (stearic acid) and the
215 monounsaturated (z)-octadec-9-enoic acid (oleic acid) were examined as model
216 carboxylic acids. On-line flash pyrolysis-gas chromatography-mass spectrometry
217 was used to thermally decompose the carboxylic acids in the presence or absence
218 of a variety of Mars relevant iron oxides/(oxy)hydroxides. Comparing the effects
219 of pyrolysis on both saturated and monounsaturated carboxylic acids of equal
220 carbon-chain lengths with a variety of Mars relevant iron oxides/(oxy)hydroxides
221 allowed the determination of the sources and mechanisms by which any pyrolysis

222 products are formed. All carboxylic acids should behave in predictable ways when
223 compared to these 2 model molecules and so it should be possible to extrapolate
224 the results to a wider range of carboxylic acid lengths, double bond positions and
225 ultimately their parent triglycerides. Analysis of the iron oxide/(oxy)hydroxide
226 mineral substrates by X-ray diffraction (XRD) after pyrolysis will allow the
227 reactions affecting the pyrolysis products to be determined. The results will
228 provide guidance for the design of thermal extraction experiments on Mars and
229 help interpretation of any data generated by life detection missions to the red
230 planet.

231 **2. Methods**

232 **2.1. Sample preparation**

233 Quartz sand (US Silica F-35), was used as a relatively inert substrate. Magnetite,
234 haematite and goethite were obtained from Sigma-Aldrich. Due to its instability,
235 ferrihydrite dehydrates and recrystallises rapidly at room temperature (Cudennec
236 and Lecerf, 2006; Das et al., 2011) ferrihydrite had to be produced in the
237 laboratory. Ferrihydrite was synthesized following the method detailed in Cornell
238 and Schwertmann (2003). XRD analysis (see below) confirmed the produced
239 ferrihydrite to be of the amorphous/least crystalline 2-line ferrihydrite, as opposed
240 to the more (but still poorly) crystalline 6-line ferrihydrite, based on the number of
241 broad peaks (2 or 6) exhibited in the XRD pattern (Cornell et al., 2003;

242 Kukkadapu et al., 2003). Eight grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, suitable
243 for cell culture) was dissolved in 100 ml of deionised water and stirred with a
244 magnetic stirrer (which had previously been cleaned by sonication in deionised
245 water followed by 93:7 v/v DCM/MeOH solution). To this solution, 66 ml of 1M
246 potassium hydroxide (KOH) solution was continuously added to bring the pH of
247 the resulting mixture to 7.5. The final volume of KOH solution was added
248 dropwise, and the pH continuously monitored (using a pH meter which was rinsed
249 with deionised water and DCM/MeOH between measurements). Dissolved salts
250 were removed by adding deionised water, centrifuging and decanting the
251 supernatant until the conductivity was less than $10 \mu\text{S}/\text{cm}$ as measured with a total
252 dissolved solids (TDS) probe (which was rinsed with deionised water and
253 DCM/MeOH between measurements). The synthesised ferrihydrite was frozen
254 then placed in a Labcono freeze dryer at 0.133 mbar. Synthetic samples were
255 ground gently in a solvent-cleaned agate pestle and mortar, wrapped in aluminium
256 foil and stored at 4°C .

257 Quartz sand was cleaned by furnacing overnight at 450°C to remove any initial
258 organic matter contamination. Due to their reactivity the iron-oxides magnetite,
259 haematite and goethite had to be cleaned via solvent extraction rather than
260 heating; these minerals oxidise and/or dehydrate/dehydroxylate if furnaced in air
261 at the temperatures required to combust organic contaminants (Ruan et al., 2002;
262 Mazo-Zuluaga et al., 2003). Solvent extraction was carried out using a standard

263 liquid extraction protocol (e.g. Emmerton et al., 2012) as follows: 1-3 g of
264 powdered sample was suspended in a 93:7 v/v DCM/MeOH solution and agitated
265 in a sonic bath. The resulting suspension was then centrifuged and the supernatant
266 solution pipetted off. This process was repeated 3 times and the materials were
267 dried under a stream of nitrogen. As the ferrihydrite was produced in the
268 laboratory using clean materials and methods, and subsequently stored clean, it
269 was deemed unnecessary to clean this highly reactive mineral further.

270 The cleaned substrates were spiked with solutions of either (z)-octadec-9-enoic
271 acid or *n*-octadecanoic acid in pentane, which was subsequently evaporated off
272 under a nitrogen stream, to produce quartz sand/iron-oxide samples with known
273 concentrations of carboxylic acid. To test detectability, spiked substrates at 50
274 ppm, 500 ppm and 0.5 % (z)-octadec-9-enoic acid by weight (wt. %) were
275 produced. *n*-Octadecanoic acid was only tested at 0.5 wt % and was not tested on
276 the ferrihydrite substrate based on the unamiability of this substrate to detection of
277 carboxylic acids as shown by the initial experiments with (z)-octadec-9-enoic
278 acid. Unspiked quartz sand/iron-oxide samples were also analysed as control
279 samples.

280 2.2. Pyrolysis GC-MS

281 10-20 mg prepared samples were loaded into quartz pyrolysis tubes and held in
282 place with quartz wool (both tubes and wool were cleaned by overnight furnacing

283 at 450°C), (z)-octadec-9-enoic and *n*-octadecanoic acids were also pyrolyzed
284 without a substrate with 0.4 (± 0.1) mg of carboxylic acid supported by quartz
285 wool.

286 Loaded samples were placed inside the platinum coil of a Chemical Data Systems
287 5200 Pyroprobe under helium and heated at a rate of 20°C ms⁻¹ to the target
288 temperature where it was held for 15 s. Each sample was run in replicate.
289 Individual samples were run at 450°C or 650°C. These temperatures were selected
290 because the usual range for flash pyrolysis of organic matter is 400-900°C, with
291 most studies going no higher than 700°C (Hartgers et al., 1994, 1995; Watson et
292 al., 2012). Above this temperature range fragmentation is too extensive and
293 structural information is lost, except with highly refractory material (Sephton,
294 2012; Matthewman et al., 2012). Thus, 450°C and 650°C gave scope for
295 comparing relatively 'low' temperature pyrolysis where only 'weak' (e.g., C-O-C)
296 bonds should be broken and relatively 'high' temperature pyrolysis where 'strong'
297 (e.g., C=C and C-C) bonds should break. The interface was run at 350°C but not
298 turned on until after the probe had fired to avoid premature desorption of the
299 spiked samples (Zafar et al., 2017; Zafar and Watson, 2017).

300 Separation and identification of products was achieved using an Agilent
301 Technologies 6890 gas chromatograph coupled to a 5973 mass spectrometer (GC-
302 MS). The GC inlet was held at 270°C and operated in split mode (10:1) with a

column helium flow rate of 1.1 ml min^{-1} . Separation was performed on an SGE BPX5 column ($25 \text{ m} \times 220 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m}$). The GC oven was held for 2 min at 40°C and then ramped at a rate of 5°C min^{-1} to 310°C where it was held for 10 min. Mass spectra were acquired over a range of m/z 45-550. For gas phase analysis, to identify highly volatile low mass phases released, mass spectra were acquired over a range of m/z 10-150 (all other pyrolysis, interface and GC settings were kept identical). Identification of peaks in the produced chromatograms was carried out using the Agilent MSD Chemstation software package and peak identification was achieved by comparison to the NIST database, published literature and standards.

