

# The alteration of organic matter in response to ionising irradiation: Chemical trends and implications for extraterrestrial sample analysis

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## Abstract

Ionising radiation is an energy source capable of generating and altering complex organic matter. A full understanding of the radiolytic formation and evolution of organic matter is essential to appreciate the budget of organic chemicals that exist in cometary and interstellar ices, carbonaceous meteorites, and to understand the results of analyses of irradiated extraterrestrial organic matter, such as that in cometary nuclei. The effects of ionising radiation on a set of 10 naturally occurring, terrestrial organic assemblages have been revealed by pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS), carbon isotopic analysis, and stepped combustion–isotope ratio mass spectrometry (SC–IRMS). Progressive radiolytic alteration of biogenic complex–hydrocarbon mixtures induces a decrease in the average size and extent of alkylation of polyaromatic hydrocarbons (PAH) and an increase in the abundance of oxygen-containing compounds, as indicated by Py–GC–MS, and an enrichment in <sup>13</sup>C. These changes are attributed to reactions with free radicals, produced by ionising radiation. In contrast, the progressive radiolytic alteration of bitumens proposed to have derived from the radiolytic polymerisation of methane into an organic solid produces, upon pyrolysis, PAH of increasing average size and degree of alkylation. This, the opposite of the trend observed in the irradiated complex–hydrocarbons mixtures, cannot be explained in terms of the radiolytic alteration of a pre-existing array of complex organic molecules. Instead, it suggests the gradual construction of PAH from smaller molecules, supporting the hypothesis of a methane origin. Radiolytic alteration is also associated with a previously unrecognised increase in the mean combustion temperature of organic matter. This leads to predictions regarding the combustion characteristics of the irradiated organic matter present on cometary nuclei. A full understanding of the relationship between the combustion characteristics of organic polymers, radiation dose and the atomic H/C ratio should lead to the better design and implementation of in situ extraterrestrial sample analysis hardware and aid the interpretation of data from such missions. This study establishes predictable organic chemical responses of organic matter, upon exposure to ionising radiation. Our results support proposals that extraterrestrial PAH may be formed by the cosmic irradiation of simple hydrocarbons in interstellar ices. Our data may also be relevant to analogous material formed in other hydrocarbon-rich environments, such as the surface and atmosphere of Titan and other icy bodies, such as comets, and to the results of in situ analyses of extraterrestrial organic matter.

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## 1. Introduction

The evolution of life on the early Earth would have required the in situ formation, or exogenous delivery,

of significant quantities of complex organic molecules. Ionising radiation is an energy source capable of inducing a varied and complex organic chemistry in a wide range of environments, including simulated interstellar and cometary ices (e.g., Bernstein et al., 1997; Kaiser and Roessler, 1998), planetary atmospheres (e.g., Clarke and Ferris, 1997; Miyakawa et al., 2002) and the early Earth (e.g.,

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Garzon and Garzon, 2001; Parnell, 2004). However, despite representing an important process in prebiotic organic evolution, the formation and alteration of organic matter by ionising radiation is not well understood. Such an understanding is essential to determine the full inventory and relative biological utility of the organic matter that existed on the Earth coincident with the origin of life, and to understand fully the results of in situ analyses of extraterrestrial organic matter.

The natural radiolytic alteration of organic assemblages can be studied by the analysis of terrestrial bitumens containing varying concentrations of uranium and thorium. Irradiated bitumen occurs globally, in rocks of different ages. Variations in the organic chemistry and carbon isotopic composition of irradiated bitumens can be examined using a variety of techniques. The literature attributes the following variations to the effects of the radiolytic alteration of organic matter:

- An enrichment in  $^{13}\text{C}$  (Leventhal and Threlkeld, 1978);
- Greater aromaticity (Forbes et al., 1988; Kríbek et al., 1999);
- A decreased degree of alkylation of polyaromatic hydrocarbons (PAH) (Dahl et al., 1988);
- Decreased pyrolysis and solvent extract yields (e.g., Kríbek et al., 1999);
- Greater structural disorganisation (Wang et al., 1989; Landais et al., 1990);
- Lower H/C ratios and higher O/C ratios (e.g., Kríbek et al., 1999);
- Increased hardness (Moench and Schlee, 1967) and reflectance (Dubinchuk et al., 1977);
- An elevated Rock-Eval (a technique used to determine the type and thermal maturity of organic matter) peak pyrolysis temperature ( $T_{\text{max}}$ ) (Forbes et al., 1988).

These changes are attributed to radiolytic cleavage, aromatisation and polymerisation, occurring via free radical mechanisms, induced by ionising radiation. Experimental irradiation of organic chemicals and sedimentary organic matter causes dehydrogenation, polymerisation, and the production of light hydrocarbons. These effects are enhanced by the presence of water, due to the radiolytic production of reactive hydroxyl radicals (Kríbek et al., 1999; and references therein).

Most radiolytic alteration occurs in  $\sim 50\ \mu\text{m}$  haloes around radiation sources, corresponding to the calculated 40–60  $\mu\text{m}$  range of 4–7 MeV  $\alpha$ -particles in organic matter. Outside of the 50- $\mu\text{m}$  halo,  $\beta$ - and  $\gamma$ -radiation deliver a significantly lower radiation dose (Friedlander and Kennedy, 1962; Leventhal et al., 1987). It must be noted that the comparison with extraterrestrial radiation sources is not exact. Processing of organic compounds by ionising radiation (cosmic radiation) occurs in cometary and interstellar ices (e.g., Bernstein et al., 1997) and

in planetary atmospheres (Miyakawa et al., 2002). Cosmic radiation consists mainly of protons (85%), with some  $\alpha$ -particles (12%). The remainder consists of electrons and heavier nuclei. Typical energies are 1000 MeV, but energies up to  $10^{14}$  MeV have been recorded (e.g., Sigl, 2001).

Here, we report data from the analysis of terrestrial bitumens that have experienced varying levels of irradiation. Pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS), stepped combustion–isotope ratio mass spectrometry (SC–IRMS) and isotope ratio mass spectrometry (IRMS) have been applied to reveal trends in the nature of organic matter. These trends are attributed to the effects of ionising radiation and the nature and origin of the irradiated bitumen. The patterns of radiolytic organic evolution identified here will aid future interpretations of both terrestrial and extraterrestrial organic assemblages exposed to ionising radiation, such as that of Comet 67P/Churyumov Gerasimenko, the target of the Rosetta mission.

## 2. Methodology

### 2.1. Samples

Ten bitumens, from a range of geographical locations and ages, have been analysed. “Bitumen” is used here in a broad sense, to refer to organic solids derived from migrated hydrocarbons. Groups A and B comprise samples that are regarded as having formed from migrating organic liquids of biological origin. Collectively, they are referred to as *complex–hydrocarbon mixtures*, reflecting their biological origin. Group A comprises two bitumens. Electron microprobe analyses revealed no uranium or thorium mineralisation (Parnell, 1985; Parnell and Eakin, 1989). Although a very low radioelement concentration is possible, it is considered that this would not exceed around  $\sim 100$  ppm. In comparison, the radioelement concentration of the bitumen from Cerro Huemul is at least 20 times greater (0.21%; 2100 ppm). Consequently, it seems reasonable to assume that radiolytic alteration of the Group A bitumens, relative to the samples of Groups B and C, is minimal, justifying a description of *nonirradiated complex–hydrocarbon mixtures*.

Group B is a set of five bitumens, containing uranium or thorium, with reported radioelement concentrations ranging from 0.21% (Cerro Huemul) to 12.3% (Laxey), by mass. The quoted radioelement concentrations include only uranium and thorium, and not their decay products. The justification and implications of this is discussed later.

Although the natural diversity of bitumens means the Group A samples cannot be directly compared with Group B, comparisons of the behaviour of the irradiated and nonirradiated complex–hydrocarbon mixtures should prove illuminating. Furthermore, the two bitumens

samples from Nash Scar Quarry very likely formed in the same fluid migration event (Parnell and Eakin, 1989). Hence, variations in pre-irradiation hydrocarbon composition and differential thermal maturation are likely to be minimal. Consequently, differences between the nonirradiated Nash Scar Quarry A sample and the irradiated Nash Scar Quarry B sample should be due largely to the effects of radiolytic alteration. These variations should also be apparent in Group B as a whole.

The Group C samples may be different. Group C is also referred to as the (*putative*) *methane-derived bitumens*. These bitumens were proposed to have formed by the radiolytic polymerisation of methane, based on their carbon isotopic composition and field relationships (Grip and Ödman, 1944; Landais et al., 1993; Kríbek et al., 1999). This hypothesis will be discussed later, in light of the results presented here. Brief descriptions of the samples follow and are presented in Table 1.

### 2.1.1. Group A: nonirradiated complex-hydrocarbon mixtures

2.1.1.1. *Dingwall, Scotland*. A sample of radioelement-free bitumen was taken from a hydrocarbon vein in a conglomerate at the base of the Devonian Middle Old Red Sandstone, alongside the A862 road (Parnell, 1985).

2.1.1.2. *Nash Scar Quarry A, Powys, Wales*. A sample of radioelement-free, nonirradiated bitumen (Nash Scar Quarry A) was taken from a vein in the Llandovery Nash Scar Limestone of Powys, Wales, at Nash Scar Quarry. A sample of thoriferous bitumen (Nash Scar Quarry B) was also taken from the underlying Folly Sandstone at this site (Parnell and Eakin, 1989).

### 2.1.2. Group B: irradiated complex-hydrocarbon mixtures

2.1.2.1. *Cerro Huemul, Argentina*. Uraniferous and cupriferous bitumen is present in sandstones of the Upper Cretaceous

Table 1  
Details of the bitumen samples, published data and analytical results

| Bitumen Group | Sample             | Source and host rock age              | Published data                     |                            | ANCA-SLx organic $\delta^{13}\text{C}$ (‰) |       | MS86 data  |                                   |  |
|---------------|--------------------|---------------------------------------|------------------------------------|----------------------------|--|-------|--|-----------------------------------|--|
|               |                    |                                       | Radioelement concentration (% wt.) | $\delta^{13}\text{C}$ (‰)  | Values                                     | Mean  | Assigned maximum organic carbon combustion temperature ( $T_{ALL}$ ; °C) | Organic $\delta^{13}\text{C}$ (‰) | Mean combustion temperature (°C; $\pm 5$ ) |
| A             | Dingwall           | Scotland Devonian                     | n.d. <sup>a,1</sup>                | —                          | −31.7<br>−32.9<br>−32.9                    | −32.5 | 475  | −31.2                             | 350  |
|               | Nash Scar Quarry A | Powys, Wales Silurian                 | n.d. <sup>a,2</sup>                | —                          | −31.0<br>−31.2                             | −31.1 | 575  | −31.0                             | 458  |
| B             | Cerro Huemul       | Argentina Tertiary                    | 0.21 U <sup>3</sup>                | —                          | −30.2<br>−29.9                             | −30.1 | 525  | −27.8                             | 418  |
|               | Nash Scar Quarry B | Powys, Wales Silurian                 | 0.75 Th <sup>2</sup>               | —                          | −29.5<br>−28.4                             | −29.0 | —  | —                                 | —  |
|               | Temple Mountain    | Utah, USA Triassic                    | 7.0 U <sup>4</sup>                 | —                          | −24.6<br>−24.9                             | −24.7 | 400  | −26.7                             | 437  |
|               | Moonta             | South Australia Archaean <sup>b</sup> | 4.2 U <sup>5,6</sup>               | —                          | −22.2<br>−21.0<br>−20.7                    | −21.3 | 550  | −21.8                             | 279  |
|               | Laxey              | Isle of Man Irish Sea                 | 12.3 <sup>6,7,8</sup>              | −18.5 <sup>7</sup>         | −18.1<br>−18.2                             | −18.1 | 450  | −13.6                             | 402  |
| C             | Boliden            | Sweden Palaeoproterozoic              | 7.0 U<br>0.7 Th <sup>7,9,10</sup>  | −29.2 <sup>14</sup>        | −41.6<br>−43.2                             | −42.4 | 575  | −42.4                             | 458  |
|               | Cluff Lake         | Saskatchewan, Canada Mesoproterozoic  | 12.3 U <sup>11,12</sup>            | −43 to 49 <sup>11,12</sup> | −42.9<br>−43.4<br>−55.6                    | −43.2 | 550  | −46.5                             | 474  |
|               | Příbram            | Czech Republic Carboniferous          | 24.2 U <sup>13</sup>               | ~−57 <sup>13</sup>         | −55.6<br>−57.3                             | −56.2 | 575  | −59.6                             | 480  |

