

# Insights into the nature of cometary organic matter from terrestrial analogues

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**Abstract:** The nature of cometary organic matter is of great interest to investigations involving the formation and distribution of organic matter relevant to the origin of life. We have used pyrolysis–Fourier transform infrared (FTIR) spectroscopy to investigate the chemical effects of the irradiation of naturally occurring bitumens, and to relate their products of pyrolysis to their parent assemblages. The information acquired has then been applied to the complex organic matter present in cometary nuclei and comae. Amalgamating the FTIR data presented here with data from published studies enables the inference of other comprehensive trends within hydrocarbon mixtures as they are progressively irradiated in a cometary environment, namely the polymerization of lower molecular weight compounds; an increased abundance of polycyclic aromatic hydrocarbon structures; enrichment in  $^{13}\text{C}$ ; reduction in atomic H/C ratio; elevation of atomic O/C ratio and increase in the temperature required for thermal degradation. The dark carbonaceous surface of a cometary nucleus will display extreme levels of these features, relative to the nucleus interior, while material in the coma will reflect the degree of irradiation experienced by its source location in the nucleus. Cometary comae with high methane/water ratios indicate a nucleus enriched in methane, favouring the formation of complex organic matter via radiation-induced polymerization of simple precursors. In contrast, production of complex organic matter is hindered in a nucleus possessing a low methane/water ration, with the complex organic matter that does form possessing more oxygen-containing species, such as alcohol, carbonyl and carboxylic acid functional groups, resulting from reactions with hydroxyl radicals formed by the radiolysis of the more abundant water. These insights into the properties of complex cometary organic matter should be of particular interest to both remote observation and space missions involving *in situ* analyses and sample return of cometary materials.

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**Key words:** comets, cometary organic matter, irradiated organic matter, infrared spectroscopy.

## Introduction

The nature of cometary organic matter is of great interest to investigations into the formation and distribution of organic matter throughout the solar system. Studies of comets reveal conditions in the solar nebula and offer insights into the ability of comets to deliver volatiles and biologically useful compounds to the surfaces of terrestrial planets. The bulk composition of the typical comet has been estimated as a 1:1:1 mass ratio of water:silicates:carbonaceous molecules (e.g. Huebner 2002) and estimated fluxes of comets to the early Earth imply a role in providing the raw materials for an incipient biosphere (Greenberg 1993). Yet our understanding of organic chemical evolution on these complex objects is limited and new insights are required.

Comets are likely to be physically and chemically heterogeneous. Recent spacecraft missions have identified a layered stratigraphy on the nucleus of Comet 9P/Tempel (Kadono *et al.* 2007; Thomas *et al.* 2007). Laboratory simulations, modelling and observations have indicated the existence of a metre-thick carbonaceous layer at the surface of cometary nuclei (Hudson & Moore 1997; Kissel *et al.* 1997; Cottin *et al.*

1999; Strazzulla 1999; Nelson *et al.* 2004; Oberst *et al.* 2004; Kadono *et al.* 2007; Thomas *et al.* 2007). Observations of Comets Wild 2 and Borrelly imply a physical discontinuity at around 100 m depth and crater terracing on a 10-m scale (Brownlee *et al.* 2004). In addition, the topography of Comet Tempel 1 shows at least three layers of 50–200 m thickness with various thinner units also evident (Kadono *et al.* 2007; Thomas *et al.* 2007). Given the substantial organic contents of comets, these physical layers are very likely to correlate with heterogeneities in organic chemistry. Our current understanding of cometary organic matter comes from three principle sources: (i) remote spectroscopy (e.g. Cottin *et al.* 1999), (ii) the material returned to Earth from Comet Wild 2 by the Stardust spacecraft (e.g. Sandford *et al.* 2006) and (iii) laboratory-based irradiation of simulated cometary ices (e.g. Bernstein *et al.* 1997; Strazzulla 1997; Moore & Hudson 1998; Strazzulla & Palumbo 1998; Hudson & Moore 1999; Strazzulla 1999), using ultraviolet (UV) and ion irradiation to simulate the effects of the solar UV, solar energetic particle (SEP) and galactic cosmic ray (GCR) fluxes.

Here, we propose a fourth source of information. For comets far from the Sun, the dominant energy source controlling the

evolution of organic matter is ionizing radiation, such as the GCR and SEP fluxes. Hence, to understand the nature and evolution of complex organic matter in comets, it is essential to appreciate the effects of ionizing radiation on complex organic matter.

We have investigated these effects using naturally occurring irradiated bitumens, hereafter referred to as terrestrial cometary organic matter analogues (T-COMA). Studying the effects of ionizing radiation on mixtures of organic matter in different environments yields clues that can be applied to the radiation-altered organic matter in cometary nuclei and comae. Although almost all terrestrial organic matter is biological in origin and has experienced little irradiation, giving it only limited utility as an analogue to abiotic organic matter, many terrestrial bitumens contain a radiation source in the form of incorporated radioelements, such as uranium and thorium. Analyses of these can reveal processes and effects of irradiation common to both terrestrial organic matter and abiotic cometary materials. In addition, rare samples of abiotic terrestrial organic matter can act as more direct analogues to cometary organic matter. Both types of T-COMA have been investigated here. Our data also allow predictions about the nature of the organic matter formed by irradiation of simple species within the nucleus from studies of the volatiles present in the cometary coma. A coma with a high methane/water ratio indicates a nucleus enriched in methane, while a low methane/water ratio indicates one with less methane and more water. Our T-COMA can be used to infer the complex organic products of the irradiation of mixtures of simple volatiles of varying methane/water ratios, yielding clues regarding the nature and abundance of complex organic present in cometary nuclei possessing comae of different compositions.

