

**The Moon as a recorder of organic evolution in the early solar system: a lunar regolith analogue study**

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Running title: The Moon as a recorder of organic matter

## **Abstract**

The organic record of the Earth older than ~3.8 Ga has been effectively erased. Some insight is provided to us by meteorites as well as remote and direct observations of asteroids and comets left over from the formation of the solar system. These primitive objects provide a record of early chemical evolution and a sample of material that has been delivered to the Earth's surface throughout the past 4.5 Gyr. Yet, an effective chronicle of organic evolution on all solar system objects, including that on planetary surfaces, is more difficult to find. Fortunately the early Earth would not have been the only recipient of organic matter-containing objects in the early solar system. For example, a recently proposed model suggests the possibility that volatiles, including organic material, remain archived in buried palaeoregolith deposits intercalated with lava flows on the Moon. Where asteroids and comets allow the study of processes before planet formation, the lunar record could extend that chronicle to early biological evolution on the planets. In this study we use selected free and polymeric organic materials to assess the hypothesis that organic matter can survive the effects of heating in the lunar regolith by overlying lava flows. Results indicate that the presence of lunar regolith simulant appears to promote polymerisation and, therefore, preservation of organic matter. Once polymerised, the mineral-hosted newly-formed organic network is relatively protected from further thermal

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degradation. Our findings reveal the thermal conditions under which preservation of organic matter on the Moon is viable.

### **Keywords**

Moon; regolith; organic preservation; biomarkers

## 1. Introduction

### 1.1. Organic records in the solar system

The processes that drive the Earth's geological cycle continually overwrite the rock record with new geological information. Tectonic activity has destroyed rocks older than ~3.8 Ga, and the oldest rocks that we are able to examine have been heavily altered, complicating the interpretation of ancient terrestrial environments (*e.g.*, Mojzsis *et al.*, 1996; Fedo and Whitehouse, 2002; Lepland *et al.*, 2005; van Kranendonk *et al.*, 2007). We are, therefore, forced to look elsewhere for clues about the conditions on Earth and in the inner solar system at, and before, ~3.8 Ga. Meteorites have provided us with a great deal of information about the formation of the solar system. However, what is needed is a record over time of the materials that were circulating close to, and impacting on, the Earth during early phases of ocean, atmosphere and continent formation and destruction (*e.g.*, Marchi *et al.*, 2014). Such materials would have derived from primitive and processed asteroids, comets, interplanetary dust particles, as well as fragments of planetary surfaces blasted off by large impacts. Many of these bodies are known to contain organic material. In particular, the analysis of carbonaceous chondrite meteorites has revealed the wide variety of organic compounds that were generated abiotically and were available for delivery to planetary surfaces (Sephton, 2002). Some of these compounds, such as amino acids, carboxylic

acids, polyhydroxylated compounds and nucleobases, have relevance to biological systems. Some compounds appear to have a clear relationship with inorganic mineral phases (Pearson *et al.*, 2002; Garvie and Buseck, 2007; Kebukawa *et al.*, 2010; Zega *et al.*, 2010; Le Guillou *et al.*, 2014). Similarly, direct sampling by spacecraft and remote observations of comets and asteroidal bodies has revealed a range of organic compounds (Kissel and Krueger, 1987; Ehrenfreund and Charnley, 2000; Sandford *et al.*, 2006; Elsila *et al.*, 2009). These objects and the organic matter they carry are important in helping us to understand prebiotic chemical evolution in the early solar system. Yet a record of the subsequent emergence and evolution of the first biological systems on planetary surfaces is currently unavailable on Earth. However, the cratering record of the Moon and models of solar system dynamics indicate an intense period of asteroid bombardment of the inner solar system, around 4.2-3.7 Ga, known as the Late Heavy Bombardment (LHB) (Hartmann *et al.*, 2000; Kring and Cohen, 2002; Gomes *et al.*, 2005; Tsiganis *et al.*, 2005; Bottke *et al.*, 2012; Marchi *et al.*, 2012). Such impacts may have ejected fragments of terrestrial crust containing evidence of ancient rock types, trapped records of atmospheric gases, and potentially biomarkers (Armstrong *et al.*, 2002). Capture and preservation of ejected planetary material could answer outstanding questions over the chemical evolution in the inner solar system leading up to the origin of life.

The Moon may provide us with this archive (Armstrong *et al.*, 2002; Crawford *et al.*, 2008; Joy *et al.*, 2012; Burchell *et al.*, 2014b). Orbiting close to the Earth, major surface volcanic activity ceased around 3.1 Ga (Wilhelms *et al.*, 1987). The Moon is a relatively large body (3475 km diameter), causing it to readily attract material owing to its gravitational pull. It has essentially no atmosphere and is largely anhydrous, features which makes it a potentially ideal witness to the organic chemical processes occurring close to the Earth in the early solar system. The surface of the Moon is largely covered by a few metres to kilometres thickness of regolith, a fine-grained rock powder developed by impacting material and space weathering (Lucey *et al.*, 2006). After the return of the Apollo lunar samples, a number of studies assessed the lunar materials for the presence of organic matter (*e.g.*, Abell *et al.*, 1970; Burlingame *et al.*, 1970; Nagy *et al.*, 1970). Small quantities of carbon were detected (<200 ppm total C, Burlingame *et al.* 1970; Ponnampertuma *et al.*, 1970). The indigenous nature of detected organic compounds was uncertain. Measurements by Brinton and Bada (1996) quantified the level of free amino acids at around 15 ppb, however some of the detected compounds were attributed to terrestrial contamination based on enantiomeric ratios. More recent studies using highly sensitive modern instruments have indicated the presence of organic compounds in lunar samples that are not of terrestrial contamination origin but may have come from added meteoritic material (Thomas-Keppta *et al.*, 2014). A lunar impact melt breccia

returned from the Moon by Apollo 17 (sample 72255) has been shown to contain graphitic carbon which may have formed from condensation of vaporised C-rich impactors (Steele *et al.*, 2010). Understanding how these carbonaceous materials were formed, and modified, would allow us to test proposed models of preservation. The presence of well-preserved records on the Moon may be crucial in illuminating the behaviour and chemical evolution of organic matter in the early solar system.

### 1.2. Sources of organic matter to the Moon

Organic matter is prevalent throughout the solar system, and the possibility of the presence of indigenous organic matter on the Moon has been considered for some time (*e.g.*, Sagan, 1960). In addition to exogenous delivery, organic compounds may be generated *in situ* by the action of radiation on ices (*e.g.*, Moore *et al.*, 1983; Bernstein *et al.*, 1995; Lucey, 2000; Crites *et al.*, 2013). Carbon may also be directly implanted in the regolith from the solar wind (Bibring *et al.*, 1974; Pillinger and Eglinton 1977; Haskin and Warren, 1991). There would have been a number of sources which could have delivered organic and volatile material during the early history of the Earth–Moon system. Models have shown that enstatite and ordinary chondrite-type bodies would have been the dominant large impactor types during the LHB (Bottke *et al.*, 2012; Morbidelli *et al.*, 2012).