References are as follows: 1, Parnell (1985); 2, Parnell and Eakin (1989); 3, Haggan et al. (2002); 4, Kelley and Kerr (1958); 5, Radcliff (1906); 5, Davidson and Bowie (1951); 7, Eakin (1989); 8, Parnell (1988); 9, Aminoff (1943); 10, Grip and Ödman (1944); 11, Landais et al. (1993); 12, Leventhal et al. (1987); 13, Kríbek et al. (1999); 14, Welin (1966).

<sup>a</sup> Not detected (See Section 2.1 for discussion).

<sup>b</sup> Although the host rock of the bitumen at Moonta is Archaean, the bitumen is believed to have migrated from overlying Cambrian host rocks, now eroded (Parnell, 1989). See Section 2.1 for further details of the samples. The “assigned maximum organic combustion temperature ( $T_{ALL}$ )” refers to the temperature step in which the carbon evolved is no longer considered to represent organic matter, based on its abundance and carbon isotopic composition. Above that temperature, the evolved carbon represents carbonate and/or analytical blank. This temperature limit is then used to calculate the mean organic combustion temperature and the organic  $\delta^{13}\text{C}$ .

Diamante Formation, within the Neuquén Basin in Cordillera Principal of the Argentinean Andes. The mined ore contained an average of 0.21% wt. uranium (Haggan et al., 2002).

*2.1.2.2. Nash Scar Quarry B, Powys, Wales.* Underlying the Nash Scar Limestone at Nash Scar Quarry is the Llandovery Folly Sandstone. This unit contains thoriferous bitumen, containing on average 0.75% wt. thorium (Parnell and Eakin, 1989). Although this bitumen is thoriferous, the radiolytic alteration is expected to be comparable to that sustained by a bitumen with a similar uranium concentration. The Nash Scar Quarry A and B bitumens are believed to have been emplaced in the same fluid migration event (Parnell and Eakin, 1989).

*2.1.2.3. Moonta, Australia.* Veins of uraniferous bitumen occur in the Archaean metasediments of the Moonta copper mines of South Australia. Although the bitumen was originally attributed to radiolytic polymerisation of magmatic organic gases, migration of hydrocarbons into the crystalline basement from overlying rocks, now eroded, is more likely (Parnell, 1989; and references therein). Uranium concentrations of around 4.2% wt. were reported (Radcliff, 1906; Davidson and Bowie, 1951).

*2.1.2.4. Temple Mountain, Utah, USA.* Uraniferous bitumen exists at Temple Mountain, Utah, replacing the Triassic sandstones of the Colorado Plateau (Landais et al., 1987; and references therein). A uranium concentration of 7.0% wt. has been reported for this material (Kelley and Kerr, 1958).

*2.1.2.5. Laxey, Isle of Man.* Uraniferous bitumen is found in a cupriferous dolomite vein, in Ordovician shales, at Laxey, Isle of Man (Parnell, 1988). The bitumen contains complex metal sulphide inclusions and has reported uranium concentrations of 18.75% wt. (Parnell, 1988), 6.9% wt. (Eakin, 1989), and 11.2% wt. (Davidson and Bowie, 1951), giving a mean uranium concentration of 12.3% wt.

### *2.1.3. Group C: putative methane-derived bitumens*

*2.1.3.1. Boliden.* Radioactive bitumen occurs in andalusite rock of the Palaeoproterozoic, in the Boliden Au–Cu–As deposit, Sweden (Welin, 1966; and references therein). Reported radioelement concentrations (% wt.) are: 5.8% uranium and 0.82% thorium (averages of five samples, Aminoff, 1943); 10.2% uranium and 0.16% thorium (Grip and Ödman, 1944); and 9.67% uranium (Eakin, 1989). These give average concentrations of 7.0% uranium and 0.71% thorium, giving a mean total radioelement concentration of 7.7% wt.

The starting materials for the irradiated bitumen at Boliden are thought to be methane for a number of reasons. Analyses of flammable natural gas emitted from drillholes in bitumen-bearing rocks in the Boliden mine indicate abundant methane (Grip and Ödman, 1944). An origin by means of the radiolytic polymerisation of methane

was originally proposed by Grip and Ödman (1944), based on the close proximity of abundant methane, radioelements and bitumen.

*2.1.3.2. Cluff Lake.* Radioelement-containing bitumen is reported from Mesoproterozoic gneiss at Cluff Lake, Saskatchewan, Canada (Landais et al., 1993; and references therein). Uranium concentrations (% wt.) of 9.2 and 15.6% (Landais et al., 1993) and 12% (Leventhal et al., 1987) have been reported. Landais et al. (1993) also reported traces of thorium (33 and 44 ppm), giving a mean radioelement concentration of 12.3% wt. for this sample.

The literature also attributes the source of Cluff Lake bitumen to methane. Abundant methane was found during the exploration and development of the uranium mine at this site (Hoeve and Sibbald, 1978). Its presence in the bitumen was confirmed by the stepped pyrolysis of bitumen samples, which caused the evolution of significant quantities of methane, at temperatures well below the onset of pyrolysis (Leventhal et al., 1987; and references therein). The bitumen has carbon isotopic ratios of  $-43.0$  to  $-43.7$ ‰, significantly lower than the values of  $-23$  to  $-29$ ‰ reported from the surrounding country rock, but similar to the value of  $-48.4$ ‰ reported for methane occluded in the bitumen (Leventhal et al., 1987). On this basis, the bitumen was proposed to be derived from polymerised methane by Landais et al. (1993).

*2.1.3.3. Příbram.* Radioactive bitumen is found in the Permian hydrothermal uranium deposit at Příbram in the Czech Republic. The deposits extend along the boundary between the Central Bohemian Pluton and its adjacent aureole. Analyses of eight uraniferous coke-like bitumens (the type analysed here) gave a mean uranium concentration of 24.2% wt. Thorium is not reported in these bitumens (Kříbek et al., 1999). An origin by the radiolytic polymerisation of methane was proposed by these workers, based upon the carbon isotopic composition of this bitumen and those of nearby, nonirradiated organic matter, and the presence of abundant, flammable methane-rich gas, released during excavation of the mine.

## *2.2. Techniques*

### *2.2.1. Pyrolysis–gas chromatography–mass spectrometry*

Quartz pyrolysis tubes and quartz wool were cleaned by overnight heating in air at 450 °C. Approximately 1 mg of a sample was placed in a pyrolysis tube, each end of which was plugged with quartz wool. Pyrolysis was performed with a CDS Pyroprobe 1000, fitted with a 1500 valve interface held at 250 °C (CDS Analytical, Oxford, PA) and coupled to an Agilent Technology 6890 gas chromatograph and a 5973 mass selective detector. A cryotrap was not employed. During pyrolysis, the samples were heated at 20 °C ms<sup>-1</sup> to 610 °C and held at this temperature for 15 s under a flow of He. During a run, the initial

temperature of the gas chromatograph oven was 50 °C. This temperature was held for 1 min, then increased at 5 °C per minute until 300 °C was attained. This temperature was held for a further 9 min, giving a total run length of 60 min. Separation was executed on a SGE (UK) BPX5 column (30 m length, 0.25 mm internal diameter, and 0.25 µm film thickness), with He carrier gas at a constant flow rate of 1.1 ml min<sup>-1</sup>. Compounds were identified by comparison with the NIST 98 mass spectral database, elution orders and literature data. Ratios of compounds were derived by integration of the area under peaks. Coeluting peaks were decomposed by integrations based upon selected mass fragments.

### 2.2.2. Stepped combustion-isotope ratio mass spectrometry

Masses of carbon and their stable isotopic composition were measured on a completely automated instrument (MS86) that provides a highly reproducible protocol for high-resolution, multistep analysis. The automated combustion step process consists of 30 min of heating with an oxygen pressure of 10 mbar, followed by 20 min during which the oxygen is resorbed by CuO (Wright and Pillinger, 1989; Yates et al., 1992). This instrument measures δ<sup>13</sup>C with a precision of ±1‰ and the mass of carbon with a precision of ±1%. The furnace temperature readings are precise to approximately 5 °C. The abundances of stable isotopes of carbon are expressed using δ notation, describing the difference, in parts per mil (‰) between the ratio of the sample and the same ratio in the international standard (V-PDB).

### 2.2.3. Stable carbon isotope analysis

Stable carbon isotopic ratios of bulk bitumen samples were determined using a PDZ Europa ANCA-SL elemental analyser, coupled to a Geo 20-20 continuous-flow stable isotope ratio mass spectrometer, set to combustion mode. Bitumen was powdered to provide a homogenous mix and carbonate carbon was removed using 1 M HCl. Aliquots of around 500 µg were analysed. The analytical process is described by Sephton et al. (2004). Carbon isotopic compositions are reported using δ notation and the V-PDB standard.

## 3. Results

### 3.1. Pyrolysis–gas chromatography–mass spectrometry

#### 3.1.1. Variations in the products of pyrolysis

Fig. 1 displays chromatograms of pyrolysis products of the samples. The two nonirradiated samples (Group A) are dominated by *n*-alkene–alkane couplets, whereas the irradiated Group B samples contain abundant aromatic hydrocarbons, such as naphthalene. Pyrolysis of the Cerro Huemul material, which possesses the lowest radioelement concentration in Group B, produced the greatest variety of compounds, including a diverse array of alkylated PAH. In contrast, bitumen from Laxey, with its much

higher uranium concentration, produced only a few compounds of generally lower mass, including alkylbenzenes, benzaldehyde, and benzoic acid. Generally, a higher radioelement concentration amongst the complex–hydrocarbon mixtures correlates with reduced numbers of pyrolysis products. The sample from Laxey contains abundant sulphur, as chalcopyrite (Parnell, 1988). This sample was contaminated by silicone oil species—these are the cause of the peaks around 10.5, 15, 19, and 23 min (Fig. 1). Several aliquots of this sample were subjected to Py–GC–MS analysis; the chromatogram shown is the cleanest of those produced.