Data from the laboratory pyrolysis-GC-MS was assumed to be comparable to that from the SAM and MOMA experimental set ups. While differences in heating rate and environmental conditions between laboratory- and rover-based instruments (Table 1), could affect the distribution of pyrolysis products. Flash, as opposed to temperature ramped, pyrolysis can be advantageous in a laboratory analogue experiment as it may provide a ‘worst-case scenario’ ensuring the coincidence of reactions of both the inorganic and organic phases.

2.3. XRD analysis

Representative XRD patterns of iron oxides were acquired before pyrolysis and after pyrolysis at 650°C with 0.5 wt. % octadecenoic acid. A PANalytical X’Pert

323 Pro MPD Alpha-1 X-Ray Diffractometer with an X'Celerator detector was used
324 to analyse samples between 5 and 80° 2θ under copper radiation with a step size
325 of 0.033° at a speed of 5° per minute. Measurements were made at a current of 40
326 mA and a voltage of 40 kV. The diffraction patterns were analyzed using a X'Pert
327 Highscore Plus program with references from the International Centre for
328 Diffraction Data (ICDD) database.

329 **3. Results**

330 **3.1. Pyrolysis-GC-MS**

331 Control samples were analysed by pyrolyzing quartz sand and iron oxide
332 substrates post-cleaning to determine the effectiveness of the techniques used
333 (Supplementary Figure S1). The only products detected were from column-bleed
334 (siloxanes that were also detected in blank runs) and low molecular weight peaks
335 from gas phases released during the thermal decomposition of the iron oxides.
336 Product distribution and relative abundance were reproducible between
337 replicates. Release of adsorbed water and CO₂ (the main low mass phases
338 identified from all three iron oxides when the mass spectrometer was optimised
339 for low mass compounds, data not shown) from ferrihydrite was orders of
340 magnitude higher than the other iron oxides due to its adsorbent and hydrous
341 nature.

342 3.1.1. *(z)*-Octadec-9-enoic acid

343 Figure 2 shows the total ion current chromatograms (TICs) produced by
344 pyrolyzing *(z)*-octadec-9-enoic acid by itself and on the quartz sand, haematite,
345 magnetite, goethite and ferrihydrite substrates at 0.5 wt. % at 450 and 650°C.

346 3.1.1.1. *(z)*-Octadec-9-enoic acid pyrolysis products

347 The main products of *(z)*-octadec-9-enoic acid when pyrolyzed, either by itself
348 (Figure 2, ‘Octadecenoic Acid’) or on a quartz sand substrate (Figure 2, ‘Quartz +
349 Octadecenoic Acid’), were highly similar so they will be discussed together. The
350 products were as expected based on previous studies of the pyrolysis of carboxylic
351 acids (Zafar et al., 2017; Zafar and Watson, 2017; Santos et al., 2019). At both
352 450 and 650°C the signal was dominated by *n*-alkadienes, cyclic and *n*-alk-1-enes
353 and minor *n*-alkanoic acids and *n*-alkylbenzenes. A notable peak of the
354 monounsaturated aldehyde heptadecanal was observed at both temperatures when
355 *(z)*-octadec-9-enoic acid was pyrolysed by itself.

356 At the lower (450°C) pyrolysis temperature, the products were dominated by
357 products with 16 to 17 carbon atoms, particularly hexadeca-1,6-diene, heptadeca-
358 1,7-diene and heptadecanal (Figure 2).

359 At the higher (650°C) temperature the longer chain length fragments were less
360 dominant. C₈-C₁₀ fragments, particularly cyclooctene and *n*-decanoic acid, were
361 greater in relative abundance at this higher pyrolysis temperature (Figure 2).

362 Despite the similarities, differences were observed between (z)-octadec-9-enoic
363 acid pyrolysed on its own and on quartz in the relative abundances of products.
364 With the addition of a quartz sand substrate there appeared to be both an increased
365 survivability of the intact parent compound at both temperatures and a further
366 increase in the relative abundance of lower molecular weight compounds at
367 650°C.

368 Pyrolyzing various concentrations of (z)-octadec-9-enoic acid on the quartz sand
369 substrate (Supplementary Figure S2) revealed non-linear decreases in the response
370 and diversity of products with decreasing concentrations. There was a decrease in
371 the relative abundance of higher molecular weight products, especially
372 heptadecanal and the parent (z)-octadec-9-enoic acid. When 50 ppm of (z)-
373 octadec-9-enoic acid was pyrolysed at 450°C only benzene was the only
374 identifiable product.

375 3.1.1.2. (z)-Octadec-9-enoic acid on iron oxides

376 Figure 2 shows that when (z)-octadec-9-enoic acid was pyrolyzed on an iron
377 oxide/(oxy)hydroxide substrate the pyrolysis products were significantly different
378 to those produced when the carboxylic acid was pyrolysed by itself or on a quartz
379 sand substrate. Aliphatic hydrocarbons and *n*-alkyl- and *n*-allyl-benzenes
380 (benzenes with *n*-alkene or *n*-alkane aliphatic side chains) were the major
381 pyrolysis products observed when (z)-octadec-9-enoic acid was pyrolyzed in the

382 presence of iron-bearing substrates. Supplementary figures S7 and S8 show the
383 distribution of aliphatic hydrocarbons and *n*-alkylbenzenes in the pyrolysis
384 products of 0.5 wt. % (z)-octadec-9-enoic acid spiked samples at 450°C and
385 650°C and reveal changes in chain length distribution and saturation state
386 dominance between samples.

387 Figure 2 shows that out of the iron-bearing substrates tested, pyrolysis of (z)-
388 octadec-9-enoic acid on haematite exhibited the greatest diversity in pyrolysis
389 products (Figure 2 ‘Haematite + Octadecenoic Acid’). When (z)-octadec-9-enoic
390 acid was pyrolysed on a haematite substrate, aromatic hydrocarbons and pairs of
391 *n*-alkyl- and *n*-allyl-benzenes dominated the pyrolysis products at both 450 and
392 650°C. The aliphatic hydrocarbons were dominated by *n*-alkanes up to nonane
393 (C₉) but were dominated by *n*-alk-1-enes at higher carbon numbers. (Figure S7).
394 At 450°C oxygenated species in the form of both aliphatic (particularly around
395 C₈-C₁₁) and aromatic ketones were also present as minor products. When (z)-
396 octadec-9-enoic acid was pyrolysed on haematite, aromatisation of products (in
397 comparison to pyrolysis without substrate or on quartz sand) was increased at both
398 450 and 650°C pyrolysis temperatures. A variety of aromatic moieties with
399 polycyclic aromatic hydrocarbons (PAHs) up to 4 rings were detected.

400 Pyrolyzing various concentrations of (z)-octadec-9-enoic acid on the haematite
401 substrate (Figure S3) showed that as concentration was decreased the relative

402 abundance of the minor aliphatic hydrocarbons, particularly unsaturated species,
403 decreased relative to aromatic moieties. This effect was more pronounced at
404 650°C than 450°C.

405 The products of (z)-octadec-9-enoic acid pyrolysed on both magnetite (Figure 2,
406 ‘Magnetite + Octadecenoic Acid’) and goethite (Figure 2, ‘Goethite +
407 Octadecenoic Acid’) were similar. Compared to either quartz or haematite, these
408 were defined by an overall lower variety and abundance of molecular species.
409 Aromatic moieties, with *n*-alkylbenzenes and PAHs (moieties up to 4 benzene
410 rings were tentatively detected) were increased relative to non-aromatic products.
411 Hydrocarbon chain lengths of the aliphatic hydrocarbons and *n*-alkylbenzenes
412 were decreased further in length (compared to quartz or haematite substrates).
413 Unsaturated aliphatic compounds were rare, with alkanes dominating the aliphatic
414 profiles at both temperatures (Figure S7). Aromatic ketones, including the
415 symmetrical ketone fluoren-9-one, and benzaldehyde were minor products from
416 both goethite and magnetite substrates. The observed transformative effects on the
417 pyrolysis products of (z)-octadec-9-enoic acid were greater in the oxyhydroxide
418 goethite compared to the oxide magnetite, with fewer aliphatic moieties detected
419 from goethite.