These meteorite types are known to contain organic material (*e.g.*, Alexander *et al.*, 1998; Quirico *et al.*, 2003; Sephton *et al.*, 2004a). There would also have been a high flux of micrometeorites and dust particles at this time, dominated by carbonaceous material (Court and Sephton, 2014). CI carbonaceous chondrites can contain >3 % carbon (Botta and Bada, 2002), and interplanetary dust particles can contain several times this amount (Thomas *et al.*, 1994). Another potential source of organic matter would have been from the surfaces of Mars, Earth, and other planets, as large impacts would have blasted fragments of surface material into space at velocities sufficient to escape the gravitational pull of the planets (Armstrong *et al.*, 2002; Armstrong, 2010). These fragments could potentially have contained organic matter, including biological material. The potential for preservation of the earliest biotic and pre-biotic material in terrestrial or martian meteorites is a key motivation for exploration of the Moon (Crawford *et al.*, 2008; Burchell *et al.*, 2014b). Recent experimental work has shown the ability of organic biomarkers to survive the impact shock conditions that would have ejected this material from the planetary surface (*e.g.*, Parnell *et al.*, 2010; Burchell *et al.*, 2014a). The total amount of terrestrial material at the lunar surface today has been estimated as 1-2 ppm, however, the distribution of impacts will be non-uniform, and some areas of the surface may have received several times more or less than this amount (Armstrong, 2010). The proportion of organic matter in the ejected terrestrial material is unknown, however assuming organic-poor rocks

with 1% organic matter or less would result in parts-per-billion levels of terrestrial organic matter in the lunar regolith.

### 1.3. *Survival of infalling material*

#### 1.3.1. *Impact at the lunar surface*

Organic material within an ejected object travelling towards the lunar surface must survive the initial impact in order to be preserved. With a negligible atmosphere to provide deceleration, impacting bodies strike the lunar surface at high velocity, producing high temperatures and great levels of shock. The lack of atmosphere means that a fusion crust will not be developed on the meteorite by ablation, however it has been suggested that material ejected from the surface of the Earth may develop a fusion crust on its passage out of the atmosphere (Gutiérrez, 2002). The high temperatures generated during atmospheric ablation of stony meteorites falling to Earth are restricted to the outermost portion of the meteorite, and do not penetrate to significant depth. The detection of organic compounds in carbonaceous chondrite meteorites, and experimental work with artificial meteorites shows that organic compounds and biomarkers are capable of surviving infall to Earth (Sears, 1975; Parnell *et al.*, 2011). It might therefore be

expected that organic compounds would survive heating by ablation in materials ejected from the Earth's surface.

Micrometeorites impacting the lunar surface are vaporised, and the vapour material condenses out onto grain surfaces (Keller and McKay, 1997). The high impact temperatures generate the glass-bound agglutinates which are abundant in the lunar regolith (*e.g.*, McKay *et al.*, 1991). However, a fraction of impacting material can survive. Direct evidence for survival following impact comes from a small number of meteorites recovered from regolith samples collected during the Apollo missions (*e.g.*, Joy *et al.*, 2012 and refs. therein). One important example is the Bench Crater meteorite, recovered by Apollo 12. This millimetre-sized object was identified as a carbonaceous chondrite, and the hydrated mineral phases remain preserved (McSween, 1976; Zolensky *et al.*, 1996; Zolensky, 1997). Bench Crater provides encouragement that carbonaceous materials in meteorites may be identifiable and characterisable *in situ* on the Moon (see also Joy *et al.*, 2012). Terrestrial meteorites would have had a lower range of impact velocities than asteroidal or cometary fragments. Armstrong (2010) calculated terrestrial meteorite impact velocities as typically occurring at  $\sim 3 \text{ km s}^{-1}$ , with a substantial proportion of impactors having relatively low vertical impact velocities. Computer modelling has shown that portions of larger impactors ( $0.125 \text{ m}^3$ ) experience relatively moderate conditions upon impact within the

range of  $2.5\text{-}5 \text{ km s}^{-1}$ , well within the survivability window for many biomarkers (Crawford *et al.*, 2008; Burchell *et al.*, 2010).

### 1.3.2. *The lunar regolith environment*

Despite the absence of tectonics, biodegradation, and other destructive agents that are present on the Earth, the lack of an atmosphere means that the surface of the Moon is subject to space weathering (*e.g.*, Lucey *et al.*, 2006). Space weathering constitutes impacts from micrometeorites and larger impactors (comminution), and irradiation from the solar wind, energetic solar events and galactic cosmic rays. The radiation causes sputtering on grain surfaces, and the more energetic particles can generate a cascade of particles within the regolith, which damages the mineral grains. It has been shown that ionising radiation can change the structure of organic matter by formation of free radicals during radiolysis, causing aromatisation, a reduction in the degree of alkylation of aromatic units, and polymerisation of smaller organic molecules into larger aromatic networks (Court *et al.*, 2006). In order for fragile materials to be preserved over billion-year timescales, some mechanism is required to protect them from the harsh radiation and impact environment; processes related to lunar lava flows may provide one such mechanism.

#### 1.4. Preservation of the lunar regolith

The continual process of lunar regolith formation is slow (2 to 5 mm Myr<sup>-1</sup> over the last 3.5 Ga; *e.g.*, McKay *et al.*, 1991), and subjects materials to repeated vertical and lateral reworking and direct surface exposure. Given the current rate of overturn, it would take a considerable length of time to build up a thickness of regolith sufficient to completely protect material from ionising radiation and impacts. Therefore, a more rapid mechanism of burial is required. Burial under an ejecta blanket or an impact melt flow from a nearby large impact is one possible method, but identification of discrete regolith horizons within the layers of pulverized rock and mixed regolith material would be a challenging task. A recently-proposed alternative method of rapid burial is by lava flows (Crawford *et al.*, 2010; Fagents *et al.*, 2010; Rumpf *et al.*, 2013). In this model, a layer of regolith that has accumulated on an exposed rock surface is covered by a lava flow, which quickly cools. Subsequent space weathering develops a new regolith layer on the lava surface, which in turn is covered by another flow. This process repeated again would result in a succession of palaeoregolith deposits separated and protected from the space environment by layers of igneous rock. Analogous processes occur on Earth, with the development of soils on lava flows which are in turn buried by later flows, causing thermal alteration of soil material (*e.g.*, Olson and Nettleton, 1998; Sheldon, 2003; Marques *et al.*, 2014). The heating profiles below terrestrial lava flows have been modelled (*e.g.*, Fagents and

Greerley, 2001; Kerr, 2001) and there is an existing literature on the analysis of thermal metamorphism as a result of igneous activity (*e.g.*, Bishop and Abbott 1993, 1995; Farrimond *et al.*, 1996). However, terrestrial conditions differ markedly from those on the Moon, particularly with the absence of water in the lunar rock profile. The sequence of lunar regolith and lava flow layers would record changes in the types of meteorite infall over time, as well as changes in other parameters of interest such as the radiation environment and particle fluxes (Crawford *et al.*, 2010; Fagents *et al.*, 2010; Joy *et al.*, 2014). Combined with radiometric dating of the lava units, such a sequence could provide a tightly defined record of processes occurring at the lunar surface including the receipt of material from elsewhere in the solar system such as the Earth's surface.