The trend of decreasing diversity of the products of pyrolysis with increasing radioelement concentration is reversed among the putative methane-derived (Group C) bitumens. Although also dominated by alkylated PAH, pyrolysis of the sample least enriched in radioelements (from Boliden) produced only a few small, poorly alkylated PAH. In contrast, pyrolysis of the sample most enriched in radioelements (from Příbram) produced a significantly more diverse array of more alkylated PAH. The response, and radioelement concentration, of the Cluff Lake sample was intermediate between these two.

#### 3.1.2. Variations in PAH size and degree of alkylation

The variation in the diversity of the products of pyrolysis also hints at variations in the relative abundance of certain compounds, between bitumen samples. Variations in the degree of alkylation of PAH are shown in Figs. 2 and 3. Although these do not represent absolute abundances, correction factors are unnecessary because no comparisons are made between different groups of compounds, only between the same groups of compounds in different samples. Among the Group B samples (Fig. 2), the same trend is apparent in each plot—the degree of alkylation of each PAH, and the average PAH size, generally decrease with increasing radioelement concentration. PAH are smaller and less alkylated in the radioelement-enriched material from Laxey, compared with the radioelement-poor bitumen from Cerro Huemul.

However, this relationship is reversed among the putative methane-derived bitumens of Group C (Fig. 3). Here, the PAH in the radioelement-enriched bitumen from Příbram are larger and more alkylated than those in the radioelement-depleted bitumen from Boliden.

#### 3.1.3. Oxygen-containing compounds

The relative responses of certain oxygen-containing compounds, as produced by Py–GC–MS of the bitumens, are shown in Fig. 4. The nonirradiated Group A bitumens possess a low diversity of oxygen-containing compounds, containing alkylphenols but no other oxygen-containing species. These are not marked in Fig. 4, as this would obscure the irradiated Group B samples, as they would plot at the Phenol apex. The diversity of oxygen-containing compounds generally increases with increasing radioelement concentration. The sample from Cerro Huemul

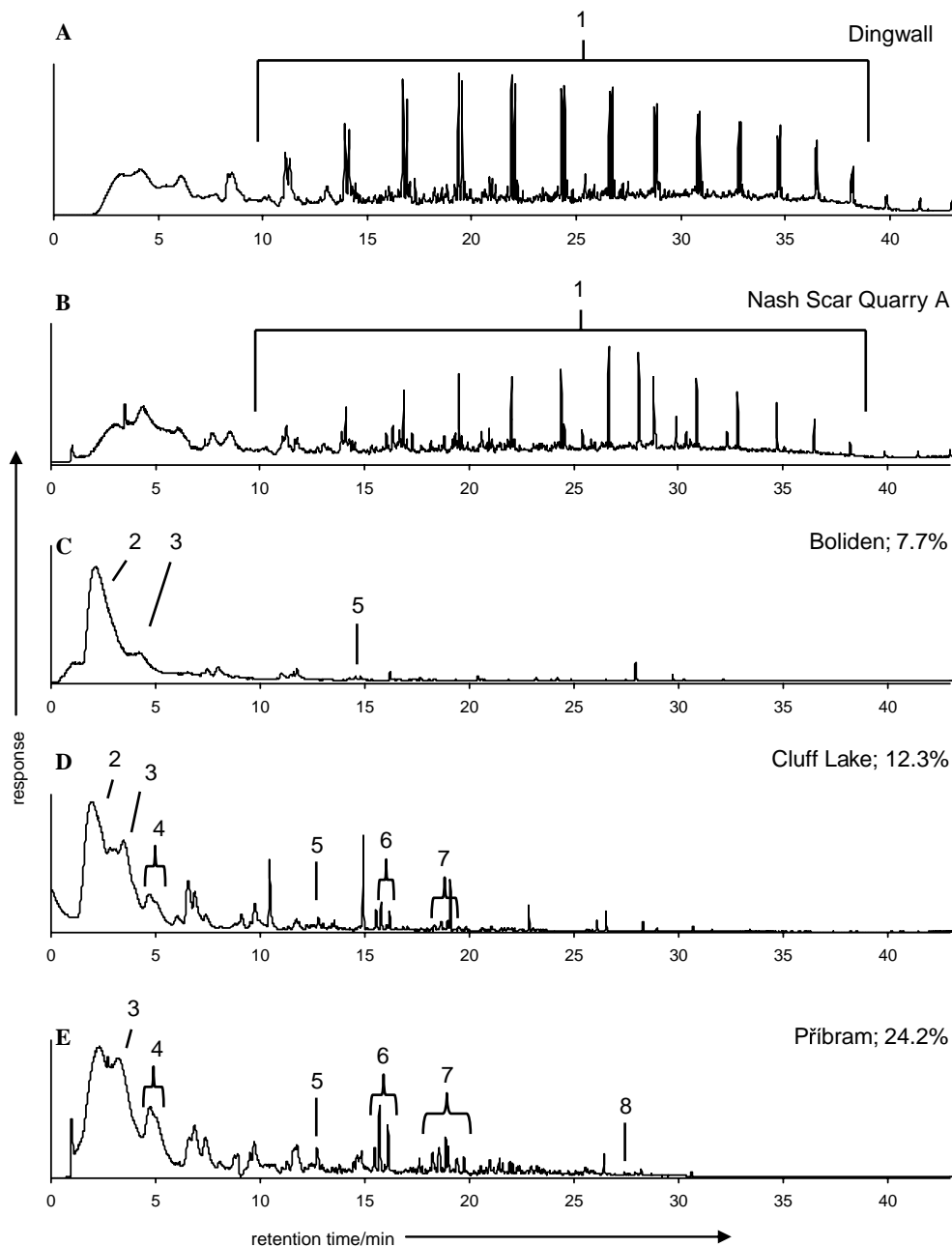


Fig. 1. Chromatograms of the pyrolysis products of the nonirradiated Group A complex-hydrocarbon mixtures (A and B), the putative methane-derived Group C bitumens (C–E) and the irradiated Group B complex-hydrocarbon mixtures (F–J). The percentages refer to the radioelement concentrations, as % wt. The Group A samples are dominated by alkene-alkane couplets, whereas the Group B samples are dominated by PAH. The diversity of products, and the average size and degree of alkylation of the PAH, decreases with increasing radioelement concentration. The putative methane-derived samples are also dominated by PAH. The diversity of products, and the average size and degree of alkylation of the PAH, increases with increasing radioelement concentration. This trend is the opposite to that observed among the irradiated complex-hydrocarbon mixtures of Group B. Oxygen-containing compounds, such as benzoic acid and benzaldehyde, are more abundant in the samples from Moonta and Laxey, than the other complex-hydrocarbon mixtures. They are not present in the pyrolysis products of the putative methane-derived bitumens. Peak assignment: 1,  $C_{11}$ – $C_{23}$  alkene-alkane couplets; 2, benzene; 3, toluene; 4, dialkylbenzenes; 5, naphthalene; 6, methylnaphthalenes; 7, dialkylmethylbenzenes; 8, phenanthrene; 9, methylphenanthrenes and methylanthracenes; 10, phenol; 11, fluorenone; 12, benzaldehyde; and 13, benzoic acid. The sample from Laxey was contaminated by silicone oil species—these are the cause of the peaks around 10.5, 15, 19, and 23 min. Several aliquots of this sample were subjected to Py-GC-MS analysis; the chromatogram shown is the cleanest of those produced.

contains alkylphenols, but Nash Scar Quarry B contains alkylphenols and small amounts of aromatic ketones. The samples from Temple Mountain and Moonta, more en-

riched in radioelements, contain, relative to alkylphenols, more aromatic ketones and aldehydes. The sample most enriched in radioelements, from Laxey, contains benzoic

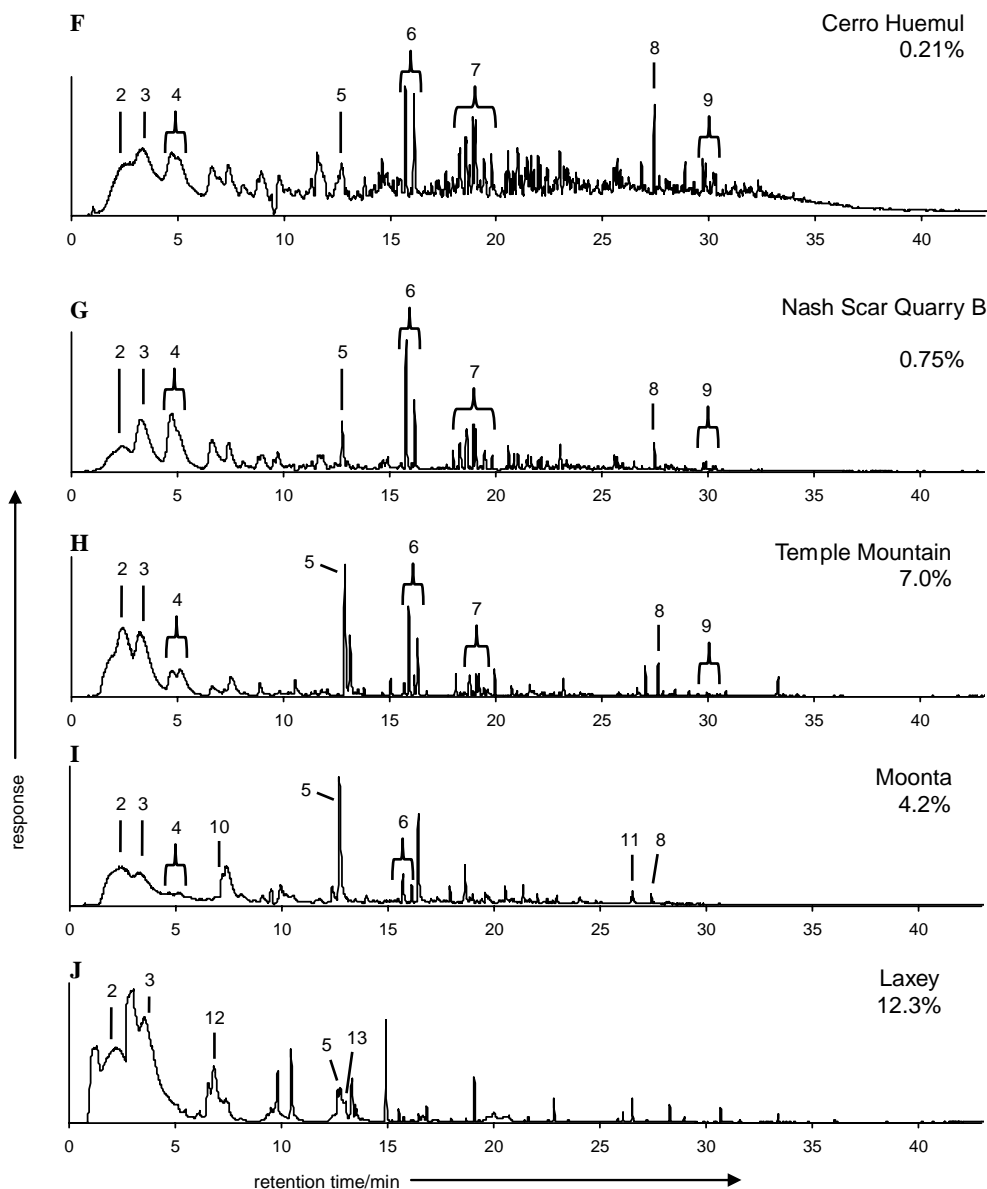


Fig. 1. (continued)

acid, in addition to the aforementioned aldehydes, ketones, and alkylphenols.