420 Pyrolyzing various concentrations of (z)-octadec-9-enoic acid on the magnetite
421 substrate (Supplementary Figure S4) showed that as concentration was decreased
422 alkanes became the dominant pyrolysis products relative to aromatic species.

423 The (z)-octadec-9-enoic acid pyrolysed on ferrihydrite showed few identifiable
424 peaks above detection limits in the TIC (Figure 2, 'Ferrihydrite + Octadecenoic
425 Acid') and XICs (Figure S7, S8 'Ferrihydrite'). Small peaks around detection
426 limits corresponding to benzene, decane, naphthalene and biphenyl were the only
427 pyrolysis products observed in the 0.5 wt. % (z)-octadec-9-enoic acid on
428 ferrihydrite data.

429 Detectable products from both the goethite and ferrihydrite substrates were
430 significantly reduced at lower concentrations of (z)-octadec-9-enoic acid
431 (Supplementary Figures S5 and S6). At both 500 ppm and 50 ppm wt. % (z)-
432 octadec-9-enoic acid on the goethite substrate, only benzene was detectable and
433 (at the same concentrations) on the ferrihydrite substrate no products were
434 identifiable.

435 3.1.2. *n*-Octadecanoic acid

436 Figure 3 shows the TICs produced by pyrolyzing *n*-octadecanoic acid by itself and
437 on the quartz sand, haematite, magnetite and goethite substrates at 0.5 wt. % at
438 450 and 650°C.

439 3.1.2.1. *n-Octadecanoic acid pyrolysis products*

440 The main products of *n*-octadecanoic acid when pyrolyzed either by itself (Figure
441 3, ‘Octadecanoic Acid’) or on a quartz sand substrate (Figure 3, ‘Quartz +
442 Octadecanoic Acid’) were similar so they will be discussed together. The products
443 were as expected based on previous studies of the pyrolysis of carboxylic acids
444 (Zafar et al., 2017; Zafar and Watson, 2017; Santos et al., 2019).

445 When *n*-octadecanoic acid was pyrolyzed at 450°C, the products were dominated
446 by hydrocarbon species with carbon numbers of 16 or 17 (particularly hexadec-1-
447 ene and heptadec-1-ene) and exhibited lower responses with decreasing chain
448 length. Alkene/alkane pairs of aliphatic hydrocarbons were strongly dominated by
449 the *n*-alk-1-ene (Figure 3 and Figure S9) and peaked at C₁₆ to C₁₇.

450 At the higher 650°C pyrolysis temperature, fragmentation of the aliphatic chain
451 was more complete with shorter chain length *n*-alk-1-enes down to hex-1-ene (the
452 lowest molecular weight detectable with the applied method) detected.

453 3.1.2.2. *n-Octadecanoic acid on iron oxides*

454 Figure 3 shows that pyrolysis of *n*-octadecanoic acid on the iron
455 oxides/oxyhydroxides haematite, magnetite and goethite produced a greater
456 abundance of aromatic moieties (compared to no substrate or quartz). The
457 dominance of longer chain lengths was also far less prevalent. With the addition

458 of iron oxides, a wider variety of products was produced from the carboxylic acid.
459 Of the non-aromatic products, alkanes were more dominant (when compared with
460 the products of *n*-octadecanoic acid pyrolysed by itself/on quartz), especially at
461 the higher 650°C pyrolysis temperature. The apparent randomization of carbon
462 chain lengths of the alkene/alkane pairs led to the loss of any clear distribution
463 pattern in the products (Figure S9). A positively skewed distribution peaking at
464 undecylbenzene ($C_{17}H_{28}$) is, however, preserved in the distribution of the *n*-
465 alkylbenzene products (Figure S9) of both haematite and magnetite substrates.
466 Ketones and aldehydes were produced as minor products from *n*-octadecanoic
467 acid pyrolysis on both haematite and magnetite with C_{13} - C_{19} aliphatic ketones
468 (with tentative acetophenone) and C_{16} - C_{17} aliphatic aldehydes on haematite and
469 aromatic ketones fluoren-9-one and tentative identifications of benzophenone,
470 acetophenone and benzaldehyde on magnetite.

471 Goethite and magnetite appeared to promote the aromatization of *n*-octadecanoic
472 acid relative to haematite, with a greater variety of aromatic molecules produced.
473 A greater abundance of higher molecular weight aromatic species was also
474 observed when *n*-octadecanoic acid was pyrolyzed on goethite as compared to
475 magnetite, with PAHs up to 4 benzene rings tentatively detected.

476 3.2. X-ray diffraction (XRD) data

477 XRD data (Figure 4) showed that phase transformations were occurring in the iron
478 oxides during pyrolysis in the presence of 0.5 wt. % octadecenoic acid. Haematite
479 was partially reduced to magnetite (from iron (III) oxide to iron (II, III) oxide),
480 although the transformation was incomplete – presumably due to the short (15 s)
481 period of heating. Goethite was dehydrated to haematite and partially reduced
482 further to magnetite, again, this transformation was incomplete. The goethite was
483 seen to be an impure sample with quartz and possible clays present. Ferrihydrite is
484 nanophase/amorphous pre-pyrolysis, which led to a lack of peaks in the XRD
485 profile, and shows the twin humps typical of 2-line ferrihydrite (Janney et al.,
486 2000; Kukkadapu et al., 2003) and on pyrolysis, in the presence of organic matter,
487 this mineral transformed to more crystalline haematite with minor reduction to
488 magnetite. Converse to these other reduction reactions, magnetite when heated in
489 the presence of (z)-octadec-9-enoic acid was partially oxidized to haematite.

490 4. Discussion

491 4.1. Pyrolysis of carboxylic acids

492 When (z)-octadec-9-enoic acid or n-octadecanoic acid were (individually)
493 pyrolyzed either without substrate or on quartz sand, the products were very
494 similar indicating that the quartz substrate had little effect on the pyrolysis
495 products (Figures 2 and 3). The pyrolysis products in all cases were as expected

496 based on previous studies on the pyrolysis of carboxylic acids (Zafar et al., 2017;
497 Zafar and Watson, 2017; Santos et al., 2019).

498 At the lower (450°C) pyrolysis temperature the pyrolysis products of both
499 carboxylic acids showed a dominance of moieties with 16 to 17 carbon atoms.
500 This indicates that, at low temperatures, cleavage preferentially occurred through
501 the loss of the carboxyl group. Decarbonylation was the dominant process of
502 carboxyl group loss, as indicated by the dominance of the heptadeca-1,8-diene
503 and hepta-1-decene peaks for (z)-octadec-9-enoic acid or *n*-octadecanoic acids
504 respectively. Chain scission was a secondary process at these lower temperatures
505 for both the unsaturated and saturated carboxylic acids leading to shortened
506 aliphatic chains.