### 1.5. *The influence of volcanic heat on organic records*

Having established a possible method of preserving regolith deposits by lava flows, consideration needs to be made of the effects of heating of the materials of interest within the buried regolith by the lava. Heating of organic materials can result in the loss of volatile compounds, degradation, and aromatisation (*e.g.*, Killops and Killops, 2005). The presence of minerals is known to affect the alteration of organic matter during heating (*e.g.*, Espitalié *et al.*, 1980, 1984; Huizinga *et al.*, 1987). Space weathering would gradually break up an organic-

bearing meteorite on the surface of the regolith, with the result that a portion of the organic material would become dispersed within the lunar regolith, with direct contact between organic material and lunar minerals. The minerals of the lunar regolith may have properties which accelerate the destruction or reconfiguration of organic materials when heated, or otherwise result in organic products different to those where the organic matter is heated in isolation, as has been investigated for the martian regolith (*e.g.*, Iniguez *et al.*, 2009).

The composition of the lunar regolith depends upon the bedrock from which it is formed, and tends to be predominantly basaltic in mare regions or anorthositic in highland areas (McKay *et al.*, 1991). As such, the regolith is chiefly composed of a complex mixture of rock fragments and grains containing plagioclase feldspar, olivine, and pyroxene in variable amounts, as well as amorphous glass (Papike *et al.*, 1982; McKay *et al.*, 1991). There are also quantities of ilmenite and meteoritic iron. Elemental iron also occurs as a nanoparticle distribution within the amorphous glass rims of grains, and in agglutinates, formed as a result of micrometeorite impacts and redistribution of Fe from lunar silicates (Keller and McKay, 1997; Taylor *et al.*, 2001).

In this work we performed heating experiments on various organic materials under vacuum in the presence and absence of lunar regolith analogue JSC-1 (Johnson Space Centre - 1) in order to determine any alteration effects of the

minerals on the organic materials. The aim was to assess the validity of the proposed mechanism of preservation of organic materials in lunar regolith capped by lava flows. Our results can be used to direct the search for organic records of chemical and early biological evolution in the solar system that may exist on the Moon.

## **2. Materials and Methods**

A variety of organic compounds and materials were heated under vacuum at a range of temperatures with and without lunar regolith simulant present. The products were then extracted with solvent, and these extracts were analysed by gas chromatography-mass spectrometry (GC-MS). The solvent-extracted residues were analysed by pyrolysis-gas chromatography-mass spectrometry (pyrolysis-GC-MS).

### *2.1. Lunar regolith simulant*

JSC-1 is a simulant of the lunar mare regolith, and was developed to fulfil a wide range of analogue roles. It is a basaltic volcanic ash from Arizona, USA, and the main mineral constituents are plagioclase feldspar, olivine, pyroxene, and amorphous glass of basaltic composition, with a median particle size of

approximately 100  $\mu\text{m}$  (see McKay *et al.*, 1994, and Willman *et al.*, 1995, for a complete description of JSC-1). Although primarily intended as a geotechnical and engineering analogue, it nevertheless has a similar mineralogy and particle size distribution to lunar mare regolith. Key chemical differences include a greater abundance of water in JSC-1 as a consequence of the hydrous nature of terrestrial lavas, and a lack of  $\text{Fe}^{3+}$  in the lunar regolith (McKay *et al.*, 1994). Analogue materials such as JSC-1, which are available in significant quantities, are essential for exploratory work, allowing experimental insight without sacrificing valuable authentic samples.

## 2.2. *Organic samples*

Two types of organic materials were chosen for experimentation: free organic compounds and polymeric materials.

### 2.2.1. *Free organic compounds*

The free (solvent soluble) organic compounds selected for the heating experiments have been used before to test organic detection instruments for life detection missions (Table 1; Court *et al.*, 2010). The suite of eight compounds (hereafter termed “FC-8”) comprising atrazine, hexadecane, phytane, squalene, coprostane, stigmasterol, anthracene, and pyrene, represent a range of structures

and include both biogenic compounds and compounds that can occur in the absence of life. Defining the range of temperatures that these compounds can withstand will provide insights into whether it is possible that biological organic material delivered to the Moon by terrestrial meteorites, and non-biological material from asteroid and comet debris could survive in the lunar surface in the lava flow trapping scenario.

### 2.2.2. *Polymers*

Both meteoritic and biotic carbonaceous materials contain a large proportion of macromolecular organic materials. Synthetic polymers were used as a simulant of this material. Poly( $\epsilon$ -caprolactone) (PCL) and poly[(R)-3-hydroxybutyrate] (PHB), which are both polyesters, were chosen. Although markedly different in structure to the meteoritic macromolecular organic material, the synthetic polymers have well-characterised mechanisms of thermal decomposition, allowing any deviations due to the presence of mineral matrix to be recognized.

### 2.3. *Sample preparation*

Glassware, including pyrolysis tubes, was prepared by baking in aluminium foil in air at 500 °C for a minimum of 3 hours, or by cleaning with solvent. JSC-1 was cleaned by exhaustive washing with dichloromethane in order to remove organic

contaminants. The eight compounds of FC-8 were made up in 20  $\mu$ l of methanol, which was spiked using a syringe onto JSC-1 which was pre-loaded into a pyrolysis tube to give 20  $\mu$ g per compound. The methanol was then removed by thorough drying at 37 °C. This resulted in a total of 0.5-0.8 organic wt%. For those experiments where FC-8 was heated in the absence of JSC-1, the 20  $\mu$ l of FC-8 methanol solution was spiked onto quartz wool in a quartz pyrolysis tube to give 20  $\mu$ g per individual compound, before the methanol was evaporated using a hot box at 37 °C. The quartz wool was intended to act as a simple substrate to retain the compounds and therefore a precise ratio of compound mass to quartz wool mass was not applied. In order to check for contamination, aliquots of JSC-1 (~25-40 mg each) containing no added organic material were heated alongside the other samples at each temperature step.

Finely powdered polymers were mixed with JSC-1 to give approximately 5 wt% organic content. Approximately 20-30 mg of this mixture was then loaded into quartz pyrolysis tubes, and secured with quartz wool at both ends. For organic samples heated without JSC-1, variable masses from 2 to 12 mg were loaded into pyrolysis tubes in the same manner.

For each individual experiment, the quartz pyrolysis tube with loaded sample was placed into a 200 mm length of 3 mm internal diameter borosilicate glass tubing sealed at one end with a flame. The unsealed end of the tube was connected to a

vacuum line and evacuated before the whole tube was flame sealed. Care was taken to ensure that the heat from the flame sealing process did not affect the loaded sample. The vacuum sealing process will have removed the bulk of atmospheric and adsorbed water.