This trend is not apparent in the putative methane-derived samples of Group C. These contain alkylphenols, but the aldehydes, ketones and benzoic acid apparent in the Group B samples do not occur.

### 3.2. Variations in bulk carbon isotopic composition

The bulk carbon isotopic ratios of the bitumen samples are listed in Table 1. The nonirradiated Group A bitumens possess  $\delta^{13}\text{C}$  values that are the lowest of the complex-hydrocarbons mixtures of Groups A and B. The Group B samples are enriched in  $^{13}\text{C}$ , relative to Group A. They

also display a general trend of increasing  $^{13}\text{C}$ -enrichment with increasing radioelement concentration.

However, the opposite relationship is apparent in the putative methane-derived bitumens of Group C—elevated radioelement concentrations are associated with more negative  $\delta^{13}\text{C}$  values.

Values of  $\delta^{13}\text{C}$  of some of the bitumens, published previously by other workers, are listed in Table 1. Those values are comparable to those obtained here, with the exception of bitumen from Boliden. The carbon isotopic ratio of bitumen from Boliden was previously measured to be  $-29.2\%$  (Welin, 1966). This was a single analysis of material apparently unrelated to that studied here.

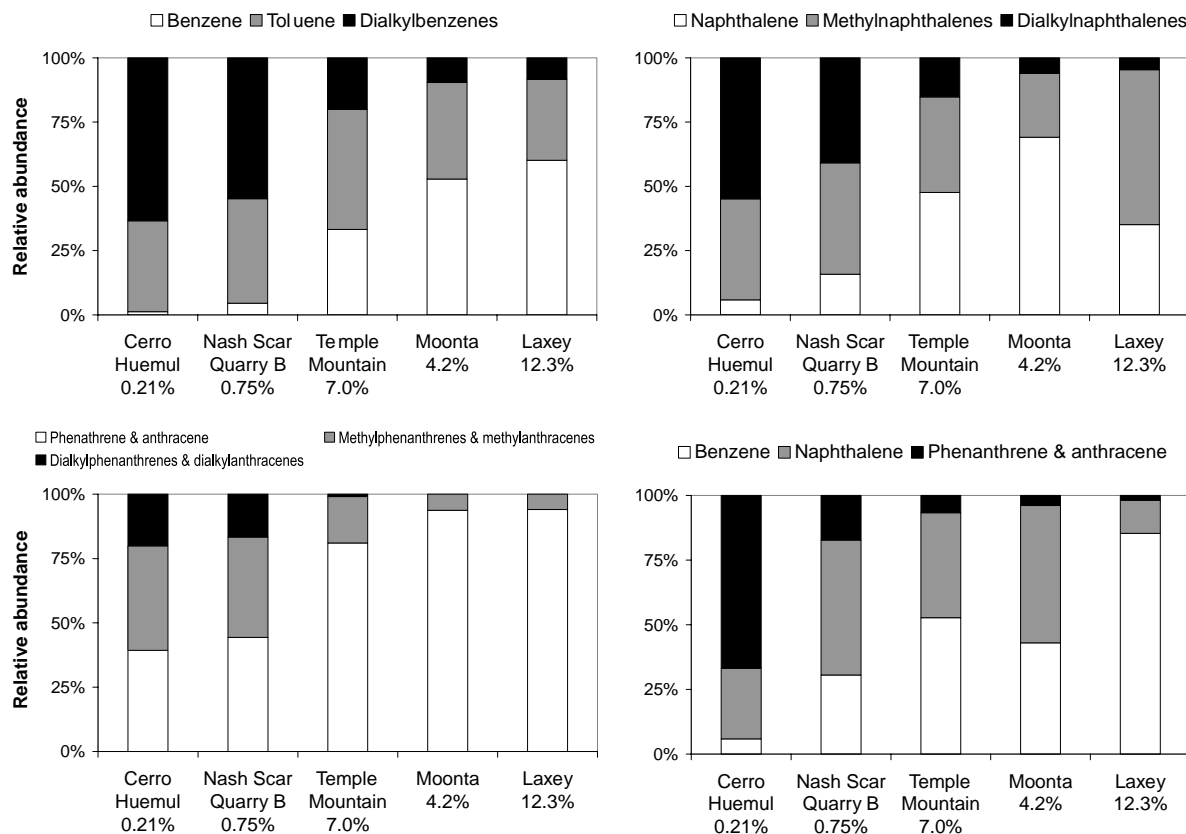


Fig. 2. Variations in the relative GC–MS responses of certain PAH, and their alkyl derivatives, and in the PAH size distribution, among the irradiated complex–hydrocarbon mixtures. The percentages (% wt.) on the horizontal axis indicate the radioelement concentration. An increase in radioelement concentration is generally associated with a decrease in the average PAH size and degree of alkylation. It is difficult to establish the accuracy of the percentages used here, due to the nature of the chromatograms. However, the range of variation present suggests that the effect observed is real.

### 3.3. Stepped combustion-isotope ratio mass spectrometry

#### 3.3.1. Variations in carbon isotopic composition with combustion temperature

Carbon release profiles of the bitumens are displayed in Fig. 5 and the data are listed in the Appendix A. The nonirradiated complex–hydrocarbon mixtures from Dingwall and Nash Scar Quarry A show profiles of carbon release that are different to each other. Trimodal carbon release is apparent in the sample from Dingwall (Fig. 5A). Relatively  $^{13}\text{C}$ -depleted carbon ( $\delta^{13}\text{C} \approx -34\text{‰}$ ) was released around 325 °C, with a further release of material ( $\delta^{13}\text{C} \approx -30\text{‰}$ ) occurring around 450 °C. A third release of carbon with distinct  $\delta^{13}\text{C}$  values of ca.  $-2\text{‰}$ , occurred around 550 °C. This last component is interpreted as carbonate, based on its  $\delta^{13}\text{C}$  value and the temperature of the carbon release (Gilmour and Pillinger, 1985). In contrast, material from Nash Scar Quarry A (Fig. 5B) released carbon over a similar temperature range, but with a single peak around 525 °C. The evolved carbon had  $\delta^{13}\text{C}$  values of ca.  $-32\text{‰}$  at 400 °C, rising to ca.  $-29\text{‰}$  at 525 °C.

Combustion of bitumen from Cerro Huemul (Fig. 5C) occurred over a broad temperature range,

around 200–525 °C, with a corresponding increase in  $\delta^{13}\text{C}$  from around  $-30\text{‰}$  to around  $-26\text{‰}$ . The  $^{13}\text{C}$ -enriched spike at 500 °C is regarded as an experimental anomaly and is omitted from calculations of the organic  $\delta^{13}\text{C}$  value. Similar combustion behaviour was encountered in bitumen from Temple Mountain (Fig. 5E), but with a secondary peak of carbon release, at 500 °C. Further carbon releases with anomalously high  $\delta^{13}\text{C}$  values occurred at 275 and 525 °C; again, these were omitted from calculations of the organic  $\delta^{13}\text{C}$  value. The isotopic composition of carbon released from bitumen from Temple Mountain varied between  $-29\text{‰}$  to around  $-25\text{‰}$  during the main release of carbon between 375 and 425 °C.

The other two samples, from Moonta and Laxey, of the irradiated complex–hydrocarbon mixtures show contrasting combustion behaviours. Peak carbon release from the sample from Moonta (Fig. 5D) occurred at lower temperatures, around 300 °C, with  $\delta^{13}\text{C} \approx -21\text{‰}$ . An anomalous  $\delta^{13}\text{C}$  value was recorded at 500 °C; again, this was omitted from calculations of the organic  $\delta^{13}\text{C}$  value. Further release of  $^{13}\text{C}$ -enriched carbon ( $\delta^{13}\text{C} \approx +1\text{‰}$ ) occurred around 650 °C. This is interpreted as carbonate, on the basis of its combustion temperature and isotopic composition



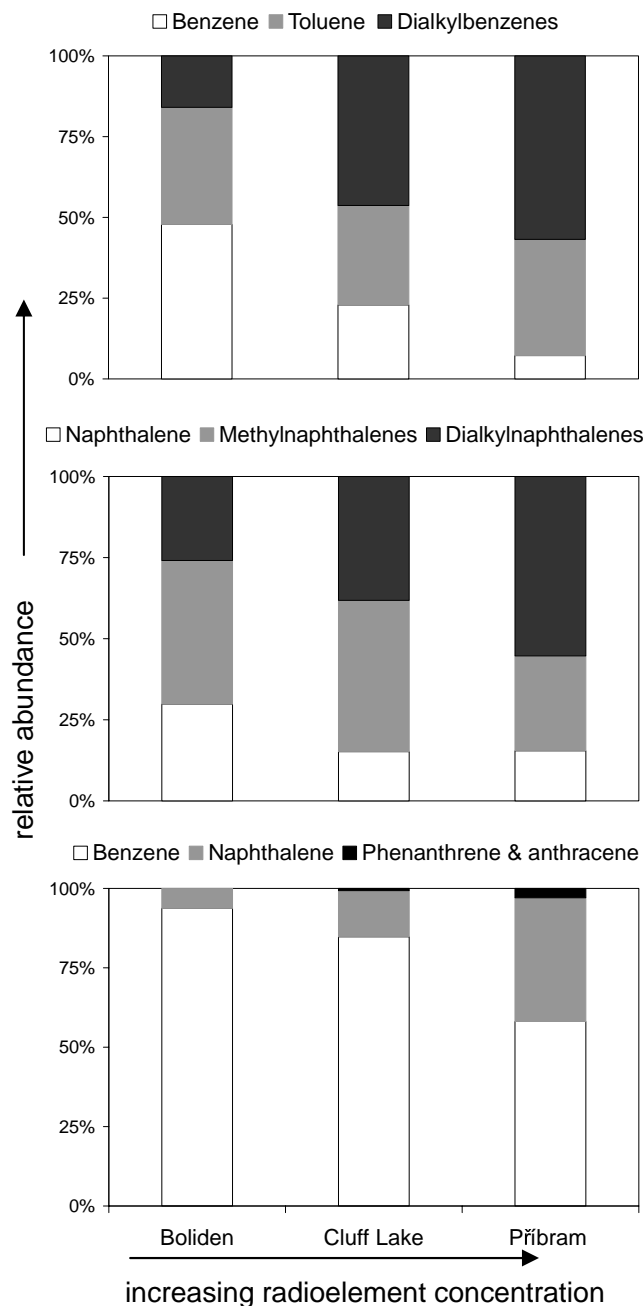


Fig. 3. Variations in the relative GCMS responses of certain PAH, and their alkyl derivatives, and in the PAH size distribution, among the putative methane-derived bitumens of Group C. The percentages (% wt.) indicate the radioelement concentration. An increase in radioelement concentration is associated with an increase in the average PAH size and degree of alkylation. This is the opposite of the trend observed among the complex-hydrocarbon mixtures.