In this paper, we assess the utility of irradiated terrestrial organic matter to act as an analogue of cometary organic matter by (i) attempting to equate Fourier transform infrared (FTIR) spectroscopy data of pyrolysis products from terrestrial analogues of cometary organic matter with that from cometary comae and (ii) relating trends in the composition of thermally degraded volatile material to features observed in the solid starting materials. The findings have implications for the interpretation of data from future cometary missions including the Rosetta mission that is en route to Comet Churyumov-Gerasimenko, to deploy the Philae lander that will conduct *in situ* analyses.

## Methodology

### Samples

We have investigated a range of T-COMA, terrestrial analogues to the organic matter found in cometary nuclei and comae. Our samples consist of a suite of ten terrestrial bitumens, previously characterized by Court *et al.* (2006, 2007). These bitumens derive from naturally occurring migrated hydrocarbons, but differ in terms of the nature of the source hydrocarbons, the level of radiolytic alteration endured and the influence of water and oxidation on the final products. The ten samples are divided into three groups, based

upon interpretations of analyses regarding their origin and evolution (Court *et al.* 2006, 2007). A single sample from each group has been subjected to analysis by quantitative pyrolysis-FTIR spectroscopy (Court & Sephton 2009a, b).

### Non-irradiated organic matter

As a benchmark of non-irradiated organic matter, a radioelement-free (according to electron microprobe analyses) non-irradiated bitumen, derived from migrating organic liquids of biological origin was obtained from a hydrocarbon vein in a conglomerate at the base of the Old Red Sandstone near Dingwall, Scotland (Parnell 1985). This bitumen contains abundant aliphatic hydrocarbons and is a poor analogue to abiotic cometary organic matter by itself, but comparisons between it and irradiated organic matter can reveal effects expected to occur in irradiated cometary organic matter.

### Irradiated organic matter with water

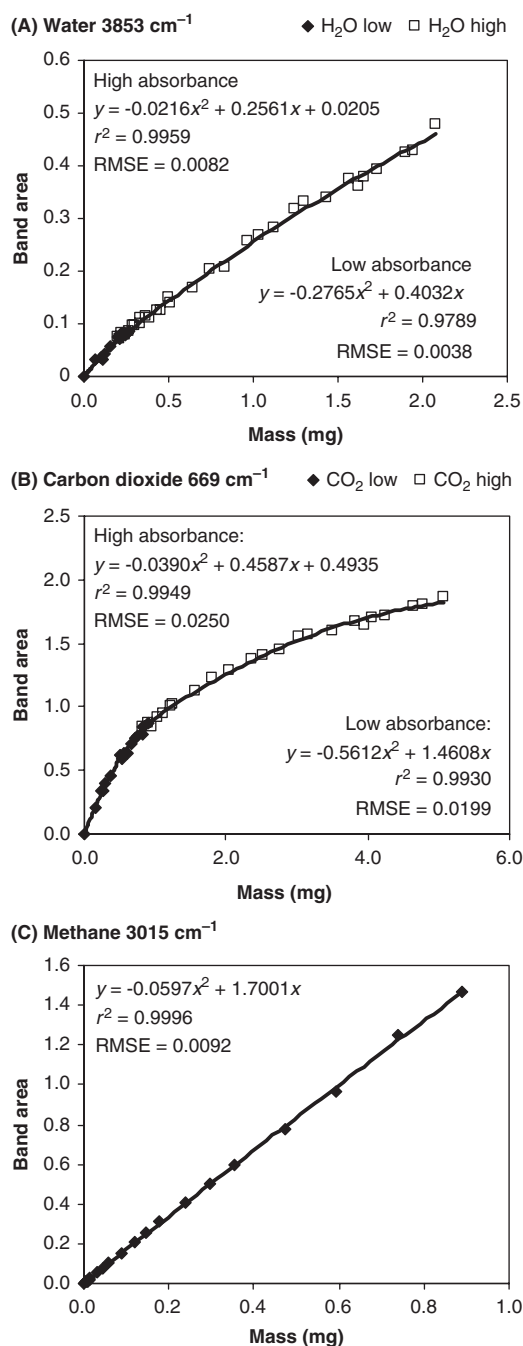
Solid bitumens, formed from organic liquids of biological origin, can be collected from veins in the Archaean meta-sediments of the Moonta copper mines of South Australia (Radcliff 1906; Davidson & Bowie 1951). The liquid hydrocarbons solidified as a result of chemical changes induced by irradiation from incorporated uranium and/or thorium. A comparison of this sample with the non-irradiated bitumen from Dingwall can be used to infer the effects of radiolytic alteration in the presence of water (Court *et al.* 2006).

### Irradiated organic matter without water

Bitumens interpreted to have formed by the polymerization of methane in water-poor conditions following irradiation can be collected from Příbram in the Czech Republic, where uraniumiferous Permian hydrothermal deposits occur along the boundary between the Central Bohemian Pluton and its adjacent aureole (Kříbek *et al.* 1999). The origin of this bitumen is revealed by its carbon isotopic composition, field relationships (Grip & Ödman 1944; Landais *et al.* 1993; Kříbek *et al.* 1999) and data generated by the analyses of Court *et al.* (2006, 2007). This sample is a rare example of terrestrial bitumen of abiotic origin; its formation by the radiation-induced processing of methane makes it an excellent candidate to be a terrestrial analogue to cometary organic. The Příbram bitumen therefore provides insights into how the radiation-induced polymerization and evolution of very simple organic compounds proceeds in the absence of water.