#### 2.4. Heating experiments

Sample tubes were heated in a furnace from room temperature (~20 °C) up to the required final temperature at a rate of 1 °C per minute. The final temperature was held for 80 minutes, and then the furnace was allowed to cool. This temperature profile was intended to simulate the gradual heating of regolith material beneath a recently-emplaced lava flow up to a maximum temperature. The four maximum temperatures chosen were 250 °C, 400 °C, 550 °C and 700 °C. This range of temperatures can be considered to correspond to a range of depths into the regolith beneath the lava flow. A thicker overlying lava flow will mean a greater temperature excursion at a given depth than for a thinner lava flow, and it will also remain hotter for longer owing to the greater volume of lava (Fagents *et al.*, 2010; Rumpf *et al.*, 2013). The minimum observed thickness of individual lava flow units on the Moon is ~1 m (Vaniman *et al.*, 1991). The maximum temperature isotherm of 700 °C modelled by Rumpf *et al.*, (2013) for a 1 m lava flow reaches a maximum depth of ~0.1 m into the regolith beneath the lava flow

after 10 days. The 300 °C isotherm reaches a maximum depth of ~0.2 m after 20 days. This temperature is slightly higher than the 250 °C step used in our heating experiments, but provides an indication that the peak temperatures chosen for our experiments correspond to the first few tens of centimetres depth below the surface of the regolith.

### 2.5. *Sample extraction*

After the sample tubes had cooled, they were carefully broken open. Soluble organic compounds were then extracted from the sample and the internal glass surface of the tube by the addition of approximately 0.5 ml of 93:7 v/v dichloromethane:methanol solution. The solvent extraction step was repeated a further two times to ensure complete removal of organic compounds. Subsequently, the quartz pyrolysis tube containing the sample was removed from the borosilicate tubing, and was dried at 37 °C to remove solvent.

### 2.6. *Analysis*

The solvent extracts were made up to 1 ml with dichloromethane for analysis by GC-MS. Samples were run using an Agilent 7890 N GC coupled to an Agilent 5975C mass selective detector (MSD). The injected sample volume was 1 µl. The

oven temperature was programmed for 50 °C (1 minute) then ramped at 4 °C min<sup>-1</sup> up to 310 °C then held for 20 minutes. Separation was carried out on an Agilent HP-5MS capillary column (30 m length, 250 µm i.d., 0.25 µm film thickness) using helium carrier gas at a flow rate of 1.1 ml min<sup>-1</sup>. The inlet was operated in splitless mode and was held at 250 °C. The MSD scan range was *m/z* 50 – 550.

The solvent-extracted residue in the quartz pyrolysis tube was subjected to pyrolysis-GC-MS. Analysis was carried out using a Chemical Data Systems 5200 pyroprobe coupled to an Agilent 6890 GC with a 5973 MSD. Pyrolysis was performed at 600 °C for 15 seconds. Separation was achieved using an Agilent J&W DB-5MS UI column (30 m length, 250 µm i.d., 0.25 µm film thickness) with helium carrier gas at a flow rate of 1.1 ml min<sup>-1</sup>. The oven was held at 40 °C for 2 minutes, before being ramped to 300 °C at a rate of 5 °C min<sup>-1</sup>, and then held at the final temperature for 8 minutes. The inlet was held at 270 °C and was operated in split mode (50:1). The MSD scan range was *m/z* 45 – 550.

Compound identification was performed based on retention times, comparison with standard compounds in the case of FC-8, and using the NIST-08 mass spectrum library.

### 3. Results

The analysis of the solvent extracts and the pyrolysis-GC-MS results are complementary; the solvent extracts reveal the unbound compounds that survive the heating process, as well as those that are generated by degradation of any polymers present in the experimental residue. The pyrolysis-GC-MS provides information about polymers that survive thermal processing, but also newly formed polymeric structures that are created by cross linking reactions. Solvent extraction of a 18.6 mg split of JSC-1 (i.e., for a typical mass used for heating experiments) showed no organic components. The aliquots of JSC-1 containing no added organic material that were heated alongside the other samples at each temperature step showed no substantial organic contamination that would affect the interpretation of results in either the solvent extracts or pyrolysis runs.

#### 3.1. Free compounds (FC-8)

##### 3.1.1. Solvent extracts

The pattern of survival of the free organic compounds (Table 1) for samples heated with JSC-1 present and those where JSC-1 was absent are similar. In both cases, at the lowest heating step of 250 °C, stigmaterol and atrazine are lost (Table 2). Squalene has a very low response where JSC-1 is absent, and was not

detected when JSC-1 was present. At 550 °C, only anthracene and pyrene remain in both the sample heated with JSC-1 and the one without. After the heating experiments at 700 °C, none of the original compounds of FC-8 are detectable in the total ion chromatogram. Aromatisation of the FC-8 compounds has also occurred, evidenced by a methylated 3-ringed ( $m/z$  192) aromatic compound in the 550 °C sample heated without JSC-1. This compound was not present in the original FC-8 suite of compounds.

### 3.1.2. Pyrolysis products

Up to 400 °C, the key products detected by pyrolysis-GC-MS were hexadecane and phytane. It is likely that these compounds were incompletely removed by solvent extraction. At the 550 °C temperature step, new compounds not initially present in the FC-8 were detected in the JSC-1 sample. Methyl-, dimethyl-, and trimethylnaphthalene are indicative that a temperature of 550 °C is sufficient to cause aromatization of the constituent compounds of FC-8. This is reflected in the formation of a methylated aromatic compound ( $m/z$  192) which was detected in the solvent extract of FC-8 heated at 550 °C in the absence of JSC-1. At 700 °C, in the sample heated with JSC-1, only naphthalene and a 3-ringed PAH ( $m/z$  178) are detectable. The increased level of condensation at the higher temperature is indicated by the lack of alkylated aromatic compounds. No compounds with a response allowing definite identification were found where FC-8 had been heated

in the absence of JSC-1 at 550 or 700 °C. It is also possible that the analytical pyrolysis temperature of 600 °C was not sufficient to completely access the refractory carbonaceous phase formed by heating at 700 °C.

### 3.2. *Polymers: Poly( $\epsilon$ -caprolactone)*

#### 3.2.1. *Solvent extracts*

The solvent extracts of PCL heated with and without JSC-1 at 250 °C both show systematic breakdown products, and do not show any major differences (Fig. 1a). Analysis of the solvent extracts at this step is complicated by the solubility of the polymers in solvent, which can break down in the inlet of the GC. This is confirmed by the generation of the same products where PCL mixed with JSC-1 was subject to solvent extraction without prior heating. Following heating at 400 °C, a more complex assemblage of polymer fragments is produced. However following heating at 550 °C, the dominant response in the solvent extracts of both samples is pyrene ( $m/z$  202). Polycyclic aromatic compounds up to  $m/z$  290 are detectable in the solvent extract of PCL heated without JSC-1 (Fig. 1a). In the solvent extract following heating at 700 °C without JSC-1, a range of aromatic compounds were detected including naphthalene, biphenyl, fluoranthene, pyrene, and an aromatic compound with  $m/z$  252. There were no peaks in the total ion

chromatogram of the solvent extract from the experiment where PCL was heated with JSC-1 at 700 °C.

### 3.2.2. *Pyrolysis products of residues*

Following heating at 250 °C, 2-oxepanone and hexenoic acids indicate the presence of surviving PCL polymer. These are products of unzipping reactions and *cis*-elimination of the polymer (Persenaire *et al.*, 2001; Aoyagi *et al.*, 2002). Comparing the pyrolysis-GC-MS results of PCL heated with and without JSC-1 present at 250 °C, reveals that there is a slightly greater diversity of products released from the residual polymer when JSC-1 is present (Fig. 1b).