(Gilmour and Pillinger, 1985). Carbon release during the combustion of bitumen from Laxey (Fig. 5F) occurred over a narrower temperature range, beginning around 275 °C, peaking around 425 °C ( $\delta^{13}\text{C} \approx -13\text{‰}$ ) and ceasing around 450 °C.

The three bitumen samples of Group C show behaviour that is broadly similar to each other (Fig. 5, Appendix A). Carbon combusts over a similar temperature range, around

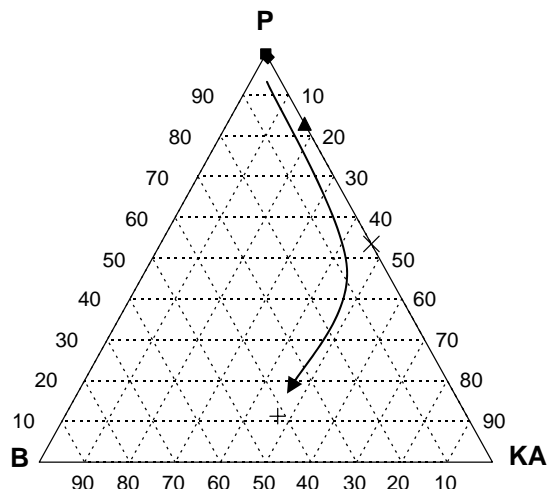


Fig. 4. Ternary diagram showing the relative abundances of oxygen-containing compounds in the irradiated samples (Group B). The nonirradiated bitumens (Group A) and the methane-derived bitumens (Group C) plot at the Phenol apex, along with the sample from Cerro Huemul. Radiolytic alteration of the complex hydrocarbon mixtures initially generates additional phenols, progressing to aromatic ketones and aldehydes and, at the highest levels of alteration, abundant benzoic acid. The arrow marks the proposed track of alteration. This contrasts with the behaviour of the methane-derived bitumens, which do not contain significant quantities of the ketones, aldehydes and benzoic acid seen in the sample from Laxey. This dichotomy is attributed to the efficient removal of hydroxyl ions, formed by the radiolysis of water, by the surrounding methane. Diagram apices, sample assignments and the radioelement concentrations are as follows: P, phenol; B, benzoic acid; KA, acetophenone, acetonaphthone, benzaldehyde, naphthaldehyde, fluorenone, and benzophenone; ■, Groups A, C, and Cerro Huemul (0.21%); ◆, Nash Scar Quarry B (0.75%); ▲, Temple Mountain (7.0%); ×, Moonta (4.2%); and +, Laxey (12.3%). The percentages (% wt.) indicate the radioelement concentration.

200–525 °C, peaking around 500 °C. The evolved carbon is relatively  $^{13}\text{C}$ -depleted, around  $-40\text{‰}$  for material from Cluff Lake and Boliden, and around  $-60\text{‰}$  for material from Přebřam (Table 1, Figs. 5G–I). The evolved carbon becomes more  $^{13}\text{C}$ -enriched with increasing combustion temperature, an effect previously observed in stepped combustion-IRMS studies of terrestrial organic assemblages (e.g., Gilmour and Pillinger, 1985).

### 3.3.2. Variations in mean organic combustion temperature

Significant variations in combustion temperatures are apparent between the bitumen samples. The stepped nature of the combustion process means that the temperature of peak carbon release (the mode) cannot be determined with precision greater than the size of the temperature step. However, by weighting the amount of carbon released in each combustion step to the temperature attained by that temperature step, it is possible to calculate an arithmetic mean. These means, calculated by the formula below, are listed in Table 1.

$$T_{\text{mean}} = \frac{\sum_{T=0}^{T=T_{\text{all}}} T_{\text{step}} \cdot m_{\text{step}}}{\sum m}$$

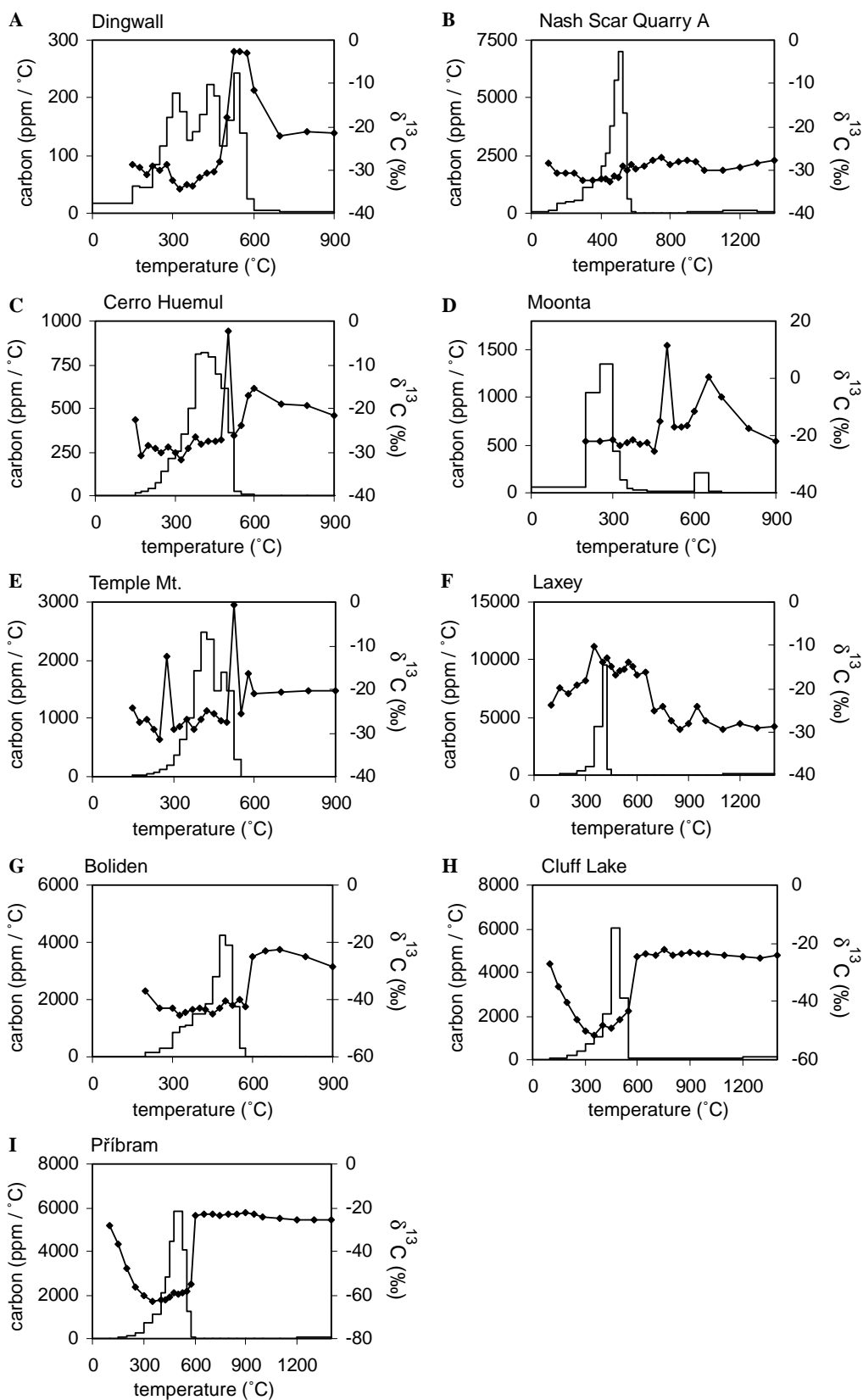


Fig. 5. Carbon yields (—) and  $\delta^{13}\text{C}$  profiles (+) for the bitumen samples. The isotopically heavy spikes around 500 °C in the samples from Cerro Huemul, Moonta, and Temple Mountain (also around 250 °C) are interpreted as experimental artefacts, not reflecting the true composition of the bitumen, and were disregarded in the calculations of the bulk bitumen  $\delta^{13}\text{C}$  values.

where  $T_{\text{mean}}$  is the mean combustion temperature,  $T_{\text{step}}$  is the temperature attained in a temperature step,  $m_{\text{step}}$  is the ppm of carbon released in that temperature step,  $T_{\text{all}}$  is the temperature at which combustion of organic carbon ceases. See Table 1 for the assigned cut-off points.  $\sum_m$  is the sum, over all temperature steps, of organic carbon released (in ppm).

The calculations of the organic mean combustion temperatures require a limit of organic combustion to be assigned. This refers to the MS86 temperature step in which the carbon evolved is no longer considered to represent organic matter, based on its abundance and carbon isotopic composition. Above that temperature, the evolved carbon is interpreted as carbonate and/or analytical blank. This temperature limit is then used to calculate the organic mean combustion temperature and the organic  $\delta^{13}\text{C}$ . The assigned maximum organic combustion temperatures ( $T_{\text{all}}$ ) used for this purpose are listed in Table 1.

Among the complex-hydrocarbon mixtures of Groups A and B, significant variations in the mean combustion temperature are apparent. The lowest (279 °C) occurs for the sample from Moonta; the highest (458 °C) in Nash Scar Quarry A. It is not possible to distinguish the irradiated bitumens from the nonirradiated samples, and no trend with radioelement concentration is apparent.

However, the putative methane-derived bitumens of Group C possess generally higher mean combustion temperatures. The bitumens from Boliden, Cluff Lake and Příbram produce values of 458, 474, and 480 °C, respectively. These combustion temperatures are higher than those of the complex-hydrocarbons mixtures and, with a precision of about 5 °C, show a trend of increasing mean combustion temperature with increasing radioelement concentration.

### 3.3.3. Variations in the organic carbon isotopic ratio

The carbon isotopic ratios of the organic matter in the bitumens have been calculated by weighting the isotopic composition of the gas evolved at each temperature step, to the mass of that gas, in a process similar to that used to calculate the mean combustion temperature, as described above. The same upper temperature limit as was used for the calculation of the mean combustion temperature was employed, to remove the isotopic contribution of the blank and carbonate carbon.

The carbon isotopic ratios of the organic matter in the bitumens are comparable with those acquired using the ANCA-SL (Table 1). Group B shows a general  $^{13}\text{C}$ -enrichment with increasing uranium concentration, an effect attributed to preferential escape of  $^{12}\text{C}$ -enriched gases, produced by radiolytic cleavage of bonds in organic matter (e.g., Leventhal and Threlkeld, 1978). However, the opposite relationship is apparent in the putative methane-derived bitumens of Group C-elevated radioelement

concentrations are associated with more negative  $\delta^{13}\text{C}$  values.

## 4. Discussion

### 4.1. A proxy for the degree of irradiation

The work presented here links variations in the chemical and isotopic composition of these bitumens to variations in their radioelement concentration. However, the correlation between radioelement concentration and the subsequent degree of radiolytic alteration is not straightforward; a range of influences can be significant:

- Radiation intensity (influenced by, e.g., the ambient radiation field or local radioelement concentration and source);
- Duration of irradiation;
- Dissemination of radioactive grains in the organic matter;
- Density of the organic matter;
- Abundance of water.