### Quantitative pyrolysis-FTIR spectroscopy

Bitumen samples were subjected to flash pyrolysis, with the products of pyrolysis being analysed using FTIR spectroscopy, using the technique outlined by Court & Sephton (2009a, b). Briefly, samples of bitumen were pyrolysed using a platinum coil heated to 610 °C at 20 °C millisecond<sup>-1</sup> and held for 15 seconds, in a helium atmosphere within a CDS Analytical Brill Cell™, attached to a Thermo-Nicolet 5700 FTIR spectrometer and a CDS Analytical Pyroprobe 5200. Samples were loaded into quartz pyrolysis tubes and immobilized by plugging the ends with quartz wool, both previously cleaned



**Fig. 1.** Calibration curves for water, carbon dioxide and methane. The equations describe the curves formed by the data, along with the correlation coefficient  $r^2$ , while the root means square error (RMSE) describes the difference between the measured data points and those predicted by the equations. A single equation could not be found to satisfactorily describe the water and carbon dioxide data, so two quadratic equations are shown, each describing different areas of the data, as indicated by the different data point markings  $\blacklozenge$  and  $\square$ . From Court & Sephton (2009a).

by baking in air at 450 °C. The temperature of the Brill Cell was held at 250 °C to hinder condensation of the pyrolysis products. The Brill Cell was purged with helium after loading the sample, but not during pyrolysis, to allow the accumulating

pyrolysate to produce stronger infrared absorbance bands. Background spectra were acquired before, and subtracted from, each sample spectrum. The background was accumulated from 64 individual spectra; the sample spectra were accumulated from 256 spectra. Both sample and background spectra were produced at a resolution of 4  $\text{cm}^{-1}$  using a deuterated triglycine sulphate detector. The masses of the samples were recorded before and after pyrolysis, allowing the results to be understood in terms of production per unit mass, and to identify the mass lost upon pyrolysis. Quantification of the yields of water and carbon dioxide was achieved using calibration curves constructed from FTIR measurements of known masses of these compounds (Fig. 1).

## Results

### *Quantitative pyrolysis–FTIR of complex hydrocarbons (Dingwall)*

Pyrolysis of the non-irradiated organic matter from Dingwall (Fig. 2(a) and Table 1) produced substantial yields of water (0.8 wt%) and carbon dioxide (1.0 wt%, respectively), as shown by absorption around 3500–4000  $\text{cm}^{-1}$  for water, and around 670  $\text{cm}^{-1}$  and 2300  $\text{cm}^{-1}$  for carbon dioxide. There is also a small response from methane around 3015  $\text{cm}^{-1}$ , difficult to quantify because of strong superimposed absorption from aliphatic hydrocarbons around 2900–3000  $\text{cm}^{-1}$ . No absorption from bonds such as C–O, C=O or O–H is detectable, indicating an absence of significant amounts of alcohol, carbonyl or carboxylic acid functional groups, representing a bitumen that has not been subjected to significant oxidation via, for example, reaction with hydroxyl ( $\text{OH}^\cdot$ ) radicals.

### *Quantitative pyrolysis–FTIR of organic matter irradiated with water (Moonta)*

Pyrolysis of the organic matter irradiated in the presence of water from Moonta (Fig. 2(b) and Table 1) also yielded substantial abundances of water and carbon dioxide (8.9 and 14.8 wt%, respectively). However, in contrast to the non-irradiated bitumen from Dingwall, no absorption from methane around 3015  $\text{cm}^{-1}$  or from aliphatic hydrocarbons around 2900–3000  $\text{cm}^{-1}$  is apparent. The absence of aliphatic material in the products of pyrolysis suggests its absence in the solid bitumen, implying that the Moonta bitumen possesses a structure with abundant oxygen-containing species, such as hydroxyl, carbonyl and carboxyl groups, but few labile aliphatic species.

### *Quantitative pyrolysis–FTIR of organic matter irradiated without water (Přibram)*

Pyrolysis of the organic matter irradiated in water-poor conditions from Přibram (Fig. 2(c) and Table 1) produced a yield of water (4.5 wt%) intermediate to those of the samples from Dingwall and Moonta, and a yield of carbon dioxide (2.2 wt%) similar to that of the Dingwall sample. Abundant methane was produced, with a yield of 2.6 wt%. No absorption resulting from aliphatic methyl or methylene groups was