At 400 °C, pyrolysis-GC-MS generates a much greater diversity of products from the residual polymer. The product with the greatest response for both the sample heated with JSC-1 and the one without was hexenoic acid. The broad ‘fingerprint’ of the chromatograms was similar between the two, however the sample heated with JSC-1 showed greater responses for benzene and alkylbenzenes relative to hexenoic acid than the sample without (Fig. 1b). This indicates that aromatisation of the polymer is facilitated by the presence of the mineral matrix. At 550 °C, aromatisation of both samples is more complete. However, the proportion of di- and trimethylnaphthalenes and fluorene relative to naphthalene is much greater in the sample heated with JSC-1 than the one without (Fig. 1b). Responses at *m/z* 178 that correspond to the 3-ring PAH anthracene and phenanthrene are minor in

the pyrolysis-GC-MS chromatograms for both samples, and 4-ring or larger aromatic PAHs were not detected. This indicates that whilst relatively large free aromatic compounds are released during the heating experiments, the polymer residue is composed of smaller aromatic units.

After heating PCL without JSC-1 at 700 °C, only benzene and a response at  $m/z$  178 are detectable in the pyrolysis-GC-MS total ion chromatogram, indicating that the polymer residue has been further condensed relative to the previous temperature step. In the pyrolysis-GC-MS total ion chromatogram for the sample of PCL heated with JSC-1, benzene, naphthalene, biphenyl, and anthracene or phenanthrene are detectable, along with minor responses for alkylated aromatic compounds.

### 3.3. *Polymers: Polyhydroxybutyrate*

#### 3.3.1. *Solvent extracts*

The thermal decomposition of PHB follows a broadly similar pattern to that of PCL (Fig. 2a). After heating at 250 °C, the solvent extracts of PHB with and without JSC-1 show the presence of crotonic acid and its oligomers, which are produced from the polymer as a result of *cis*-elimination reactions. Crotonic acid is recognized by characteristic  $m/z$  68, 69 and 86 (Aoyagi *et al.*, 2002). However,

these products are again likely to be at least partly the result of solubilised polymer breaking down in the heated GC inlet.

At 400 °C, both the pyrolysis-GC-MS and solvent extraction chromatograms reveal a wide range of products with an unresolvable complex mixture (Figs. 2a and b). However, there are some differences in the responses of individual compounds in the solvent extracts. A peak with signals at  $m/z$  67, 136, 154 gives a greater relative response in the PHB heated without JSC-1. This compound gives a major response in the pyrolysis-GC-MS chromatogram where JSC-1 was present. This may be due to incomplete extraction of the compound from the minerals by solvent extraction. Another two peaks, one with signals at  $m/z$  99 and the other at  $m/z$  110 and 152 are prominent in the solvent extract of the sample heated with JSC-1, but are minor peaks in the PHB sample heated in isolation (Fig. 2a). After heating of PHB in isolation at 550 °C, the solvent extract is very similar to that of PCL heated in isolation at the same temperature, with a broad range of condensed and alkylated aromatic compounds present. The key responses are for naphthalene, methylnaphthalenes, and pyrene. However, the solvent extract of PHB heated with JSC-1 at 550 °C shows a different pattern to that of PHB heated on its own. Where JSC-1 is present, pyrene is a weak response, and methylphenol is a strong response relative to naphthalene. Where JSC-1 is absent, pyrene is a strong response, and methyl phenol is a weak response relative to naphthalene. The polymer has interacted with the mineral

matrix to produce a different distribution of organic products. As with PCL, low responses of simple aromatic compounds are detected in the solvent extract chromatograms and pyrolysis-GC-MS chromatograms of PHB heated both with and without JSC-1 at 700 °C.

### 3.3.2. *Pyrolysis products of residues*

Pyrolysis-GC-MS of the residue of PHB heated with JSC-1 at 250 °C also shows crotonic acid; no crotonic acid was detected by pyrolysis-GC-MS where PHB was heated in isolation. The pyrolysis-GC-MS chromatograms of the residues of the PHB heated at 550 °C also show a similar pattern to the PCL samples. After heating with JSC-1, the residual PHB polymer gives a greater pyrolysis-GC-MS response for di- and trimethylnaphthalenes and fluorene relative to naphthalene than when PHB is heated in isolation. There is also a strong response for methylphenol relative to naphthalene in the pyrolysate where JSC-1 is present, reflecting the strong methylphenol response in the corresponding solvent extract.

## **4. Discussion**

### 4.1. *Alteration of organic materials in a lunar regolith simulant*

We have performed heating experiments to determine the viability of preserving organic compounds in lunar regolith material beneath a lava flow. Particularly, we

have tested to see whether the lunar regolith, simulated by JSC-1 analogue material, has any deleterious effects on the preservation of organic materials under heating.

For the free organic compounds, JSC-1 does not appear to have any dramatic destructive effect. As in the experiments without JSC-1, all compounds except atrazine, squalene and stigmasterol are detectable after the 400 °C experiment. FC-8 comprises a variety of terrestrial biomarker compounds; the fact that these compounds can survive at high temperature under vacuum in the presence of lunar regolith analogue lends credibility to the possibility that biomarkers in terrestrial meteorites from the early Earth could remain preserved on the Moon in regolith at tens of centimetres depth under lava flow units.

For the polymers PCL and PHB, increasing the temperature of heating firstly apparently causes the compounds to depolymerise into monomers and oligomers at 250 °C, a process which is well characterised (Persenaire *et al.*, 2001; Aoyagi *et al.*, 2002). These systematic breakdown products can be seen in both the solvent extracts and the residues (Figs. 1 and 2). However, due to the nature of the analytical techniques employed, it is likely that some of the detected compounds are not primary products from the experiments, but instead result from breakdown of the solubilised polymer in the hot (250 °C) GC inlet. At 400 °C, breakdown of the polymers is more complete, with a wide variety of smaller molecules being

generated. At 550 °C, the polymers are charred i.e., they have been extensively aromatised by heating in the absence of oxygen, and aromatic hydrocarbons are the main responses from both the solvent extracts and pyrolysis of the residues. Charring is almost complete at 700 °C, with low responses for simple aromatic hydrocarbons and a loss of compound diversity compared with the previous heating step.