However, determination of many of these parameters is not simple. Although parameters like radioelement concentration and density can be measured relatively easily, quantitative determination of others is less simple. Microscopy can indicate the dissemination of radiation sources in the organic matter, but relating that to a degree of efficiency or effectiveness of radiolytic alteration is more difficult. An accurate determination of the duration of irradiation is also problematic. Though the age of the host rock may be known, this may bear little relation to the timing of hydrocarbon migration and bitumen formation. Reliable estimates of the abundance of water (which can accelerate alteration by the production of reactive hydroxyl ( $\text{OH}^-$ ) radicals, by the radiolytic cleavage of water) throughout that estimated duration are even more difficult. Consequently, previous workers have successfully used radioelement concentration as a proxy for the degree of alteration (Leventhal and Threlkeld, 1978; Dahl et al., 1988). This proxy is also used here. The presence of thorium, rather than, and in addition to, uranium in certain samples is not expected to cause significant differences in alteration, for similar radioelement concentrations. It should be noted that a proxy of radioelement concentration disregards the contribution of radiation from the decay series of these elements. However, an accurate correction for this factor would require knowledge of not just the timing of incorporation of the radioelements, but also the degree of retention of their daughter products. Reliable determination of these factors does not currently seem possible for these samples or, given the other difficulties discussed above, particularly useful.

## 4.2. Discerning the effects of radiation

The natural diversity of terrestrial bitumens means that variations in the properties of irradiated bitumens cannot be immediately assigned to variations in the degree of radiolytic alteration. Other factors, such as variations in the pre-irradiation bitumen composition, or differential thermal maturation or oxidation may be responsible for the observed differences.

Furthermore, differences observed between irradiated and nonirradiated bitumens may still be due to the variations mentioned above. Consequently, the nonirradiated complex-hydrocarbon mixtures of Group A are, in themselves, of limited utility as standards. The possibility and extent of variations in pre-irradiation composition and thermal maturation needs to be minimised or known, to enable chemical and physical variations to be ascribed with confidence to the effects of radiolytic alteration.

This can be achieved by the analysis and comparison of irradiated and nonirradiated bitumens that formed in the same fluid migration event and occur in close stratigraphical proximity. Such materials, having formed from the same hydrocarbon fluids, would possess very similar pre-irradiation chemical and isotopic compositions. Similar stratigraphical positions would minimise differential thermal maturation. This appears to have occurred at Nash Scar Quarry in Wales. Here, bitumen occurs in outcrops of the Folly Sandstone and the overlying Nash Scar Limestone. The bitumen from the Nash Scar Limestone is not mineralised (Nash Scar Quarry A), whereas the material from the Folly Sandstone contains thorium (Nash Scar Quarry B). The field relationships of the bitumen, occurring as veins and along bedding planes, and the close proximity of the units strongly suggests that the same fluid migration event was responsible for the bitumen deposits in both strata (Parnell and Eakin, 1989). Consequently, the bitumens would have possessed very similar pre-irradiation compositions. Furthermore, the close proximity of the samples suggests that differential thermal maturation has been minimised. Consequently, variations between Nash Scar Quarry A (nonirradiated) and Nash Scar Quarry B (irradiated) can be ascribed confidently to the effects of radiolytic alteration. These variations can then be compared with those among the other irradiated bitumens, in an attempt to build a comprehensive picture of the effects and nature of the radiolytic alteration of terrestrial biogenic complex-hydrocarbon mixtures.

### 4.3. What are the effects of ionising irradiation upon the complex-hydrocarbon mixtures?

#### 4.3.1. Comparison of the irradiated and nonirradiated samples from Nash Scar Quarry

Two bitumen samples were obtained from Nash Scar Quarry, Wales. These are believed to have formed during

the same fluid migration event, but only one contains thorium mineralisation and, hence, is irradiated. Therefore, comparisons between these samples offer the best available indication of the effects of ionising radiation upon naturally occurring organic assemblages, over geological timescales.

The effects of irradiation are apparent in Fig. 1. The chromatogram of the pyrolysis products from Nash Scar Quarry A is dominated by *n*-alkene-alkane couplets, whereas that of Nash Scar Quarry B is dominated by alkylated PAH. This difference is attributed to the radiolytic aromatisation and cracking of the aliphatic material, converting it into more radiation-resistant aromatic compounds, coupled with the greater resistance of aromatic compounds to radiolytic cleavage (Bovey, 1958).

Comparisons of the relative abundance of PAH, as shown in Figs. 2 and 3 are not useful, however. The PAH in the nonirradiated Nash Scar Quarry A bitumen are not derived from radiolytic alteration and so cannot be compared meaningfully with the distribution of those that are, as in Nash Scar Quarry B.

The variations in the occurrence and abundance of oxygen-containing compounds can be related to irradiation. Pyrolysis of Nash Scar Quarry A produced only phenols, and not the aldehydes and ketones found in Nash Scar Quarry B (Fig. 4). This supports reports of elevated atomic O/C ratios in irradiated bitumens (Nash et al., 1981; Landais et al., 1987). This can be attributed to reactions with hydroxyl radicals, formed by the radiolysis of water.

Carbon isotopic differences are also apparent between these two samples. Nash Scar Quarry A has a  $\delta^{13}\text{C}$  value of  $-31.1\%$ , whereas the irradiated Nash Scar Quarry B sample is more enriched in  $^{13}\text{C}$ , with a value of  $-29.0\%$  (Table 1). A similar positive shift in  $\delta^{13}\text{C}$ , associated with the effects of ionising radiation, was reported by Leventhal and Threlkeld (1978). This was attributed to preferential escape of isotopically light volatiles, formed by radiolysis of the organic matter, leaving a  $^{13}\text{C}$ -enriched residue.

Unfortunately, a further sample of Nash Scar Quarry B was unavailable for analysis by stepped-combustion-isotope ratio mass spectrometry. Consequently, a comparison of the mean combustion temperatures of the two Nash Scar Quarry samples cannot be made. However, the relationship between this parameter and the radioelement concentrations of the other Group B bitumens will be discussed below.

#### 4.3.2. Extension to the other complex-hydrocarbon mixtures

Differences between the two Nash Scar Quarry samples have been attributed to radiolytic alteration, as discussed above. If that conclusion is correct, then similar variations should be present in Group B bitumens containing significantly different radioelement concentrations.

The difference between the chromatograms of pyrolysis products from the Nash Scar Quarry samples is repeated with the other complex–hydrocarbon mixtures (Fig. 1). The nonirradiated bitumen from Dingwall is, like Nash Scar Quarry A, dominated by *n*-alkene–alkane couplets. In contrast, the irradiated Group B samples are similar to Nash Scar Quarry B: they produced only a few, mostly aromatic compounds. Furthermore, the diversity of pyrolysis products decreases with increasing radioelement concentration. This relationship is examined in detail in Fig. 2, indicating the relative abundances of certain PAH. An increased radioelement concentration is associated with a general reduction in the average size of PAH, and in a decrease in their degree of alkylation. This can be regarded as an extension of the processes of aromatisation and radiolytic cracking that produced the aromatic-dominated material of Nash Scar Quarry B from the mostly aliphatic material of Nash Scar Quarry A. These variations in the products of pyrolysis are in harmony with those observed for PAH in solvent extracts of irradiated organic matter (Dahl et al., 1988).

The relationship of a greater diversity of oxygen-containing compounds in radioelement-rich, relative to radioelement-poor, bitumen from Nash Scar Quarry is also observed amongst samples from other locations (Fig. 4). Nonirradiated bitumens (Group A) contain alkylphenols. The Group B complex–hydrocarbon mixtures contain other oxygen-containing compounds, such as 1- and 2-ring aromatic ketones and aldehydes. Further irradiation produces the additional compound, benzoic acid, which occurs in Laxey only, and is the dominant oxygen-containing species at elevated levels of alteration. Fig. 4 illustrates how the relative abundance of groups of these compounds varies with radioelement concentration. The oxygen in these molecules is presumably derived from hydroxyl radicals, formed by the radiolysis of water. These highly reactive species are capable of oxidising organic species in their vicinity. Although the presence of these compounds could be coincidental, reflecting variations in the pre-irradiation composition, the correlation with radioelement concentration suggests that this is unlikely. The link with radiolytic alteration is also supported by the elevated atomic O/C ratios observed in irradiated organic matter by various workers (Nash et al., 1981; Landais et al., 1987).

This is also supported by analyses of experimentally irradiated coronene-bearing water–ice (Bernstein et al., 2002; Bernstein et al., 2003). These workers reported that UV- and MeV-ion irradiation of a mixture of coronene and water–ice resulted in the attachment of functional groups. These functional groups, including alcohol (–OH), ketone (>C=O) and carboxylic acid (CO<sub>2</sub>H), are similar to those present in the pyrolysis products of these irradiated bitumens.

The <sup>13</sup>C-enrichment of the Nash Scar Quarry B sample, relative to Nash Scar Quarry A, is attributed to the effects of radiolytic alteration. The other Group B bitumens show a general trend of <sup>13</sup>C-enrichment with increasing radioelement concentration. Although the pre-irradiation carbon isotopic compositions of the other Group B bitumens and, hence, the actual isotopic shift induced by radiolytic alteration are unknown, the observed correlation suggests that extensive radiolytic alteration is the dominant influence upon the present-day isotopic composition.

Overall, variations in radioelement concentration can be matched to variations in the diversity and nature of the products of pyrolysis and of carbon isotopic composition. The differences observed in comparisons of the irradiated and non-irradiated samples from Nash Scar Quarry are evident in the wider sample set. This is strong evidence for the influences of radiolytic alteration.

#### 4.4. Variations in the mean combustion temperatures of the complex–hydrocarbon mixtures

The combustion behaviour of organic matter is related to the atomic H/C ratio. Variations in the atomic H/C ratio from 1.2 to 0.8 have been associated with an increase in the peak combustion temperature of ~70 °C (Gilmour, 1986; Wright and Pillinger, 1989). Normally, the H/C ratio of organic matter is influenced by the degree of thermal maturation, which causes the preferential depletion of H, leaving a carbon-enriched, aromatic residue. This process can, ultimately, create graphite, with an H/C ratio of close to zero.

However, radiolytic alteration can also modify the atomic H/C ratio of organic matter. Analyses of terrestrial, biogenic organic matter from the Akouta deposit in Niger indicate that organic matter with U concentrations of a few % wt. have H/C ratios that are around 0.15–0.20 lower than nonirradiated counterparts (Forbes et al., 1988). A single sample, containing 19.6% wt. U, gave an H/C ratio of 0.520, significantly less than the values of ~0.8, as observed for the nonirradiated samples. This supports previous work by Pierce et al. (1958) and explains the general hydrogen-depletion of uraniferous organic matter (e.g., Leventhal et al., 1986). A similar effect has been observed during the experimental irradiation of organic matter (Colombo et al., 1964). These workers reported that the gas evolved during irradiation was enriched in H<sub>2</sub>, relative to CH<sub>4</sub> and CO<sub>2</sub>, indicating that C–H bond cleavage was more common and that the residue was being depleted in hydrogen, relative to carbon.

The radiation-induced depletion in H/C ratios indicates that radiolytically altered organic matter should also possess elevated combustion temperatures. Variations of around 0.15–0.25 in the H/C ratios of irradiated organic matter, from around 0.8 to around 0.6, (Forbes et al., 1988) correspond to an offset in the combustion temperature of around 50 °C (Gilmour, 1986).