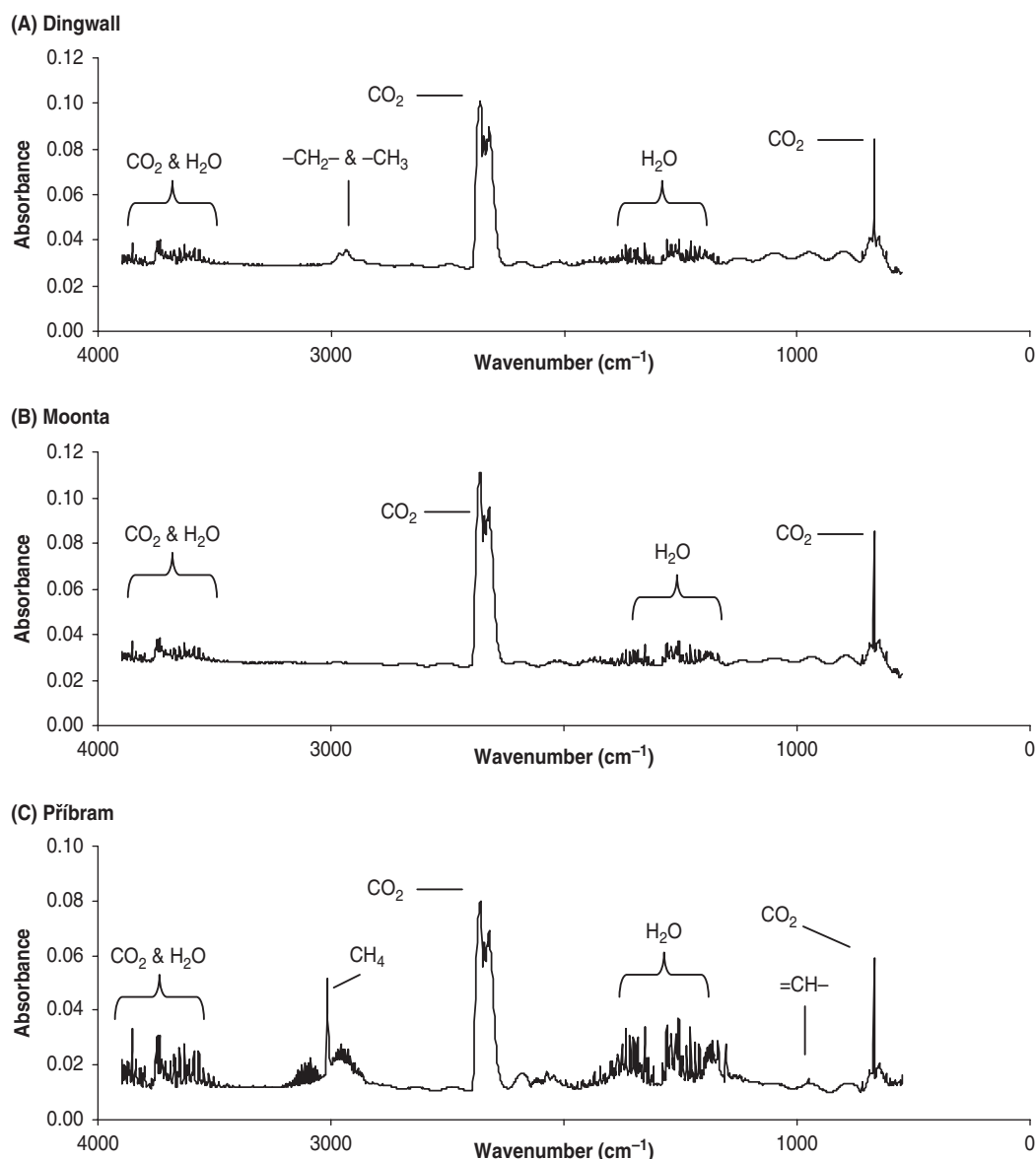


Fig. 2. FTIR spectra of the pyrolysis products of the T-COMA samples.

detected, but the pyrolysate contained some species with alkene ( $=\text{CH}-$ ) bonds, causing absorption around  $950\text{ cm}^{-1}$ . These data suggest a parent structure with abundant methane monomers presumably inherited from its ultimate source material.

## Discussion

### *Chemical trends in response to irradiation of terrestrial organic matter*

Pyrolysis–FTIR of these three bitumens reveals the effects of ionizing irradiation on terrestrial organic matter. Pyrolysis of the non-irradiated bitumen from Dingwall produced water, carbon dioxide, some methane and abundant aliphatic hydrocarbons, indicating a bitumen comprised of biologically derived long-chain aliphatic species. In contrast, pyrolysis of

the irradiated bitumen from Moonta produced no methane or aliphatic hydrocarbons. Given that this bitumen formed from migrating biological hydrocarbons (Parnell 1989), a substantial biological aliphatic component would be expected. Its absence can be understood in terms of radiolytic alteration, which has effectively removed or transformed aliphatic material, producing a bitumen dominated by aromatic hydrocarbons (Court *et al.* 2006). Similarly, the detection of abundant water and carbon dioxide in the pyrolysis products of the Moonta bitumen reveals the presence of oxygen-containing organic units, such as ketones, aldehydes and carboxylic acids, reflecting reactions between organic matter and hydroxyl radicals formed by the radiolysis of water (Court *et al.* 2006). Pyrolysis of the third bitumen, from Příbram, yielded markedly different products. Here, the pyrolysis products contain abundant methane but almost no aliphatic hydrocarbons. This stands in contrast to the other irradiated

Table 1. Yields (wt%) of water, methane and carbon dioxide upon pyrolysis of the bitumen samples, as determined using the calibration curves of Fig. 2 (Court & Sephton 2009a)

	Yield (wt%)		
	Water	Carbon dioxide	Methane
Dingwall	0.8	1.0	0.0
Moonta	8.9	14.8	0.0
Příbram	4.5	2.2	2.6

bitumen from Moonta and supports an origin for the Příbram sample by the radiolytic polymerization of methane in a water-poor environment (Court *et al.* 2006).

The data demonstrate that the pyrolysis products of irradiated organic-rich materials depend on the nature of the starting material and on the environment in which the irradiation took place. Pyrolysis of the non-irradiated Dingwall bitumen, formed in the presence of water, yielded aliphatic hydrocarbons, reflecting its biogenic, aliphatic origin. Radiolytic alteration of material similar to the Dingwall bitumen in its original composition, containing biogenic aliphatic hydrocarbons, produced the Moonta bitumen, rich in aromatic hydrocarbons and oxygen-containing functional groups such as ketones, aldehydes and carboxylic acids and yielding, upon pyrolysis, abundant carbon dioxide and water. The Příbram bitumen represents solid organic matter formed by the radiolytic polymerization of methane; its pyrolysis products include abundant methane, in contrast to the other irradiated bitumen from Moonta, but almost no aliphatic hydrocarbons. Moreover, the absence of oxygen-containing functional groups reflects a lack of reactions involving hydroxyl radicals generated by the radiolysis of water. The data indicate that the pyrolysis products of organic matter provide useful information regarding the irradiation history and original composition of the source organic matter.