It can be seen in the back-to-back comparisons of the chromatograms in Figures 1 and 2 that the presence of JSC-1 influences the types and proportions of compounds produced at different temperatures. The pyrolysis of the residues where JSC-1 is present shows a greater variety of responses. In the pyrolysis residues at 400 °C, JSC-1 appears to be promoting aromatisation; benzene and alkylbenzenes are prominent relative to other responses in the chromatograms of the residues where JSC-1 was present. With both PCL and PHB, after heating with JSC-1 at 550 °C the residual polymer, when subject to pyrolysis-GC-MS, releases a greater proportion of alkylated naphthalenes relative to naphthalene than when the polymers were heated in isolation. The distribution and responses of soluble aromatic compounds generated from PHB and PCL heated in isolation at 550 °C are very similar, however, it can be seen that the presence of JSC-1 alters the distribution of responses of the generated compounds (Figs. 1a and 2a). It is apparent that the presence of the JSC-1 material affects the ability of the dichloromethane:methanol solvent to efficiently extract soluble organic

compounds from the samples after the heating experiments, complicating interpretation of the results. However, particularly in the case of the aromatic compounds generated at the 550 °C step for the synthetic polymers, a range of distributions of responses is seen which cannot be attributed to solvent extraction efficiencies, and is instead a result of organic-mineral interactions during the heating experiments. The chromatograms of the PCL and PHB polymers at the 700 °C step show similar behaviour. Where JSC-1 was absent, there are readily detectable aromatic compounds in the solvent extracts, however, this is not the case where JSC-1 was present. Conversely, a wider variety of aromatic compounds are present in the pyrolyzed residues of the polymers where JSC-1 was present. The data indicate that the mineral and glass surfaces of JSC-1 are adsorbing and retaining the products of aromatisation. The JSC-1 lunar analogue consists of a mixture of different mineral types, the main constituents being feldspar, pyroxene, and olivine. The catalytic properties of these minerals have been investigated in a number of industrial and natural settings (*e.g.*, Rapagnà *et al.*, 2000; Demiral and Şensöz, 2008; Tian *et al.*, 2013). However, for this study we have simply focused on the overall effects of the natural JSC-1 mineral assemblage as a representative of reactions that may occur in the lunar regolith.

#### 4.2. *General mechanism*

The results from the heating experiments with free compounds and with polymers can be synthesised into a general mechanism (Fig. 3). The lunar regolith simulant appears to promote polymerisation and cross linking (reflected by the production of more diverse pyrolysis products at lower heating experiment temperatures) and retard degradation and depolymerisation (indicated by the continued production of pyrolysis products at high heating experiment temperatures; the mineral surface must be acting as a protective adsorbent). The lunar regolith with a similar basaltic chemistry, glass content, and grain size as the JSC-1 simulant may, therefore, aid in the preservation of its organic matter when encapsulated and heated by lava flows.

#### 4.3. *Preservation of organic materials in a lava-capped regolith layer*

Thermal alteration of organic matter can be considered to have both positive and negative impacts in the context of preservation. Thermal alteration of an assemblage of organic molecules destroys information about the nature of the original material, but the process of aromatisation and polymerisation renders the organic material more resistant to damaging environmental processes. It may in fact be a requirement to have a moderate level of alteration of organic material to

a more robust aromatic structure in order to ensure long-term survival in an energetic environment.

An ideal scenario for the preservation of organic materials within palaeoregolith layers has a number of competing factors. Whilst it would be advantageous to reduce the surface exposure time of organic-containing rock fragments to a minimum to protect from radiation and impacts, there nevertheless needs to be sufficient elapse of time in order to build up a regolith layer thick enough to effectively insulate against the overlying lava flow (Fagents *et al.*, 2010; Rumpf *et al.*, 2013). There also needs to be time to allow the organic-containing material to build up in the regolith to a concentration sufficient that a drill core (or other sampling technique) will have a reasonable chance of intercepting a useful quantity of the material. Understanding the role of radiation in the alteration of organic matter will, therefore, be extremely informative in refining the model. It has been well established that ionizing radiation can have a variety of effects on organic materials (Lewan and Burchardt, 1989; Bernstein *et al.*, 2003; Court *et al.*, 2006; Kminek and Bada, 2006; Dartnell, 2011).

Duration of heating in the lava flow palaeoregolith model is another key consideration. Modelling work (Fagents *et al.*, 2010; Rumpf *et al.*, 2013) shows that the regolith can remain at temperatures substantially elevated above ambient for timescales up to months. This is substantially longer than the timescales

employed in the experiments described here. The minimum lava flow thickness observed on the Moon is approximately 1 m (Vaniman *et al.*, 1991), however, many lunar lava flows are known to be substantially thicker than this. Thicker lava flows would increase both the duration of heating and the depth of heating into the underlying regolith (Fagents *et al.*, 2010; Rumpf *et al.*, 2013). Thicker lava flows also have the potential to overprint the thermal profile of thinner lava flows and regolith horizons lying beneath. These factors would increase the degree of thermal alteration of the organic matter compared to a thinner flow. Although not explored in this work because of the generally accepted anhydrous nature of lunar surface materials in regoliths between latitudes  $<70^\circ$ , water may also play a role in preservation. In terrestrial environments, the presence of water has a substantial effect on how organic matter is preserved (*e.g.*, Killops and Killops, 2005). This also extends to space environments: the parent asteroidal bodies from which type 1 and 2 carbonaceous chondrites originated have experienced varying levels of aqueous alteration which has affected the composition and structure of the organic material (*e.g.*, Sephton *et al.*, 2004b). The Moon is essentially an anhydrous environment, although local sources of hydration may be provided by the hydrated silicate minerals of meteorites (Court and Sephton, 2014), hydrated volcanic pyroclastic glass beads (Hauri *et al.*, 2011; Saal *et al.*, 2008, 2013), indigenous minerals like apatite, and implanted solar

wind (Pieters *et al.*, 2009; for reviews see Anand *et al.*, 2014, and Robinson and Taylor, 2014).

When subjected to heating by volcanic or other processes, water can be driven from these minerals. This water can then interact with other materials within the host regolith. Recent observations have suggested the presence of water ice in permanently shadowed craters at the poles of the Moon (Colaprete *et al.*, 2010). This water, which may be exogenous or endogenous in origin, could host organic compounds (Pierazzo and Chyba, 1999; Lucey, 2000). It is, therefore, important to take the role of water into account when considering the preservation of organic materials on the Moon. For the experiments in this study, although vacuum sealing of the samples before heating will have removed the majority of the water from the vessel, it is likely that minor amounts of atmospheric water will have remained adsorbed on mineral surfaces. Water may also have been released from clays in the JSC-1 analogue, however since clay is a minor mineral phase (McKay *et al.*, 1994), the quantity of water released from this source is assumed to be low. In the case of the synthetic polymers PCL and PHB, water would be eliminated from the polymer structure during thermal degradation (Persenaire *et al.*, 2001) and would be available for reaction with other products or the polymer residue.

## **5. Conclusions**

We have shown that organic matter is capable of surviving within a chemical and physical analogue of the lunar regolith, even when subjected to a demanding thermal regime intended to simulate the effects of an overlying flow of lava. However, we have seen that the aromatisation of polymers is affected by the presence of the mineral matrix, producing a different distribution of responses for individual products than where compounds were heated on their own.

Using a range of heating temperatures intended to simulate different depths in the regolith beneath a lava flow, we have shown that for a 1 m thick flow, organic compounds have the potential to survive in regolith only a few tens of centimetres deep, due to the highly insulating properties of the lunar soil. These include compounds of biological origin, indicating the potential for biomarkers to be preserved in terrestrial meteorites on the Moon. Our work suggests that the palaeoregolith of the lifeless Moon may be a valuable location to search for records of organic chemical evolution in the early solar system and, perhaps, the transition from prebiotic to biotic processes on the early Earth.

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## **Author Disclosure Statement**

The authors declare they have no competing interests.