507 At the higher (650°C) pyrolysis temperatures, for (z)-octadec-9-enoic acid
508 pyrolysed both without substrate and on quartz sand, the decreased abundance of
509 longer chain length ($C \geq 16$) fragments compared to shorter chain length ($C \leq 10$)
510 shows that this higher temperature enhanced homolytic C=C cleavage at the
511 double bond or at the allylic positions (the sites adjacent to the unsaturated carbon
512 atoms), due to the lower bond dissociation energies. The high abundances of
513 cyclooctene and *n*-decanoic acid produced at 650°C are the expected products of
514 (z)-octadec-9-enoic acid undergoing cleavage at the allylic position. In contrast, *n*-
515 octadecenoic acid, with no internal double bond to provide a weakness, produced

516 a series of *n*-alk-1-enes and *n*-alkanes decreasing in abundance with decreasing
517 carbon number from a peak at C₁₇, indicating that chain scission primarily occurs
518 at the end of this molecule. As these alkane-alkene pairs were strongly dominated
519 by the *n*-alk-1-ene, it appears decarbonylation was still the main process of
520 carboxyl group loss, even at this higher temperature. Elevated peaks at hexadec-1-
521 ene and tetradec-1-ene in the *n*-octadecanoic acid products may be due to
522 secondary β -scission of the aliphatic chain on ionization within the mass
523 spectrometer (Beyer and Walter, 1996). Aldehydes, such as heptadecenal, present
524 in the products of both carboxylic acids, are intermediate products in the
525 incomplete reduction of carboxylic acids (Fréty et al., 2014).

526 There is a tendency of the pyrolysis products of unsaturated carboxylic acids to
527 cyclize, due to their doubly unsaturated carbon chains, after loss of the carbonyl
528 group. This is evidenced by the abundance of cyclic and aromatic moieties in the
529 products of (z)-octadec-9-enoic acid (Hartgers et al., 1995), particularly the
530 produced series of *n*-alkyl- and *n*-allylbenzenes (Figure 2 and S8). The *n*-
531 alkylbenzene series observed in the pyrolysis products of *n*-octadecenoic acid
532 (Figures 3 and S10) was less prominent than it was for (z)-octadec-9-enoic acid.
533 This is presumably because the *n*-octadecanoic acid parent molecule lacked the
534 internal double bond that aided aromatisation in the case of the unsaturated acid
535 (Hartgers et al., 1995).

536 The observed differences in relative abundances of products between (z)-octadec-
537 9-enoic acid pyrolysed by itself and on the quartz sand substrate are only minor
538 but are of interest. There was an increased survival of intact (z)-octadec-9-enoic
539 acid and increased relative abundance of higher molecular weight *n*-octadecanoic
540 acid products on quartz. This may be due to the relatively poor thermal
541 conductivity of the quartz shielding adsorbed carboxylic acids towards the centre
542 of the sample so that they were subjected to lower temperatures and thermally
543 desorbed intact.

544 Also of interest is the non-linear decrease in detectable pyrolysis products as (z)-
545 octadec-9-enoic acid concentration was reduced on the quartz substrate
546 (Supplementary Figure S2). Lower concentrations decreased the relative
547 abundance of high molecular weight products, especially the heptadecanal and
548 parent (z)-octadec-9-enoic acid, which were no longer detectable at the lower
549 concentrations despite being amongst the most abundant species at 0.5 wt. %. Our
550 experiments demonstrated that even a non-reactive substrate will result in some
551 surface effects; compounds that are released during heating can be actively
552 reabsorbed onto the surface. This will preferentially affect the higher molecular
553 weight compounds, especially those with functional groups that are readily
554 attracted to surfaces like carboxylic acids. This effect on the distribution of
555 products will be more pronounced at lower concentrations.

556 4.2. Pyrolysis of carboxylic acids in the presence of iron oxides

557 Figures 2 and 3 show that the presence of iron oxide/(oxy)hydroxide substrates
558 had a clear effect on the pyrolysis of (z)-octadec-9-enoic acid.

559 Out of the iron-bearing substrates tested, pyrolysis of carboxylic acids on
560 haematite exhibited the greatest diversity in pyrolysis products. Pyrolysis of (z)-
561 octadec-9-enoic acid at 450°C on haematite formed minor aliphatic hydrocarbon
562 products comparable to those observed when pyrolyzing (z)-octadec-9-enoic acid
563 on a quartz substrate at the higher temperature of 650°C, alongside many new
564 alteration products (Figure 2). In the aliphatic products (Figure S9, 'Haematite +
565 Octadecenoic Acid') at 450°C there is still a dominance of dienes and alkenes
566 over alkanes although there is a greater relative abundance of shorter chain
567 products. This implies that decarbonylation and cleavage around the C=C double
568 bond dominated pyrolytic breakdown from lower pyrolysis temperatures on a
569 hematite substrate when compared to pyrolysis on a quartz substrate of the
570 carboxylic acid by itself. At 650°C, the relative abundance of saturated versus
571 unsaturated aliphatic hydrocarbons was increased. This implies that either
572 decarboxylation took over as the dominant mechanism leading to the loss of the
573 carboxyl group, or that secondary hydrogenation of the products occurred at this
574 increased temperature. At 650°C, the abundance of aliphatics and *n*-alkylbenzenes
575 over C₁₂ was decreased. This reduction in carbon-chain lengths indicates that
576 bond cleavage occurred at the site of the unsaturated double bond more readily.

577 This suggests that the presence of a hematite substrate has a catalytic effect,
578 lowering the temperature necessary for cleavage of the double bond (compared to
579 a quartz substrate or free carboxylic acid).

580 Similar effects were observed in the pyrolysis of *n*-octadecanoic acid on haematite
581 (Figure 3). Compared to the products of *n*-octadecanoic acid pyrolysed by itself or
582 on a quartz substrate, the carbon numbers of aliphatic fragments are reduced and
583 there was a greater relative abundance of saturated products. Again, this shows
584 that the presence of the haematite substrate had a transformative effect on the
585 pyrolysis products, lowering the temperature necessary for increased levels of
586 internal C-C bond cleavage and hydrogenation of products.

587 Aldehydes were produced during the pyrolysis of carboxylic acids both without
588 substrate and on quartz through partial reduction of the carboxyl group (COOH)
589 to a carbonyl group (C=O). With the addition of haematite, this
590 reduction/hydrogenation was enhanced to produce a series of alcohols (hydroxyl
591 functional group, -OH), this process is known to be catalysed by metal oxide
592 catalysts (Manyar et al., 2010). The observed ketones produced may be the result
593 of the addition of methyl radicals to the carbonyl groups of aldehydes or oxygen
594 addition at the sites of terminal alk-1-enes produced after C-C cleavage has
595 occurred.

596 The transformative effects of magnetite, goethite and ferrihydrite were further
597 pronounced than those of haematite, with the products of carboxylic acids
598 pyrolysed on these substrates bearing little resemblance to those of the carboxylic
599 acids pyrolysed either on quartz or by itself (Figures 2 and 3). There was a clear
600 increased severity of the transformative effects through haematite, magnetite,
601 goethite and ferrihydrite with the detectability, molecular diversity, and the
602 average molecular weight of products decreased throughout this sequence.

603 In the products of both goethite and magnetite, the hydrocarbon chain length of
604 both aliphatic hydrocarbons and in the aliphatic side chains of *n*-alkylbenzenes
605 appear to have been less influenced by aliphatic bond position suggesting
606 hydrocarbon bond scission was more randomised.