This gives a rough indication of the magnitude of the variations in combustion that might be apparent in biogenic uraniumiferous organic matter.

However, Fig. 5 and Table 1 indicate that no such relationship is apparent, among the complex-hydrocarbon mixtures of Groups A and B. The substantial variations in combustion temperature cannot be related to the radioelement concentrations.

This is most likely because of variations in the pre-irradiation composition of the organic matter from which these bitumens formed, or to the effects of differential thermal maturation, or a combination of those two processes, serving to obscure the effects of radiolytic alteration.

#### 4.5. Comparison of the samples from Moonta and Temple Mountain

A dichotomy exists between the analytical results of the samples from Moonta and Temple Mountain, and their radioelement concentrations. Published analyses indicated a uranium concentration around 4.2% wt. for bitumen at Moonta (Radcliff, 1906; Davidson and Bowie, 1951), whereas the sample from Temple Mountain is more enriched, at 7.0% wt. (Kelley and Kerr, 1958). However, these specimens are often found in positions in the trends described that are the reverse of those expected. For example, the trend of decreasing PAH size and degree of alkylation with increasing radioelement concentration (Fig. 2) is upset by these two samples, whose properties should ideally be reversed. A similar feature is also apparent in Fig. 4. The sample from Moonta contains fewer than expected ketones and aldehydes, compared with its more irradiated companion from Temple Mountain, in contrast to the overall trend. The carbon isotopic compositions of these samples would also fit the observed general trend better if their positions were reversed (Table 1), although both samples produced similar pyrolysis products (Fig. 1). However, a certain degree of radioelement heterogeneity should be expected amongst these bitumens, especially with the small masses used for these analyses.

#### 4.6. The Group C (putatively methane-derived) bitumens

##### 4.6.1. Does the data support an origin for the Group C bitumens by the radiolytic polymerisation of methane?

The irradiated bitumens analysed here are divided into two groups. Group B comprises irradiated solid organic matter, derived from mixtures of complex hydrocarbons. In contrast, the Group C samples have been proposed to have formed by the radiolytic polymerisation of methane.

Is the radiolytic polymerisation of methane to an organic solid feasible? The effects of the irradiation of methane have been modelled and experimentally illus-

trated by many workers, seeking to understand the effects of ionising radiation on the simple organic compounds present in cometary and interstellar ices. Irradiation of solid methane at 15 K with 6 keV  $\text{H}_2^+$  ions produced a solid organic residue that, after warming to room temperature, released molecules containing at least twelve carbon atoms (de Vries et al., 1984). This work was expanded by Kaiser et al. (Kaiser et al., 1992; Kaiser and Roessler, 1992, 1997, 1998), who produced PAH upon irradiation of methane ice at a range of temperatures with MeV protons and  $\alpha$ -particles. It must be noted, though, that the low temperatures and solid phases used are hardly representative of the terrestrial conditions under which the Group C bitumens described here were proposed to have formed. However, irradiation of methane (pure and mixed with helium, nitrogen or argon) with 6.5 MeV protons at room temperature and pressure is also capable of producing aromatic hydrocarbons (Sack et al., 1990). This suggests that the radiolytic polymerisation of methane into an organic solid is possible under geological conditions. The products should be expected in environments where ionising radiation and methane have coexisted over geological time.

An origin for the bitumen from Cluff Lake and Příbram by the radiolytic polymerisation of methane was originally based largely on isotopic grounds, and the presence of methane in the vicinity of the bitumen outcrops. The extreme  $^{12}\text{C}$ -enrichment of these materials was explained by the influence of  $^{12}\text{C}$ -enriched methane (Landais et al., 1993; Kríbek et al., 1999). However, other organic matter with very low  $\delta^{13}\text{C}$  values has also been reported. For example, the biogenic organic matter, derived from methanotrophic biomass, in the Be'eri sulphur deposit of Israel has  $\delta^{13}\text{C}$  values below  $-80\%$  (Burhan et al., 2002). Consequently, it could be argued that the  $^{12}\text{C}$ -enrichment of the Group C bitumens is a product of a similar process, rather than the radiolytic polymerisation of methane.

However, bitumen derived from methanotrophic biomass would comprise of a mixture of complex hydrocarbons, like the Groups A and B samples. Consequently, progressive radiolytic observation would induce decreases in PAH size, degree of PAH alkylation and diversity of pyrolysis products similar to those observed in the Group B samples (Figs. 1 and 2). These relationships are not apparent in the Group C samples. Instead, the opposite relationship is observed: the average size and degree of alkylation of PAH and the diversity of pyrolysis products increase with increasing radioelement concentration (Fig. 3). This cannot be explained in terms of the gradual radiolytic cleavage and aromatisation of a mixture of complex hydrocarbons, as suggested for the other bitumens. Instead, it suggests the gradual construction of PAH from smaller molecules. This trend concurs with that observed in experimentally irradiated coronene, where ionising irradiation was observed to cause the progressive addition of

Table 2  
Comparison of the effects of ionising radiation upon the studied organic assemblages

| Parameter                   | Behaviour of bitumen type with increasing radioelement abundance |   |
|-----------------------------|--|---|
|                             | Complex-hydrocarbon mixtures                                     | Methane-derived bitumens                    |
| Average PAH size            | Decreases  | Increases                                   |
| Degree of PAH alkylation    | Decreases  | Increases                                   |
| Degree of oxidation         | Increases  | Remains similar                             |
| $\delta^{13}\text{C}$       | Increases  | Decreases: probably unrelated to radiolysis |
| Mean combustion temperature | No relationship apparent   | Increases                                   |

methyl groups (Bernstein et al., 2002; Bernstein et al., 2003).

This relationship suggests that the Group C samples have been assembled from smaller hydrocarbons, supporting an origin by the polymerisation of methane. The variations in the products of pyrolysis probably reflect the difference between the radiolytic aromatisation and cracking of a pre-existing array of high molecular weight aliphatic hydrocarbons, and the radiolytic assembly of alkylated PAH from simple precursors such as methane (Table 2). The radiolytic assembly of complex organic matter from simple precursors is based on free radical chemistry. Radiolysis of methane produces methyl radicals, capable of combining to form larger hydrocarbons. Simultaneous assembly and cleavage of aliphatic oligomers would eventually produce radiation-resistant PAH (György, 1981; Sack et al., 1990; Landais et al., 1993; Kaiser et al., 1997; Kaiser and Roessler, 1998). This process is very different to the progressive radiolytic cleavage and aromatisation of a pre-existing mixture of complex hydrocarbons, so different paths of chemical evolution should be expected.

Further differences between Groups A, B, and C are indicated by the relative abundance of a range of oxygen-containing compounds present in the pyrolysates. Fig. 4 illustrates how radioelement enrichment of the complex-hydrocarbon mixtures is associated with the progressive formation of ketones, aldehydes and, in the sample from Laxey, benzoic acid. This is supported by detection of similar functional groups after the experimental irradiation of a coronene-water mixture (Bernstein et al., 2002; Bernstein et al., 2003). These oxygen-containing compounds are not present in significant quantities in the Group C bitumens, despite their elevated radioelement concentrations. This can be attributed to the different environments of formation. The presence of methane, from which these bitumens formed, would reduce hydroxyl ions, formed by the radiolysis of water. This would prevent significant oxidation of the organic matter, but only whilst the bitumen was surrounded by methane; exposure to the atmosphere and hydrosphere would remove the methane, enabling subsequent gradual oxidation of the organic matter. The degree of radiolytic oxidation

appears to be related to the local redox conditions: an excess of water over methane would allow oxidation by hydroxyl radicals, which would otherwise be reduced by methane. The influence of the nature of the organic starting material is summarised in Table 2.

The calculated mean combustion temperatures, as derived from the stepped combustion data, provide further evidence for an origin by the polymerisation of methane for the Group C samples. The complex-hydrocarbon mixtures possess a wide range of mean combustion temperatures that are unrelated to the radioelement concentration of the host bitumen (Table 1). In contrast, the putative methane-derived bitumens of Group C show a much narrower variation of mean combustion temperatures, and a relationship between that parameter and radioelement concentration. The absence of this relationship in the complex-hydrocarbon mixtures was attributed to variations in the pre-irradiation composition of the organic matter, and differential thermal maturation. The presence of such a relationship among the putative methane-derived bitumens of Group C suggests that variations in those factors have been minimised. The potential for variations in the pre-irradiation organic composition would be minimal if that organic source material was methane.

Furthermore, the increase in mean combustion temperature with increasing radioelement concentration matches the effect expected from PAH formed by the polymerisation of methane. The addition of methyl groups to bitumen surfaces would increase the atomic H/C ratio and drive down the combustion temperature. However, irradiation of the bitumen core would form larger PAH with lower atomic H/C ratios. Since the ratio of surface area to volume decreases with increasing volume, progressive radiolytic alteration would allow the hydrogen-depleted core material to dominate, causing the mean combustion temperature to increase. The extent of the observed variations in the mean combustion temperature (a few 10 of degrees) is comparable with that expected, as described in Section 4.4.

Consequently, we believe that the Group C bitumens are derived from the radiolytic polymerisation of methane. An alternative explanation—that these variations are coincidental, reflecting pre-irradiation variations that

have survived subsequent radiolytic alteration—seems less likely.

#### 4.6.2. Carbon isotopic composition of the Group C bitumens

The Group B complex–hydrocarbon mixtures show enrichment in  $^{13}\text{C}$  with increasing radioelement concentration. This was attributed to radiolytic alteration (Leventhal and Threlkeld, 1978). In contrast, the Group C bitumens show a correlation of  $^{12}\text{C}$ -enrichment with increasing radioelement concentration (Table 1). However, this is not necessarily due solely to radiolytic alteration.

This difference may also be due to differences in the mechanism of isotopic change between complex–hydrocarbon mixtures and putative methane-derived bitumens. In complex–hydrocarbon mixtures, preferential escape of  $^{12}\text{C}$ -enriched material, liberated by radiolysis, enriches the organic residue in  $^{13}\text{C}$  (Leventhal and Threlkeld, 1978). In contrast, the isotopic composition of methane-derived bitumen may be dominated by the preferential capture and immobilization of  $^{12}\text{C}$ -rich molecules. Alternatively, variations in  $\delta^{13}\text{C}$  may be inherited from isotopic variations in the source methane. The carbon isotopic composition of methane can vary tremendously, from  $-23\text{‰}$  to  $-93\text{‰}$  (e.g., Breas et al., 2002), and further fractionation can occur during migration (Zhang and Krooss, 2001). It seems likely that a combination of these two processes produced the final carbon isotopic composition of these bitumens, implying that, for methane-derived bitumens,  $\delta^{13}\text{C}$  values are not useful as a proxy for the degree of radiolytic alteration, without knowledge of the isotopic composition of the source methane.

#### 4.7. Implications for extraterrestrial sample analysis

The data presented here indicates that radiolytic alteration is capable of causing the mean combustion temperature of organic matter to increase. This is attributed to a radiation-induced decrease in the atomic H/C ratio (Colombo et al., 1964; Wright and Pillinger, 1989; Lewan et al., 1991).