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Compound	Compound type	Formula	Molecular Weight	Properties relevant to this study
Atrazine	Triazine	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	215.68	Control compound
Hexadecane	Alkane	C <sub>16</sub> H <sub>34</sub>	226.44	Terrestrial biomarker
Phytane	Isoprenoid	C <sub>20</sub> H <sub>42</sub>	282.55	Terrestrial biomarker
Squalene	Isoprenoid	C <sub>30</sub> H <sub>50</sub>	410.72	Terrestrial biomarker
Coprostane	Sterane	C <sub>27</sub> H <sub>48</sub>	372.67	Terrestrial biomarker
Stigmasterol	Sterol	C <sub>29</sub> H <sub>48</sub> O	412.69	Terrestrial biomarker
Anthracene	Aromatic	C <sub>14</sub> H <sub>10</sub>	178.23	Meteoritic (carbonaceous type)
Pyrene	Aromatic	C <sub>16</sub> H <sub>10</sub>	202.25	Meteoritic (carbonaceous type)

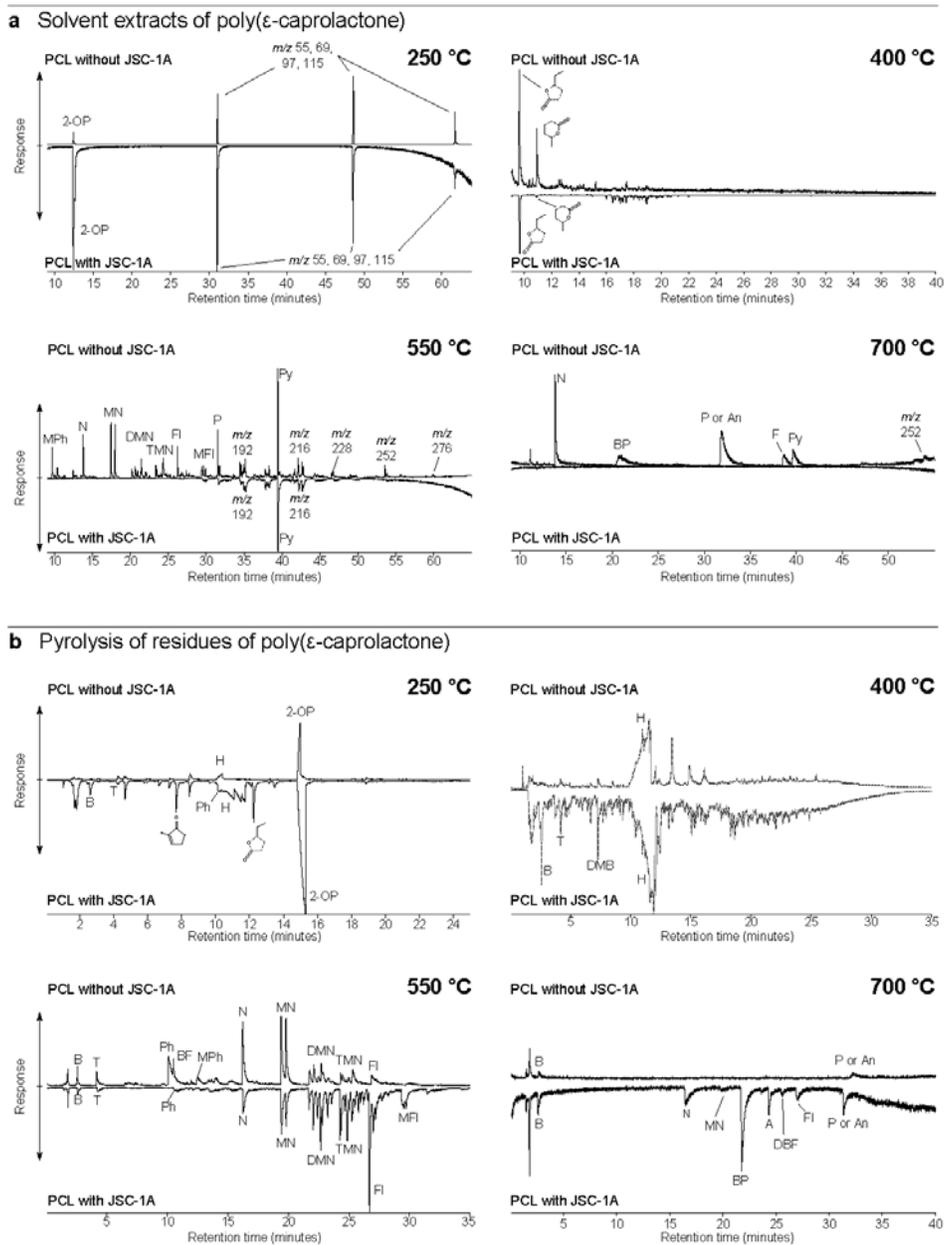
**TABLE 1.** Free organic compounds used in heating experiments.

Temperature of heating experiment (°C)	Matrix type	Mass of matrix (mg)	Compounds detected	
			Solvent soluble	Pyrolysis
20	None	-	n.d.	n.d.
	JSC-1	20.8	Hex, Phy, Cop, An, Py, At, Sq, Sti	n.d.
250	None	-	Hex, Phy, Cop, An, Py, Sq	Phy
	JSC-1	27.6	Hex, Phy, Cop, An, Py	Hex, Phy
400	None	-	Hex, Phy, Cop, An, Py, Breakdown products of Sti, aliphatic fragments.	Hex, Phy
	JSC-1	22.5	Hex, Phy, Cop, An, Py	Hex, Phy, An (tentative), TMN and cyclic, aromatic, and aliphatic fragments (tentative)
550	None	-	An, Py, PAH <i>m/z</i> 192	None
	JSC-1	28.3	An, Py	MN, DMN, TMN (tentative), PAH <i>m/z</i> 178
700	None	-	None	None
	JSC-1	31.7	None	N, PAH <i>m/z</i> 178

**TABLE 2.** Summary of the products of the heating experiments using FC-8 (see Table 1). An = anthracene; At = atrazine; Cop = coprostane; DMN = dimethylnaphthalene; Hex = hexadecane; MN = methylnaphthalene; N=