607 The presence of aryl-aryl bonded moieties (e.g. diphenyl, diphenylnaphthalene) in
608 the pyrolysis products of both carboxylic acids on all iron oxide/(oxy)hydroxide
609 substrates is significant. This suggests that the Fe^{3+} surface ions acted as electron
610 acceptors, forming aryl free radicals, which could then react with other molecules
611 to form dimers (e.g. biphenyl) and other, higher molecular weight polymers
612 through oxidative coupling reactions (Grzybowski et al., 2013; Watson and
613 Sephton, 2015).

614 The only detectable species in the TIC of (z)-octadec-9-enoic acid on ferrihydrite
615 were benzene, naphthalene, biphenyl and decane (Figure 2). These were only

616 observable in the 0.5 wt. % concentration, which was the highest tested, lower
617 concentrations showed no identifiable peaks (Figure S6). It may be that these
618 simple aromatic species are the ‘end member’ products of a near-complete
619 transformation series where organic compounds are transformed into low
620 molecular weight species such as CO and CO₂. Gas phase data was collected, in
621 separate experimental runs, however large releases of H₂O from this particularly
622 hydrous mineral phase swamped the signal (data not shown) so that these low
623 mass phases were unidentifiable.

624 For the substrates to have had such a strong effect, the transformative reactions
625 discussed must have occurred where the carboxylic acid and iron oxides were in
626 contact. Thus, for efficient reactions to occur, the carboxylic acids may have
627 adsorbed onto the iron oxide mineral surfaces. Fourier transform infrared
628 experiments to confirm adsorption were inconclusive even at high (5 %)
629 carboxylic acid concentrations due to the nature of the iron oxide substrates,
630 although previous studies have shown that organic matter readily adsorbs to iron
631 oxide surfaces via carboxyl groups (Gu et al., 1994). Carboxylic acids may act as
632 negatively charged ions as the polar carboxyl group is attracted to the positive
633 charge of the iron oxide (Wainipée et al., 2010; Chernyshova et al., 2011). The
634 structure of ferrihydrite means that numerous free Fe atoms are situated on the
635 crystal surface (Cornell et al., 2003) and these are readily available to react with
636 the OH group of the carboxylic acid, increasing the adsorption per unit area and

637 thus increasing the rate of reactivity. Furthermore, the nanophase crystal size will
638 also add to the increased transformative effect of this substrate as there is a greater
639 (by orders of magnitude) reactive surface area (Hiemstra, 2015) over which
640 adsorption, and therefore subsequent oxidative reactions may occur.

641 Unlike with the quartz substrate, as (z)-octadec-9-enoic acid concentration was
642 decreased on the iron oxide/(oxy)hydroxide substrates, the abundance and
643 diversity of pyrolysis products decreased relatively linearly. Haematite
644 (Supplementary Figure S3) and goethite (Supplementary Figure S5) were the only
645 iron-bearing substrates where any of the ‘normal’ pyrolysis products of (z)-
646 octadec-9-enoic acid, most notably unsaturated aliphatic hydrocarbons, were even
647 detected as minor products at 0.5 wt. %. The relative abundances of these
648 unsaturated aliphatic hydrocarbons were greatly reduced, relative to aromatic
649 moieties, as concentration was decreased. This shows that transformation of
650 pyrolysis products was more complete at lower concentrations of carboxylic acid;
651 at 500 ppm and below only benzene is detected from goethite. This is to be
652 expected as at lower concentrations of carboxylic acid there will be a greater
653 availability of reactive Fe sites and therefore increased potential for monolayer
654 over multilayer adsorption of the carboxylic acid (and subsequently its pyrolysis
655 products) on the reactive iron oxide/(oxy)hydroxide surface, leading to higher
656 levels of mineral surface promoted transformation (Zafar and Watson, 2017).
657 With decreasing (z)-octadec-9-enoic acid concentration on the magnetite (Figure

658 S4) and ferrihydrite (Figure S6) substrates, abundances of the transformation
659 products decreased until they passed below detection limits, suggesting the same
660 processes were occurring at all concentrations.

661 The increased transformative power of ferrihydrite means that the pyrolysis
662 products of carboxylic acids (and other potential aliphatic biomarkers) will be
663 more thoroughly altered in a substrate rich in this mineral. For a positive detection
664 to be made in a sediment dominated by ferrihydrite, carboxylic acids must be
665 present in much higher concentrations than in a similar sediment dominated by
666 other iron oxide phases.

667 4.3. Transformation of iron oxides & mechanisms for the transformation 668 of carboxylic acid pyrolysis products

669 The XRD data (Figure 4) show that when heated in an inert atmosphere and in the
670 presence of organic matter, haematite was reduced to magnetite; a simple redox
671 reaction with the oxidation state of the iron changing from Fe^{3+} to Fe^{2+} , Fe^{3+} (iron
672 (III) to iron (II, III) oxide). Minor surface water adsorbed onto the haematite
673 during storage was released during heating (observed in low mass pyrolysis-GC-
674 MS data, not shown) and this, alongside water gas shift reactions catalysed by the
675 iron oxide surface, would have produced free radical $\text{H}\cdot$ and $\text{OH}\cdot$ ions to promote
676 bond cleavage in the hydrocarbon chains (Bukur et al., 2016). These radicals will
677 have increased the rate of bond scission and hydrogenation, leading to the

678 observed decreased abundance of detectable molecules, increased saturation and
679 shorter aliphatic hydrocarbon chain lengths observed in the pyrolysis products of
680 both carboxylic acids. Similar processes of free radical generation during the
681 reduction of iron oxides/(oxy)hydroxides are well recognised as astrobiologically
682 relevant methods of organic matter oxidation in Fenton-like reactions (e.g.
683 Foustoukos and Stern, 2012; Shuai et al., 2019).

684 The presence of both Fe (II) and Fe (III) in the magnetite means that there are
685 both oxidising and reducing valence states available to react with the organic
686 matter in different ways. While Fe (III) will scavenge H^+ ions in the same way as
687 haematite, promoting cyclization and aromatization, Fe (II) will react with the
688 hydrogen poor aromatics produced during pyrolysis of the organic matter,
689 oxidizing to Fe (III) and forming haematite (as shown by the XRD data in Figure
690 4). This multistep redox process may explain the reduction in products between
691 haematite and magnetite substrates as seen in Figures 2 and 3.

692 In contrast to the simple redox reactions observed in haematite and magnetite,
693 goethite and ferrihydrite undergo phase transformations involving exothermic
694 reactions when subjected to these conditions (Cornell et al., 2003). Goethite
695 recrystallizes to haematite over 250°C (Gualtieri and Venturelli, 1999), with the
696 XRD data (Figure 4) showing that this was partially further reduced to magnetite.
697 The metastable ferrihydrite readily dehydrates to either goethite or haematite,

698 dependant on pH (Cudennec and Lecerf, 2006), and under the high temperature
699 subjected to in these pyrolysis experiments dehydration to haematite (with minor
700 further reduction to magnetite due to the presence of organic matter (Carlson and
701 Schwertmann, 1981)) was observed.

702 Dehydration, dehydroxylation and the recrystallization of these phases to
703 haematite and magnetite, especially for the hydrous ferrihydrite, would have
704 produced many free radical $H^\cdot$ and $OH^\cdot$ ions as water and hydroxyl ions react with
705 free Fe atoms on the crystal surface and dissociate (Stanjek and Weidler, 1992;
706 Cornell et al., 2003). The two way water gas shift reaction, also catalysed by iron
707 oxide surfaces, is a further source of $H^\cdot$ radicals (Bukur et al., 2016). The
708 increased temperature at the microscale, due to the exothermic energy release
709 during dehydration and decarboxylation (Schwertmann and Fischer, 1973), may
710 have also further increased the reaction rate of hydrocarbon bond thermal
711 dissociation. It is possible that the formation of iron carboxylate salt complexes
712 (Hartgers et al., 1995) and/or cross-linked carboxylic acid polymers (Fjällström et
713 al., 2002) occurred on iron (oxy)hydroxides, which may have led to some of the
714 randomisation of product chain lengths observed, however direct evidence of this
715 process was overprinted by further degradation. The clay impurities in the
716 goethite sample may also be affecting the pyrolysis products as clays have been
717 shown to have catalytic effects on hydrocarbon breakdown (e.g., Davis and

718 Stanley, 1982), however, as the clays are a minor component of the sample, this
719 should be secondary to the effect of the goethite.