#### Application to cometary environments

As noted above, the pyrolysis products of organic matter reflect the irradiation history and original composition of the source organic matter. The application of this insight into a cometary environment indicates that material in the cometary coma will reflect the effects of radiolytic processing of its source material in the cometary nucleus. First, however, it is necessary to examine the relationships between cometary environments and the organic matter and volatiles that they contain.

#### The nucleus

A comet approaching perihelion typically includes an active nucleus surrounded by a coma of vapour and particulates. The surface of the nucleus typically possess a very low albedo, 0.04 for Comet Halley, and is processed by ionizing radiation in the form of cosmic rays, SEP and solar UV photons, and by solar heating. Cosmic rays are heavy atomic nuclei with energies up to  $10^{14}$  MeV, although energies of 1000 MeV are more normal, while SEPs are rather less energetic, generally possessing

energies up to a few hundreds of MeV (e.g. Ryan *et al.* 1999). UV photons can penetrate depths measured in micrometres, while SEP can irradiate material at centimetre-scale depths. Most penetrating are cosmic rays, capable of inducing chemical changes in material at a few metres in depth, resulting in irradiation being most intense near the surface and decreasing at depth. The nature of the radiation will also vary with distance from the Sun; while the GCR flux remains roughly constant, the solar UV and SEP fluxes will diminish towards aphelion. The low temperatures of a nucleus, particularly around aphelion, hinder kinetic chemistry, but suprathreshold reactions induced by the impact of energetic ions continue irrespective of the distance from the Sun (e.g. Kissel *et al.* 1997). Closer to the Sun, solar radiation incident upon the dark surface layer heats the interior, vaporizing ices and producing volatiles that can recondense elsewhere inside a porous nucleus, or can escape into the coma.

Radiation incident on the surface of the nucleus drives chemistry in the organic phases present and causes the sublimation and removal of volatile ices. The result is the formation of a low-albedo carbonaceous layer, probably around a metre thick, enriched in silicates and complex organic matter but depleted in volatile ices (Hudson & Moore 1997; Kissel *et al.* 1997; Cottin *et al.* 1999; Strazzulla 1999; Nelson *et al.* 2004; Oberst *et al.* 2004; Kadono *et al.* 2007; Thomas *et al.* 2007). Some of the volatiles sublimed by solar radiation may escape into the coma, but modelling and simulations indicate that sublimation of volatiles from a porous substrate can also cause vapour to flow inwards, subsequently refreezing at depth, forming a dense ice crust beneath a dusty, organic-rich, permeable and volatile-depleted upper layer (Priáznik & Mekler 1991; Podolak & Priáznik 1996; Bar-Nun *et al.* 2007). The scales of these features are rather uncertain; Priáznik & Mekler (1991) estimated that a surface layer of dust and organic matter of millimetre to centimetre scale would exist above a dense crystalline ice layer of metre-scale thickness. Although this is a generalization (spectroscopy of the nucleus of Tempel 1 revealed surface areas containing 3–6% water ice particles; Sunshine *et al.* 2006), stratification undoubtedly exists and provides different chemical environments in which the irradiation of organic material will take place. Near the surface, energetic particles would bombard organic matter in a dry, dusty environment. Deeper, within an icy layer of organics/silicates cemented by condensed water vapour (Bar-Nun *et al.* 2007), or within pristine cometary material, radiolytic alteration of less-concentrated organic matter would occur in the presence of abundant water.

#### Radiation and chemical environments

With the radiation environment and the relative abundances and composition of organic matter and ices varying with depth, a simple history of complex organic matter in a cometary nucleus can be outlined. Initially, relatively simple organic species are embedded with ices and silicates at depth, shielded from radiation. Subsequent perihelia cause vaporization of overlying ices, bringing the organic matter closer to the surface and exposing it to additional ionizing radiation in the

form of GCR and SEP, driving chemistry such as aromatization of aliphatic species and the incorporation of volatiles such as methane and water. Further perihelia result in further erosion and the incorporation of the irradiated organic matter into the dark, volatile-depleted, organic-rich surface crust, where further radiolytic processing occurs. Organic matter initially at depth therefore experiences decreasing volatiles abundances and increasing radiation dose rates as the surface approaches.

These environments can be simplified into two end-members. In the subsurface, material is processed by the attenuated and relatively weak flux of cosmic rays in an environment rich in simple organic molecules. At the surface is a drier, volatile-depleted layer of dusty carbonaceous material, formed via sublimation of ices and the accumulation and further irradiation of more refractory phases such as organic matter and minerals. It was noted among the T-COMA that the abundances of water and methane, two species abundant in comets (Gibb *et al.* 2003), were of particular importance to the nature of the organic material produced by long-term irradiation. Hence, rather different patterns of radiolytic alteration should be expected in the two different chemical environments of cometary subsurface and carbonaceous crust. Because material in the subsurface can become part of the carbonaceous crust given sufficient loss of overlying and surrounding volatiles, an abrupt partition between the two environments should not be expected.

#### Relating nucleus and coma

As a comet approaches the Sun, thermal radiation promotes the vaporization of volatile ices, adding further species such as water, carbon dioxide and methane to the coma, along with entrained silicate and organic particulates. The relative abundances of the volatiles in the coma indicate the abundance of these species in the nucleus itself, and hence can be used to infer the chemistry operating in response to ionizing irradiation within the nucleus. For example, a coma with a high methane/water ratio indicates a nucleus enriched in methane. Our results, indicating the chemistry occurring in response to the irradiation of organic matter, can therefore be used to infer information about the products of the irradiation of mixtures of simple organic species in cometary environments.