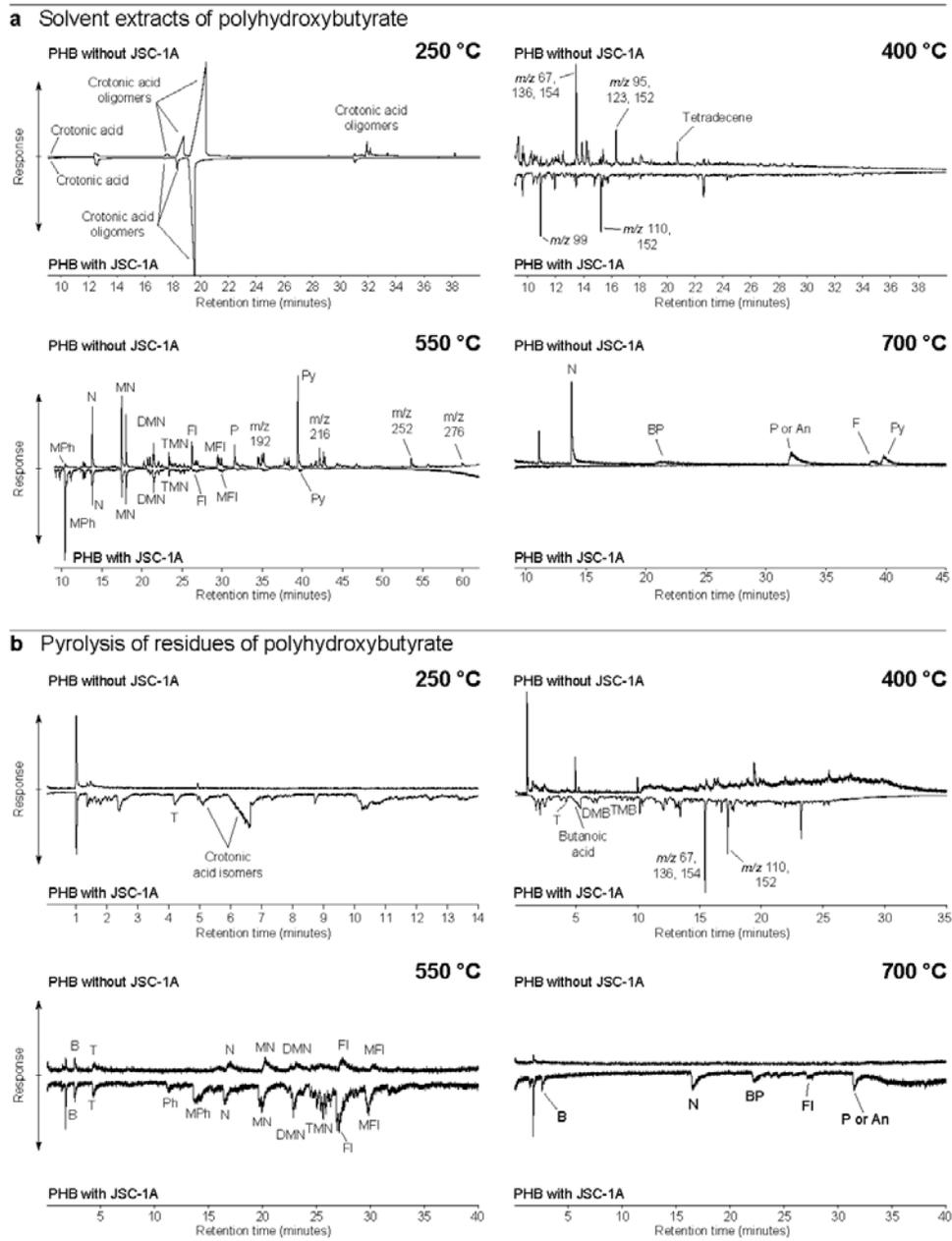
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naphthalene; PAH  $m/z$  # = polycyclic aromatic hydrocarbon with  $m/z$  ratio for main response indicated; Phy = phytane; Py = pyrene; Sq = squalene; Sti = stigmasterol; TMN = trimethylnaphthalene; n.d. = not determined.



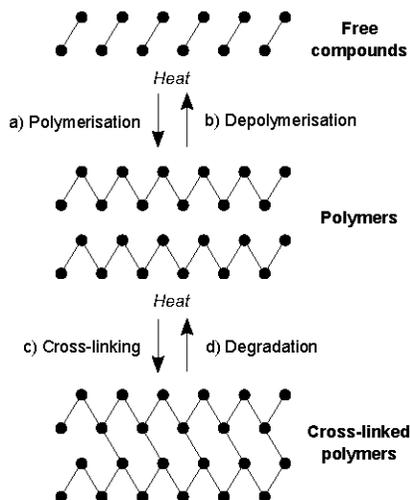
**FIG. 1.** Chromatograms of (a) the solvent extracts and (b) the pyrolyzed residues of poly( $\epsilon$ -caprolactone). Chromatograms are displayed back-to-back, with the

chromatogram where JSC-1 was absent on top, and where it was included underneath. The temperature of the heating experiment is shown in the upper right for each chromatogram couple. At 250 °C, the systematic breakdown products of PCL are detected in the extracts and residues, before more complete breakdown of the polymer structure at 400 °C. At 550 °C the polymer has charred, with polycyclic aromatic hydrocarbons (PAHs) as the dominant responses. However, the responses of the compounds in both the solvent extracts and the residues varies between the experiment where JSC-1 was present and the experiment where it was absent. At 700 °C there are only small responses for mainly non-alkylated PAHs. Compound labels: 2-OP = 2-oxepanone; A = acenaphthene; An= anthracene; B = benzene; BF = benzofuran; BP = biphenyl; DBF = dibenzofuran; DMB = dimethylbenzene; DMN = dimethylnaphthalenes; F = fluoranthene; Fl = fluorene; H = hexenoic acids; MFl = methylfluorenes; MN = methylnaphthalenes; MPh = methylphenol; N = naphthalene; P = phenanthrene; Ph = phenol; Py = pyrene; T = toluene; TMN = trimethylnaphthalenes. Other compounds of note are labelled with structures or principal mass spectral  $m/z$  responses. The vertical axes of the chromatograms have been scaled to allow easier comparison; responses are non-quantitative.



**FIG. 2.** Chromatograms of (a) the solvent extracts and (b) the pyrolyzed residues of polyhydroxybutyrate. Chromatograms are displayed back-to-back, with the

chromatogram where JSC-1 was absent on top, and where it was included underneath. The temperature of the heating experiment is shown in the upper right for each chromatogram couple. As for poly( $\epsilon$ -caprolactone), systematic breakdown products occur in the extracts and residues at 250 °C, before more complete breakdown takes place at 400 °C. At this temperature, there are some differences in the proportions of the response of products on the chromatograms, indicating that the presence of JSC-1 is having an effect on the thermal degradation of the polymer. At 550 °C, polycyclic aromatic hydrocarbons (PAHs) are the main responses in the extracts and residues, with PAHs up to  $m/z$  290 detectable. As with the PCL polymer, the presence of JSC-1 has affected the distribution of responses of compounds in both the extract and the residue. At 700 °C, low responses of simple PAHs are detectable. An = anthracene; BP = biphenyl; DMB = dimethylbenzene; DMN = dimethylnaphthalenes; F = fluoranthene; Fl = fluorene; MFl = methylfluorene; MN = methylnaphthalenes; MPh = methylphenol; N= naphthalene; P = phenanthrene; Ph = phenol; Py = pyrene; T = toluene; TMB = trimethylbenzene; TMN = trimethylnaphthalene. Other compounds of note are labelled with key mass spectral  $m/z$  responses. The vertical axes of the chromatograms have been scaled to allow easier comparison; responses are non-quantitative.



**FIG. 3.** Schematic summarising the processes occurring during heating of the organic compounds. The relevant chemical reactions can be divided into four processes. a) polymerisation of free compounds into polymers, b) depolymerisation of polymers into free compounds and gases, c) cross linking of polymers to form more intractable organic residues and d) degradation of cross linked polymers into polymers, fragments of polymers (oligomers) or free compounds and gases.