720 4.4. Identifying the original carboxylic acid from its pyrolysis products

721 Based on the results presented here it will be difficult to establish the provenance
722 of the breakdown products of carboxylic acids pyrolysed/thermally extracted in
723 the presence of iron oxides. Saturated carboxylic acids appear to be more resistant
724 to these transformative effects, due to not having a weak double C=C bond that is
725 relatively susceptible to thermal break down and subsequent production of an
726 extra terminal double bond, promoting further cyclization, aromatization and
727 hydrogenation. A saturated carboxylic acid is most likely to be identified by the
728 presence of a cluster of breakdown products (predominantly *n*-alk-1-enes,
729 benzenes with aliphatic side chains and potentially intermediate cycloalkanes)
730 with C_{n-1} that of the original carboxylic acid. The products of unsaturated
731 carboxylic acids will be much more ambiguous due to breakdown at the internal
732 double bond and associated allylic positions, alongside chain scission from the
733 end of the molecule, producing less of an obvious dominance of one carbon
734 number in the pyrolysis products.

735 If the concentration of the carboxylic acid on the substrate is high enough,
736 however, it may be possible to distinguish between a saturated and unsaturated
737 carboxylic acid based on the distribution profile of the *n*-alkylbenzenes (Figure 5).

738 For saturated carboxylic acids, the total carbon number of the *n*-alkylbenzene
739 molecules should increase in both value and abundance up to C_{n-1} of the original
740 saturated carboxylic acid molecule. Molecules larger than this modal peak will be
741 minor or absent owing to addition reactions occurring pre-cyclization. For
742 unsaturated carboxylic acids the *n*-alkylbenzenes will be distributed about a modal
743 total C_n corresponding to the position of the double C=C bond ± 1 (for breakdown
744 at the allylic positions) and decrease relatively symmetrically from this point.
745 However, as seen in the experimental data (Figure S8) there may be a shift to
746 higher values, modal peak is around 11-12 rather than 7-10, if breakdown at the
747 double bond is incomplete with chain scission competitively occurring from the
748 end of the molecules.

749 4.5. Relevance to Mars

750 The minimal alteration of the pyrolysis products between the carboxylic acids
751 pyrolysed without a substrate and those pyrolysed on quartz sand demonstrates
752 that, in comparison to iron oxide/(oxy)hydroxide rich units, sediments rich in
753 quartz will be less destructive to biosignature detectability using classical
754 pyrolysis techniques on Mars. This is in line with other work that has shown the
755 amenability of silica-rich sediments to characterisation of associated organic
756 matter (Reinhardt et al., 2020). Hydrated silica (opal) has been detected at the
757 ExoMars designated landing site of Oxia Planum (Carter et al., 2016) and there

758 are reports of >3.5 Ga old organic molecules being preserved in terrestrial
759 sedimentary hydrated silica (chert) deposits (Duda et al., 2018), making these
760 deposits an ideal target.

761 However, with iron oxides/(oxy)hydroxides being ubiquitous across the martian
762 surface, and with their potentiality to be co-deposited with and aid preservation of
763 organic matter, it would neither be possible, nor advisable to avoid them
764 completely. Haematite, magnetite and goethite have been detected (Evans and
765 Adams, 1980; Bell et al., 1993; Klingelhöfer et al., 2004, 2005; Morris et al.,
766 2006a, 2006b; Bish et al., 2013; Blake et al., 2013; Treiman et al., 2016) and,
767 while not directly identified due to its poor crystallinity, nanophase ferrihydrite is
768 believed to be a major component of the iron-rich amorphous soil component
769 (Dehouck et al., 2017). Mössbauer data collected by the Mars Exploration Rovers
770 *Spirit* and *Opportunity* found evidence for poorly crystalline/nanophase iron
771 oxide phases in samples from various localities at both Gusev crater and
772 Meridiani Planum (Morris et al., 2006a; Morris et al., 2006b). All samples
773 collected by *Curiosity* rover and analysed by the Chemistry and Mineralogy
774 (CheMin) X-ray diffraction instrument have been shown to contain a significant
775 iron-rich X-ray amorphous component (Blake et al., 2013; Vaniman et al., 2014;
776 Treiman et al., 2016), which has been suggested to be dominated by a mixture of
777 both ferrihydrite and amorphous silica (Rampe et al., 2016; Dehouck et al., 2017).

778 Oxidising and dry conditions at the surface of Mars means that in the uppermost
779 regolith, haematite will be the most stable form of iron, however exposed martian
780 surface conditions are not amenable to habitability nor the survivability of organic
781 matter (e.g. Moores and Schuerger, 2012) . On Earth, goethite is by far the most
782 common iron oxide in soils and sediments due to its high thermodynamic stability
783 (Schwertmann and Taylor, 1989). This is likely also the case in the martian
784 regolith beneath the surface out of reach of oxidizing effects of UV radiation
785 (Pollack et al., 1970) and ferrihydrite is likely to increase in concentration beneath
786 the surface for the same reason. Based on the results of this study, this is likely to
787 have a negative effect on organic matter detection and characterization efforts in
788 drilled subsurface samples by the future ExoMars *Rosalind Franklin* and
789 Mars2020 *Perseverance* rovers.

790 Ferrihydrite is metastable under oxic conditions and readily recrystallises to either
791 haematite or goethite depending on temperature and pH; at high temperatures,
792 regardless of pH, haematite is formed, at low temperatures with high (>10) or low
793 (<4) pH goethite will form, while haematite will form at neutral pH levels
794 (Cudennec and Lecerf, 2006). However, if oxidising conditions continue for an
795 extended period haematite will end up as the dominant product regardless of
796 temperature and pH (Das et al., 2011). Goethite dehydroxylates around 200-300
797 °C (Gualtieri and Venturelli, 1999; Gialanella et al., 2010); in a reducing
798 environment with a high pH this will form magnetite (Usman et al., 2013), in an

799 oxidising environment with neutral or acidic pH haematite will form (Walter et
800 al., 2001). Magnetite will oxidise to haematite (Lagoeiro, 2004), while haematite
801 may reduce to magnetite depending on the redox potential of fluids. Thus,
802 haematite will be the most stable of the iron oxides in settings which have been
803 subjected to longer term, high temperature, oxidizing and neutral/acidic fluid
804 flow.

805 There is evidence of hydrothermal systems on Mars from *in situ* observations,
806 martian meteorites and remote sensing of mineral deposits. Brine water activities
807 may have persisted all the way from Mars' early history to the present day (Chen
808 et al., 2015), potentially providing a wide range of these environments to explore
809 of varying age, in a suite of different host rocks representing a range of redox and
810 pH conditions.