#### *Terrestrial analogues to cometary organic matter*

The ability of pyrolysis–FTIR data to reflect the chemical composition of solid starting materials is of particular interest considering the repeated attempts to examine comae to understand the constitution of comets as a whole (e.g. Schulz 2006). First, however, the ability of terrestrial analogues to offer information relating nucleus and coma must be established.

#### Suitability of terrestrial analogues

Most terrestrial organic matter is biological in origin and has experienced little irradiation. In contrast, complex organic matter in cometary nuclei and comae is abiotic in origin and has experienced prolonged irradiation, resulting in chemical

changes not normally seen in terrestrial environments. Hence, two of the T-COMA analysed here include radiation sources in the form of incorporated radioelements, such as uranium and thorium. One of the two irradiated bitumens, the sample from Moonta, formed from biogenic hydrocarbon fluids, in contrast to the abiotic organic matter in comets, but a comparison of this sample with the non-irradiated bitumen from Dingwall can reveal the effects of ionizing radiation on complex organic assemblages. Even more useful is the third bitumen, from Příbram, which was formed via the radiation-induced polymerization of methane (Grip & Ödman 1944; Landais *et al.* 1993; Kribek *et al.* 1999; Court *et al.* 2006, 2007). This sample is a close natural terrestrial analogue to the irradiated abiotic complex organic matter in comets, as it represents irradiated complex organic that formed from simple precursors in an irradiated environment.

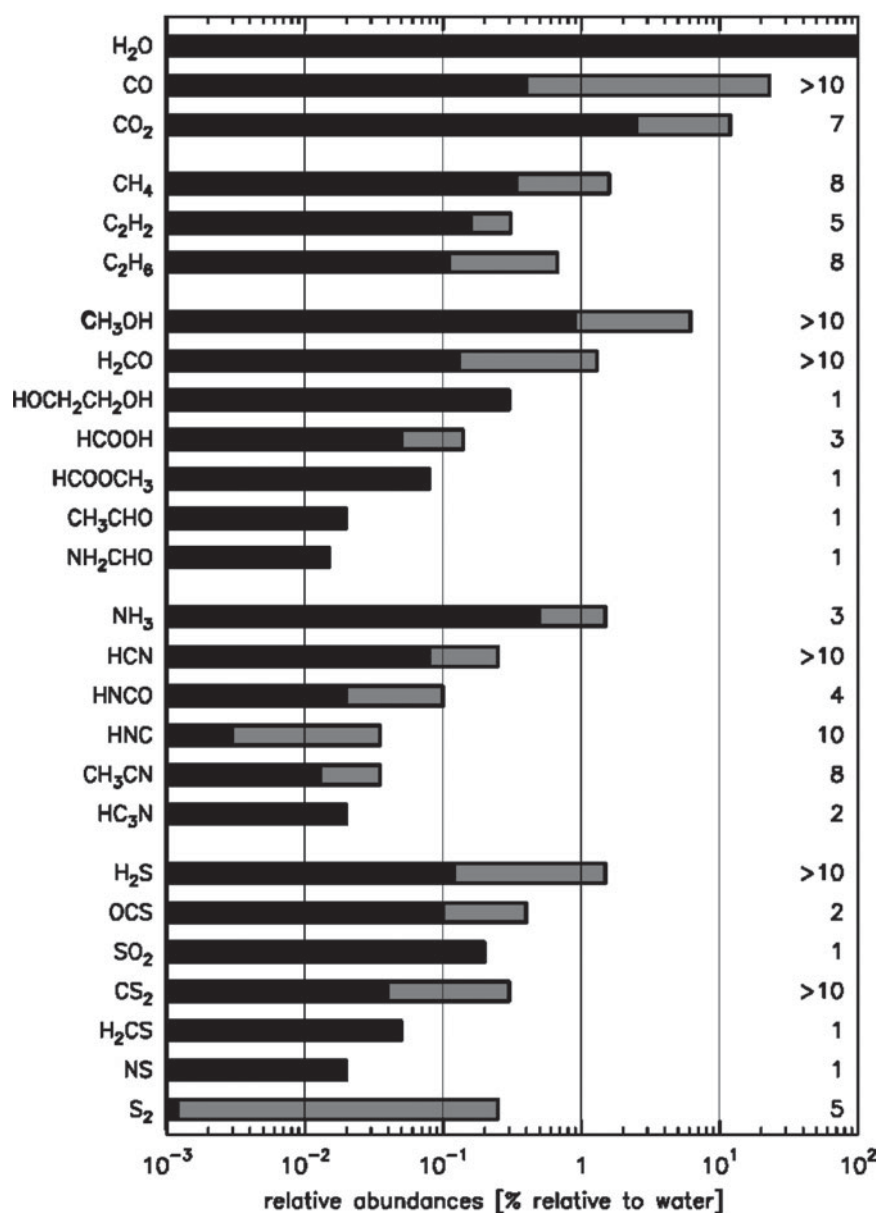
The ability of volatiles liberated by the pyrolysis of these bitumens to offer information regarding the nature of the source material can be related to volatiles produced by the irradiation of complex organic matter in a cometary nucleus. Pyrolysis is a degradation mechanism whose effects are comparable to those of radiolysis, as both pyrolysis and radiolysis cleave weakly bound organic units in complex organic matter, giving them the opportunity to escape into the surrounding environment. Therefore, the volatile pyrolysis products of the cometary analogues analysed here can be used to infer the properties of their sources. The chemical trends identified as occurring in response to ionizing radiation can then be applied to the complex organic matter inside a cometary nucleus.