811 While experimental work has shown that ferrihydrite can survive the short-term,
812 low temperature (<40 °C), nonacidic aqueous alteration that is typical of the
813 sediments of Aeolis Palus at Gale Crater, and ferrihydrite conversion to haematite
814 may be retarded by the presence of amorphous silica even under high temperature
815 hydrothermal conditions (Dehouck et al., 2017). Even very brief, strongly acidic
816 episodes of aqueous alteration will rapidly convert ferrihydrite into haematite or
817 goethite; this is suggested to account for the lack of nanophase ferric oxides in the
818 Burns formation at Meridiani Planum (Dehouck et al., 2017), where other phases

819 such as jarosite are evidence for the presence of strongly acidic fluids
820 (Klingelhöfer et al., 2004). As discussed above, the longer these conditions
821 prevailed for, the more the intermediate goethite phase would have been replaced
822 by haematite (Das et al., 2011). The presence of oxidising and acidic brines is also
823 evidenced from the mineral (and organic) assemblages in the Tissint meteorite
824 (Chen et al., 2015; Steele et al., 2018; Jaramillo et al., 2019). These hydrothermal
825 systems, coupled with the presence of reducing organic matter may have provided
826 a habitable environment with energy generation from brine-mineral interactions
827 and the oxidation of iron (and sulfate, chlorate, etc) bearing minerals (Fernández-
828 Remolar et al., 2008; Steele et al., 2018). Concentrated regions of haematite-rich
829 layers detected from orbit may be evidence of past or present large scale active
830 iron oxidation. On Earth, this is a process that is extensively mediated by
831 chemolithotropic microorganisms (Weber et al., 2006; Fraeman et al., 2013).

832 While oxidizing environments are often associated with the poor preservation of
833 organic matter (Sumner, 2004), this is not necessarily the case. Biomarker
834 preservation in ferruginous sediments from recent and ancient deposits from
835 acidic, oxidising environments such as hot springs (Parenteau et al., 2014), acidic
836 mine drainage (e.g. Rio Tinto) (Colín-García et al., 2011), and acidic streams
837 (Tan et al., 2018) show this not to be the case. Due to the preservation potential of
838 iron oxides on organic carbon (Schelble et al., 2004; Oudemans et al., 2007;
839 Lalonde et al., 2012), and the relative amenability of haematite (compared to

840 goethite, magnetite and ferrihydrite) to thermal decomposition analysis, these
841 areas could be a prime target in the search for extinct martian life.

842 Thus, we recommend targeting areas where any initial ferrihydrite would have
843 been converted to iron oxide phases which are more amenable to detection.
844 Specifically, areas that show evidence of acidic hydrothermal fluid flow should be
845 targeted. Localities with evidence of hydrothermal fluid flow should also have the
846 added advantage of decreased concentrations of soluble perchlorates, further
847 increasing the amenability of these sediments for thermal decomposition analysis
848 of organic matter (Royle et al., 2018; Montgomery et al., 2019).

849 One concern with this strategy is that adsorbed organics on iron oxide surfaces
850 may be significantly degraded by the recrystallisation process. However, initial
851 conclusions from experiments focussing on the degradation of soluble organic
852 matter in ferrihydrite-rich environments suggest that ferrihydrite-magnetite
853 recrystallisation has little to no effect on the rate of degradation of organics (Tan,
854 2020). While these conclusions cannot simply be expanded to insoluble
855 macromolecular organic or other iron mineral transformations, it does provide
856 some insight on organic degradation during recrystallisation processes.
857 Nevertheless, the potential loss in ancient organic material due to the
858 recrystallisation of iron minerals must be discussed and considered before

859 committing to a strategy that targets more stable iron minerals derived from
860 ferrihydrite.

861 It must be considered that there are significant differences between the laboratory
862 flash pyrolysis GC-MS set up used in this study and the SAM and MOMA flight
863 modules. The much slower temperature ramps of the flown instruments, compared
864 to the laboratory experiments described here (see Table 1), will mean that any iron
865 oxides/(oxy)hydroxides and putative organic matter in the analysed sediments will
866 be subjected to elevated temperatures for longer. Therefore, transformation
867 reactions have more time to go to completion, raising the catalytic potential for
868 processes associated with these reactions.

869 However, flash pyrolysis does represent a ‘worst case scenario’, forcing
870 coincidence of iron oxide/(oxy)hydroxide transformation and pyrolytic
871 breakdown of organic molecules which will maximise the alteration/destruction of
872 products (Royle et al., 2018). Under martian experimental conditions (ramped
873 pyrolysis), thermal alteration of the iron oxide/(oxy)hydroxide phases may not
874 coincide with the pyrolytic breakdown/thermal desorption of organic matter. The
875 most labile/volatile phases are likely to be effected by surface effects and the
876 release of water and free radicals from ferrihydrite ($\geq 25^{\circ}\text{C}$ (Cudennec and Lecerf,
877 2006; Das et al., 2011)) and goethite ($\geq 200^{\circ}\text{C}$ (Gualtieri and Venturelli, 1999;
878 Gialanella et al., 2010)) dehydration and dehydroxylation, whereas

879 macromolecular phases may be too refractory to thermally decompose until after
880 these most reactive phases have recrystallised. Thus, the high, 500-820°C
881 temperatures of release of organic molecules at Mojave and Confidence Hills
882 (Eigenbrode et al., 2018) would mean that any goethite and ferrihydrite in these
883 samples would have already dehydrated/dehydroxylated and so only haematite or
884 magnetite would still be available to catalyse reactions at these temperatures.

885 The catalytic potential of iron oxides/(oxy)hydroxides on the thermal
886 decomposition of macromolecular or refractory organic matter, representative of
887 meteoritic macromolecular matter, in contrast to the relatively labile monomers
888 tested here, is therefore an interesting avenue to be explored by future studies.

889 Our data shows that iron oxides promote the transformation of organic matter
890 during pyrolysis. The transformative process can be so complete that biomarkers
891 of extant life, such as MCFAs and LCFAs, may appear to have a non-biological
892 macromolecular source (e.g. meteoritic (Simmonds et al., 1969; Sephton et al.,
893 2004)). Detectability of any pyrolysis products of potential biomarkers in an iron
894 oxide rich sediment will also be greatly reduced, increasing their concentration
895 necessary for detection. This demonstrates that iron (oxy)hydroxide-rich areas
896 present yet another complication for the search for potential biomarkers (and by
897 extension life) on Mars. We have shown an example iron (oxy)hydroxide
898 catalysed breakdown and transformation of non-macromolecular aliphatic

899 molecules, during thermal decomposition experiments, could potentially be
900 another way of forming pyrolysis products that appear to be from (abiotic)
901 macromolecular material similar to those already detected on Mars (Eigenbrode et
902 al., 2018). This means that, in iron-rich sediments the structural information held
903 in (potential biomarker) organic molecules will be lost due to the catalytic effects
904 of iron (oxy)hydroxides.

905 The specific issues presented here are with classical pyrolysis-GCMS as used by
906 Viking Landers (Biemann et al., 1977), Phoenix's Thermal Evolved Gas Analyser
907 (TEGA) (Hoffman et al., 2008) and MSL-SAM (Mahaffy et al., 2012). However.
908 Both SAM and MOMA have wet chemistry capabilities with the ability to carry
909 out derivatized pyrolysis-GCMS. In these techniques a derivatization agent is
910 used to transform astrobiologically relevant organic molecules (including
911 carboxylic acids) into species that are sufficiently volatile and amenable to GC
912 column chromatography (Mahaffy et al., 2012). MOMA will have an advantage
913 over SAM by having two derivatization techniques that occur at low temperatures
914 MTBSTFA/DMF ($\approx 250^{\circ}\text{C}$) and DMF-DMA ($\approx 140^{\circ}\text{C}$) (Goesmann et al., 2017).
915 The iron oxide/oxy(hydroxide) catalysed reactions described here are likely to be
916 slow at these low temperatures, especially with the DMF-DMA technique which
917 should be within the stability range of all but ferrihydrite dehydration.

918 MOMA will also have an advantage over previously employed thermal
919 decomposition methods as its Laser Desorption – Mass Spectrometry capability
920 will allow the targeting of heavier non-volatile organic compounds (up to 1000 u)
921 which may be present in the martian sediment. This technique is non-destructive,
922 will preserve more structural information (Goesmann et al., 2017; Li et al., 2017)
923 and is less likely to suffer from catalytic mineral surface reactions or the effects of
924 oxidant species (e.g. perchlorates) as the nanosecond duration of the laser pulse
925 mitigates heating of the substrate (Li et al., 2015; Goesmann et al., 2017).

926 **5. Conclusions**

927 Iron oxides act as both oxidative and reductive catalysts during the pyrolysis of
928 carboxylic acids. Pyrolysis products are transformed, decreasing both the
929 abundance and variety of molecular species detected. This effect must be taken
930 into consideration when analysing martian data in iron-rich sediments. Any
931 carboxylic acids, or similar biomarker molecules, may be subjected to oxidative
932 coupling and aromatization or hydrogenation and reduction as well as enhanced
933 pyrolytic breakdown, this will be more pronounced with unsaturated than
934 saturated carboxylic acids. The pyrolysis products of these carboxylic acids will
935 appear very similar to mature hydrocarbons; thus, a recent biomarker molecule
936 present at low concentrations could easily be mistaken for meteoritic
937 macromolecular carbon if only classical pyrolysis GC-MS is used. The enhanced

938 derivatization pyrolysis-GCMS and LD-MS capabilities of MOMA may provide a
939 way of mitigating these effects. Therefore, iron oxides, along with the previously
940 studied perchlorates and sulphates, are yet another complication for attempts to
941 detect indigenous martian organic matter and the search for extraterrestrial life
942 itself.

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947

948 **Tables**

949 *Table 1 SAM data from Freissinet (2015) and Eigenbrode et al. (2018), MOMA data from Goesmann (2017)*
 950 *and Guzman (2020)*

	SAM Flight Module	MOMA Flight Module	Laboratory Py-GC-MS
<u>Pyrolysis oven and transfer lines</u>			
Initial (°C)	~35-50	~30	~21
Final (°C)	~835	850	450/650
Ramp rate	35 (°C/min)	200 (°C/min)	20 (°C ms ⁻¹)
He pressure (mbar)	25		1013
He flow rate (ml min ⁻¹)	~0.8		
Transfer line (°C)	135	135	270
<u>GC-MS</u>			
Column type	MXT-CLP	MXT Q BOND MXT CLP MXT 5 CP Chirasil Dex CB	SGE BPX5
He flow rate (ml min ⁻¹)	~0.4	0.8 to 1.4	1.1
Split flow (to MS or GC)	~250:1 (MS)		10:1 (GC)
Initial temperature (°C)	50	30	40
Hold (min)	4		2
Ramp rate (°C/min)	10	1-15	5
Final temperature (°C)	220	250 (220 for CP Chirasil Dex CB)	310
Final hold (min)	3		10
Scan range (m/z)	2-535	50-500	10-150

951

952 **Figures**

953

954 **FIG. 1.** Saturated (a) and unsaturated (b) long chain (C₁₈) carboxylic acids used in this study.
 955 Pyrolysis reactions of *n*-octadecanoic acid (bi) at low (450°C) temperatures where decarbonylation
 956 is dominant; (bii) at high temperatures (650°C) where decarboxylation is dominant. Pyrolysis
 957 reactions of (z)-octadec-9-enoic acid (bi) at low (450°C) temperatures where decarbonylation is
 958 dominant; (bii) at high temperatures (650°C) where decarboxylation is dominant
 959

FIG. 2. TICs of 0.5 wt. % (z)-octadec-9-enoic acid pyrolyzed on various substrates. Numbers with symbols refer to the aliphatic carbon chain length of the molecule. Abbreviations used: Benzene (Bz), Toluene (T), Styrene (St), Naphthalene (N), Phenanthrene (P), Biphenyl (BiP), Dibenzo-furan (DBF), Fluorenone (9-F), Phenyl-naphthalene (PN), Fluoranthene (Fl).

FIG. 3. TICs of 0.5 wt. % *n*-octadecanoic acid pyrolyzed on various substrates. Numbers with symbols refer to the aliphatic carbon chain length of the molecule. Abbreviations used: Benzene (Bz), Toluene (T), Styrene (St), Naphthalene (N), Phenanthrene (P), Biphenyl (BiP), Dibenzofuran (DBF), Fluorenone (9-F), Phenylanthracene (PN), Fluoranthene (FI).

FIG. 4. XRD profiles of iron (oxy)hydroxides before pyrolysis (Pre) and after being pyrolyzed along with 0.5 wt% (z)-octadec-9-enoic acid (Post). Inset shows ferrihydrite with 3x vertical axis exaggeration to emphasise twin humps typical of 2-line ferrihydrite. Elevated background is due to Fe fluorescence under Cu X-ray radiation. C? = unidentified Clay; F= Ferrihydrite; G= Goethite; H = Haematite; M = Magnetite; Q = Quartz

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FIG. 5. Cartoon showing distribution of *n*-alkylbenzenes in the breakdown products of unsaturated and saturated carboxylic acids C_{n-1} corresponds to the total number of carbon atoms in the original carboxylic acid minus one (due to loss of carboxyl group); $C_{n-(n\pm 1)}$ corresponds to the double bond position in the original unsaturated carboxylic acid molecule (± 1 for breakdown at the allylic position).

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2075 *Figure S1 Total Ion Chromatograms (TICs) of procedural blank (no sample in probe) and control samples of*
 2076 *unspiked minerals used as substrates, pyrolyzed at 650 °C post cleaning procedures*

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Figure S2 TICs of oleic acid pyrolysed on quartz at varying concentrations.

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Figure S3 TICs of oleic acid pyrolysed on haematite at varying concentrations.

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Figure S4 TICs of oleic acid pyrolysed on magnetite at varying concentrations.

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Figure S5 TICs of oleic acid pyrolysed on goethite at varying concentrations.

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Figure S6 TICs of oleic acid pyrolysed on ferrihydrite at varying concentrations.

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Figure 1 Extracted Ion Chromatograms (XICs) of oleic acid pyrolyzed on various substrates, m/z 55, 57 selected to show aliphatic hydrocarbons, numbers represent carbon chain length i.e 10 = decane/decene; 17

2092

17al = heptadecenal
450°C

650°C

2093

2094

2095

2096

Figure 2 XICs of oleic acid pyrolyzed on various substrates, m/z 91 selected to show n -alkylbenzenes, numbers represent the number of carbons in the molecule i.e. 7 = toluene (C_7H_8); 17 = undecylbenzene ($C_{17}H_{28}$).

Figure S9 XICs of steric acid pyrolyzed on various substrates, m/z 55, 57 selected to show aliphatic hydrocarbons, numbers represent carbon chain length i.e 10 = decane/decene; 17-al = heptadecenal.

Figure S10 XICs of steric acid pyrolyzed on various substrates, m/z 91 selected to show n -alkylbenzenes, numbers represent the number of carbons in the molecule i.e. 7 = toluene (C_7H_8); 17 = undecylbenzene ($C_{17}H_{28}$).