The most abundant volatile compounds identified in cometary comae are water, carbon monoxide, carbon dioxide, methane, methanol, formaldehyde, ammonia and hydrogen sulphide (Fig. 3) (Crovisier 2006), while only water, carbon dioxide and methane are readily detectable in the pyrolysis–FTIR analyses of the T-COMA. While the discrepancy in detected volatiles indicates that these bitumens are imperfect analogues, it does not prevent their chemical responses to irradiation from offering useful insights into cometary chemistry.

For those components that are present in both T-COMA and comae, useful comparisons can be made. Figure 4 compares the relative abundance of water, carbon dioxide and methane in the pyrolysis products of the T-COMA and in cometary comae. Examination of the three terrestrial samples reveals that it is the products of dry irradiation of simple organic assemblages in Příbram that displays the closest match to the cometary responses. The two other T-COMAs generate more carbon dioxide, presumably reflecting their greater non-refractory organic matter contents than the proposed 1:1:1 mass ratio of water:silicates:organic matter for comets (Huebner 2002), while their absence of methane reflects their biogenic, long chain aliphatic sources.

#### Chemical trends in irradiated terrestrial organic matter

The FTIR observations of the pyrolysis products of irradiated bitumens reported here can be combined with prior reports



**Fig. 3.** The rates of production for common cometary volatiles (Crovisier 2006). The grey section of each bar indicates the variation observed between comets. The number of cometary comae in which the species were detected is indicated on the right.

(Court *et al.* 2006, 2007) to deduce that progressive irradiation of organic matter results in:

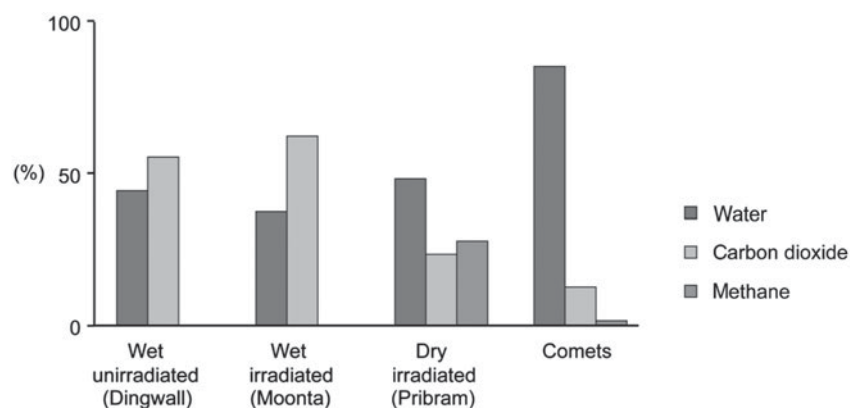
- Polymerization of lower molecular weight compounds.
- Aromatization of aliphatic hydrocarbons and a reduced yield of volatiles upon pyrolysis.
- Increased disorganization of organic matter.
- Enrichment in <sup>13</sup>C.
- Reduction in atomic H/C ratio and elevation of atomic O/C ratio.
- Increase in temperature required for thermal degradation.
- A lower yield of pyrolysis products containing a lower abundance of aliphatic hydrocarbons but more carbon dioxide and more water.

Irradiation of simple hydrocarbons induces the formation of larger molecules, with more stable polycyclic aromatic

hydrocarbons particularly favoured, such as occurred in the Příbram bitumen. Irradiation of aliphatic hydrocarbons causes cross-linking of the aliphatic chains, again promoting the formation of aromatic species. Increased disorganization manifest itself as disruption of the aromatic networks away from a graphitic structure, as can be detected using Raman spectroscopy (Court *et al.* 2007). Enrichment of irradiated organic matter in <sup>13</sup>C occurs by the preferential loss of <sup>12</sup>C-enriched gases, produced by radiolysis of the organic material (Leventhal & Threlkeld 1978).

#### Application to cometary organic matter

The trends reported for irradiated terrestrial organic matter can be applied to organic matter in cometary environments. However, the differences in chemical environment and the



**Fig. 4.** Relative yields (wt%) of water, carbon dioxide and methane upon pyrolysis of the T-COMA samples alongside the relative abundance of these components in cometary comae (Crovisier 2006). The dry irradiation of the simple organic assemblage that produced the Přibram sample displays the closest match to the cometary responses.

**Table 2.** Summary of effects seen for solid materials and their gaseous products following irradiation of a hydrocarbon mixture in water-containing and water-free environments

Feature	Irradiated with water	Irradiated without water
<i>Solid material</i>		
Molecular weight	Increase	Increase
PAH content	Increase	Increase
Organization	Decrease	Decrease
$^{13}\text{C}/^{12}\text{C}$ ratio	Increase	Increase
H/C ratio	Decrease	Decrease
O/C ratio	Increase	–
<i>Gas products</i>		
Gas yield	Increase (large)	Increase (medium)
Methane	–	Increase
Carbon dioxide	Increase (large)	Increase (medium)
Water	Increase (large)	Increase (medium)

source materials of cometary organic matter mean that caution is required. For example, the trend of radiation-driven aromatization of aliphatic hydrocarbons to aromatic species is difficult to apply to cometary organic matter, because the biological aliphatic hydrocarbons are not present in comets. Notwithstanding this restriction, the chemical trends resulting from irradiation of organic matter in two different cometary environments can be considered—in volatile-rich ices and in the volatile-depleted carbonaceous crust. These trends are summarized in Table 2.

In the subsurface, material is irradiated by the relatively attenuated GCR flux. The environment is rich in volatiles, with a mixing ratio of methane to water of about 0.5–1.5% (Gibb *et al.* 2003). By comparison with the methane-derived irradiated simple hydrocarbon mixtures of Přibram, the methane present should provide hydrocarbons for polymerization and incorporation into pre-existing organic matter, while the abundant water provides a source of hydroxyl radicals to produce oxidized functional groups, as seen with the irradiated complex hydrocarbon mixtures (Court *et al.* 2006). Given the abundance of water in the local environment, relative to methane, it seems reasonable to assume that incorporation of

oxygen into complex organic matter is more efficient than the incorporation of hydrocarbons. Hence, continued irradiation of complex organic matter in the subsurface is inferred to be associated with oxidation and the production of functional groups such as alcohols, aldehydes, ketones and carboxylic acids, favouring the accumulation of these entities as radiation dose increases, along with an increase in atomic O/C ratio.

Organic evolution in the carbonaceous crust will exhibit features that are also common to the volatile-rich cometary subsurface. Within the carbonaceous crust, the local environment is much drier, being depleted in ices and subjected to more intense irradiation. Fewer volatiles are available to provide oxygen for incorporation into complex organic matter, and the considerably more intense irradiation from the GCR and SEP fluxes increase the efficiency of radiolytic cleavage of vulnerable groups. Continued irradiation is expected to favour the aromatization of organic matter, producing a refractory, PAH-dominated residue that is enriched in  $^{13}\text{C}$ , possesses a lower atomic H/C ratio, is less soluble in organic solvents and is more resistant to thermal degradation. Differences in organic modification in the crust and subsurface will also be evident. The abundance of oxygen in irradiated organic matter reflects the balance between the incorporation of new oxygen-containing species, such as hydroxyl radicals, and their loss via radiolysis. The relative paucity of water in the carbonaceous crust, together with more efficient radiolytic cleavage, would seem to favour the loss of oxygen-containing groups in this environment, thereby causing the atomic O/C ratio of the material to decrease.

Information regarding the link between organic matter in the nucleus and the volatiles in the coma can also be inferred. A coma is composed of volatiles freed from the nucleus by sublimation of volatile ices by solar heating, and hence provides information about the bulk composition of the ices present in the nucleus. For example, a nucleus almost exclusively composed of water, with little carbon dioxide or methane, would produce a coma highly enriched in water. Such a comet would be expected to be poor in complex organics, and the species that did exist would be expected to be



well oxidized, containing abundant alcohol, carbonyl and carboxylic acid functional groups, formed by reactions with hydroxyl groups created by the radiolysis of water, as indicated by the Moonta bitumen. In contrast, a coma rich in methane indicates a nucleus enriched in simple hydrocarbons. As indicated by the Přibram bitumen that was formed via the polymerization of simple hydrocarbons such as methane, irradiation of such a nucleus would favour the formation of aromatic hydrocarbons and complex organic matter. While there would very likely be sufficient water present to promote pervasive oxidation and incorporation of oxygen-containing functional groups, it seems likely that this oxidation would not be as thorough as would occur in a more water-rich, methane-poor nucleus.

## Conclusions

1. Pyrolysis–FTIR has been used to investigate the effects of irradiation in a set of T-COMA. The results support prior analyses of the samples by alternative methods. Data reveal that the products of the irradiation of organic assemblages depend not only on the material being irradiated but also on its environment. Predictions of the nature of complex organic matter in cometary nuclei will be of great benefit to the Philae lander, upon arrival of the Rosetta mission at Comet Churyumov-Gerasimenko in 2014.
2. Pyrolysis–FTIR data illustrate how volatile organic products can be used to infer the chemical composition of solid starting materials, such as when attempting to examine comae to understand the makeup of comets. Irradiation of organic matter in comets can be considered in two end-member environments – cometary subsurfaces enriched in volatiles and cometary surfaces which are volatile-depleted. Radiolytic processing of complex organic matter in these rather different environments is expected to yield distinct products, although certain trends are expected to be common to material in both environments.
3. The cometary subsurface is enriched in volatiles and experiences relatively low irradiation rates from the attenuated global cosmic radiation flux. Here, radiolysis of water produces reactive hydroxyl radicals that react with organic matter to form oxidized species such as alcohols, carbonyls and carboxylic acids, producing organic matter with a high atomic O/C ratio. Irradiation of methane leads to polymerization and aromatization with a corresponding reduction in atomic H/C ratio, a decrease in solubility in organic solvents and an increase in thermal stability. Concomitant loss of more reactive volatiles produces an enrichment in  $^{13}\text{C}$ .
4. The carbonaceous crust is an irradiated, dry environment, rich in complex organic matter that is depleted in volatiles. Here, irradiation continues to favour the aromatization of organic material with an associated reduction in atomic H/C ratio, a decrease in solubility, an increase in thermal stability and enrichment in  $^{13}\text{C}$ . However, with fewer volatiles available to provide oxygen for incorporation into organic matter, it is likely that continued irradiation will cause a reduction in atomic O/C ratios, with radiolytic cleavage of bonds causing the production and escape of species such as hydrogen and carboxyl groups.
5. Observations of the composition of a cometary coma can indicate the relative abundance of water, methane and carbon dioxide ices in the nucleus. The nature of the complex organic products of the irradiation of simple precursors depends on the chemical environment in which irradiation occurs. A comet possessing a low methane/water ratio would be expected to possess a relatively low abundance of complex organic matter, highly enriched in oxygen containing functional groups, such as alcohols, carbonyls and carboxylic acids, resulting from reactions with hydroxyl radicals formed by the radiolysis of water. In contrast, a coma and nucleus enriched in methane would favour the formation of aromatic hydrocarbons and complex organic matter, with a lower degree of oxidation, from the relatively less abundant water and hydroxyl radicals.

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