Observations of icy solar system bodies such as Kuiper Belt objects and comets have produced estimates of their composition. Although water is the dominant species, simple organic compounds, including methane, and solid organic matter are important minor constituents (e.g., A'Hearn et al., 1995; Brown, 2002; Gibb et al., 2003).

Ionising radiation is the dominant energy source for the alteration and processing of these bodies and the interstellar ices from which they coalesced (e.g., Moore et al., 2003). Despite the low temperatures, suprathreshold chemistry, induced by the impact of energetic ions, can cause the polymerisation of simple organic molecules, including methane, into more complex, relatively hydrogen-depleted organic materials, including PAH (Kaiser and Roessler,

1997, 1998; Strazzulla and Palumbo, 1998; Cottin et al., 1999; Ehrenfreund et al., 2001; Hudson and Moore, 2001; Baratta et al., 2003).

The experimental irradiation of organic materials in simulated cometary and interstellar ices by these workers indicates that radiation-induced decreases in the atomic H/C ratio are not constrained to biological materials. Consequently, radiation-induced variations in combustion temperature should also be expected in extraterrestrial organic matter. This previously unrecognised effect has interesting implications for analyses of extraterrestrial organic matter, involving the technique of stepped combustion.

Ionising irradiation can only affect the surface materials of these icy bodies. Ultraviolet radiation can only penetrate a few micrometers of typical materials, although this can be extended by the movement of material by impact gardening. Energetic particles are more penetrative, and can cause the alteration of material at depths of many metres. However, the comparative scarcity of such energetic particles limits significant alteration to depths of about a metre (e.g., Johnson, 1989; Moore et al., 2003). The organic products of such alteration have been proposed as the cause of the very low albedos of bodies, such as Comets Halley, Borrelly, and Wild 2, which all possess albedos around 0.03 (Soderblom et al., 2002; Brownlee et al., 2004).

However, cometary nuclei are not uniform in albedo. Images of the nucleus of Comet Borrelly, returned by the Deep Space One mission in 2001, revealed significant variations in albedo, from 0.012 to 0.045. Analyses of stereo imagery indicate that the dark areas (“dark spots”) are not shadowed, but are actually topographically higher than the surrounding, more reflective material (Britt et al., 2004). These workers suggested that these elevated dark spots had been exposed at the surface for longer, sustaining a greater dose of ionising radiation, than surrounding material. This relationship is in harmony with the expected progressive radiolytic and photolytic darkening of organic-rich surfaces (e.g., Cruikshank et al., 1998).

Variations in the albedo of the nucleus of Comet Wild 2, encountered by the Stardust spacecraft in January 2004, may also be apparent, although full calibration of the imagery is not yet completed (Brownlee et al., 2004).

The relationship between elevated radiation dose, lower atomic H/C ratio and elevated mean combustion temperature is discussed above. It seems reasonable that this can be extended to the organic matter present in cometary nuclei. Consequently, the “dark spots” of Comet Borrelly should include organic matter possessing elevated mean combustion temperatures, relative to the more reflective areas.

The predicted combustion temperatures of cometary organic matter are directly relevant to the Philae lander of the Rosetta spacecraft, upon arrival at Comet 67P/Churyumov-Gerasimenko in 2014. Samples of the nucleus



will be analysed by stepped combustion-IRMS, as part of the Ptolemy experiment. Studies of analogous materials, such as these, will enable better interpretation of the results of the Ptolemy experiment, advancing our understanding of the nature and formation of extraterrestrial organic material, and the significance of that material to the evolution of life on the early Earth and elsewhere. A greater understanding of the properties of radiolytically altered organic matter will also enable improvements in the designs of future experiments. For example, predictions of the likely combustion temperature of such material, possibly derived from measurements of the atomic H/C ratio, albedo and combustion behaviour of analogous ices, would enable the combustion profile to be designed to fit the material being analysed and aid interpretation of the results.

## 5. Conclusions

1. The nature of the radiolytic alteration of naturally occurring, terrestrial organic solids depends on their composition and genesis. Irradiated complex–hydrocarbon mixtures respond differently to radiolytic alteration than bitumens formed by the radiolytic polymerisation of methane.
2. The radiolytic alteration of complex–hydrocarbon mixtures proceeds by cleavage, aromatisation, and oxidation, transforming aliphatic hydrocarbons into aromatic hydrocarbons. Irradiation causes the average size and degree of alkylation of PAH in the pyrolysis products of complex–hydrocarbon mixtures to decrease, with a concomitant enrichment in  $^{13}\text{C}$ . Reactions with hydroxyl radicals, formed by the radiolysis of water, increase the degree of oxidation by the progressive formation of phenols and aromatic ketones, aldehydes and carboxylic acids.
3. Ionising radiation from the decay of uranium and thorium is capable of polymerising terrestrial light hydrocarbons, such as methane, into complex, PAH-rich solid organic matter. Methane is abundant in bodies such as comets, interstellar ices and on the surface and in the atmosphere of Titan. By analogy, it is expected that cosmic irradiation of extraterrestrial methane would produce PAH similar to those observed in their terrestrial counterparts. Our data support the proposed formation of PAH by cosmic irradiation of interstellar and cometary ices.
4. Radiolytic alteration can cause the mean combustion temperature of organic matter to increase. This is due to the progressive loss of hydrogen, causing the atomic H/C ratio to decrease. Similar effects have been observed previously in thermally matured organic matter.
5. These analyses of irradiated bitumens suggest that the combustion behaviour of cometary organic matter is related to the radiation dose. This knowledge should aid better interpretation of data from, and design and implementation of instrumentation associated with, in situ extraterrestrial sample analysis.
6. Irradiation can produce a wide variety of functionalised aromatic compounds. Such material, whether generated in situ on the early Earth or delivered from an extraterrestrial environment, would have made a significant contribution to the prebiotic organic inventory of the early Earth.

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## Appendix A

Carbon yields and isotopic compositions of the methane-derived bitumens and complex–hydrocarbon mixtures, as determined by stepped combustion-isotope ratio mass spectrometry.  $\delta^{13}\text{C}$  values in italics are interpreted as experimental anomalies and are omitted from calculations of the bulk organic and total  $\delta^{13}\text{C}$ .

| <i>T</i> (°C) | Dingwall   |                              | Nash Scar<br>Quarry A |                              | Cerro Huemul |                              | Temple<br>Mountain |                              | Moonta     |                              | Laxey      |                              | Boliden    |                              | CluffLake  |                              | Příbram    |                              |
|---------------|------------|------------------------------|-----------------------|------------------------------|--------------|------------------------------|--------------------|------------------------------|------------|------------------------------|------------|------------------------------|------------|------------------------------|------------|------------------------------|------------|------------------------------|
|               | C<br>(ppm) | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm)            | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm)   | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm)         | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm) | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm) | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm) | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm) | $\delta^{13}\text{C}$<br>(‰) | C<br>(ppm) | $\delta^{13}\text{C}$<br>(‰) |
| 100           |            |                              | 7231                  | -28.3                        |              |                              |                    |                              |            |                              | 794        | -23.6                        |            |                              | 1341       | -27.3                        | 832        | -28.2                        |
| 150           | 2519       | -28.6                        | 6970                  | -30.7                        | 595          | -22.6                        | 996                | -24.1                        |            |                              | 806        | -19.9                        |            |                              | 1845       | -34.7                        | 1065       | -36.9                        |
| 175           | 1177       | -29.5                        |                       |                              | 332          | -30.7                        | 650                | -27.6                        |            |                              |            |                              |            |                              |            |                              |            |                              |
| 200           | 1137       | -31.0                        | 20,519                | -30.6                        | 605          | -28.4                        | 810                | -27.0                        | 11,489     | -22.0                        | 3282       | -21.2                        | 3820       | -36.8                        | 4700       | -40.2                        | 2763       | -47.8                        |
| 225           | 1133       | -29.2                        |                       |                              | 1016         | -29.2                        | 1357               | -29.2                        |            |                              |            |                              |            |                              |            |                              |            |                              |
| 250           | 2099       | -30                          | 23,858                | -30.8                        | 1787         | -30.3                        | 2039               | -31.6                        | 52,447     | -21.9                        | 8491       | -19.2                        | 7657       | -43.0                        | 9013       | -46.3                        | 5399       | -56.4                        |
| 275           | 2901       | -28.8                        |                       |                              | 3429         | -28.8                        | 3241               | -12.5                        |            |                              |            |                              |            |                              |            |                              |            |                              |
| 300           | 4133       | -32.5                        | 26,940                | -32.3                        | 5255         | -30.2                        | 5077               | -29.2                        | 67,796     | -21.3                        | 16,751     | -18.1                        | 15,114     | -43.2                        | 20,796     | -50.4                        | 14,532     | -60.0                        |
| 325           | 5198       | -34.3                        |                       |                              | 6255         | -31.7                        | 9366               | -28.6                        | 10,841     | -23.7                        |            |                              | 21,663     | -45.5                        |            |                              |            |                              |
| 350           | 4394       | -33.4                        | 55,308                | -32.5                        | 8797         | -29.2                        | 16,257             | -27.0                        | 3269       | -22.4                        | 34,932     | -10.3                        | 26,626     | -44.4                        | 36,745     | -51.4                        | 34,702     | -62.9                        |
| 375           | 3177       | -33.8                        |                       |                              | 12,551       | -26.4                        | 25,240             | -29.3                        | 1310       | -21.4                        |            |                              | 28,090     | -43.4                        |            |                              |            |                              |
| 400           | 3537       | -31.6                        | 7183                  | -31.9                        | 20,363       | -28.2                        | 45,704             | -27.0                        | 876        | -22.8                        | 212,418    | -14.0                        | 37,308     | -42.9                        | 51,438     | -48.0                        | 55,605     | -62.4                        |
| 425           | 4299       | -30.8                        | 5067                  | -32.2                        | 20,457       | -27.4                        | 62,083             | -25.0                        | 599        | -22.7                        | 239,172    | -13.0                        | 37,909     | -43.6                        |            |                              | 52,559     | -62.5                        |
| 450           | 5571       | -30.4                        | 6516                  | -32.7                        | 19,948       | -27.7                        | 59,276             | -25.5                        | 398        | -25.5                        | 13,873     | -14.8                        | 46,739     | -45.1                        | 105,230    | -49.1                        | 70,598     | -60.8                        |
| 475           | 5071       | -28.1                        | 9427                  | -31.6                        | 17,436       | -27.3                        | 37,192             | -27.2                        | 495        | -14.8                        | 1403       | -16.9                        | 69,426     | -42.9                        |            |                              | 110,773    | -59.0                        |
| 500           | 2906       | -18                          | 14,403                | -31.7                        | 15,291       | -2.2                         | 45,134             | -27.5                        | 452        | 11.4                         | 675        | -15.9                        | 106,015    | -40.4                        | 302,973    | -46.4                        | 146,330    | -59.8                        |
| 525           | 4030       | -2.6                         | 17,437                | -29.1                        | 9077         | -26.3                        | 36,785             | -0.7                         | 349        | -17.2                        | 519        | -15.6                        | 97,098     | -42.0                        |            |                              | 146,364    | -58.9                        |
| 550           | 6077       | -2.6                         | 10,859                | -30.2                        | 663          | -23.9                        | 7494               | -25.6                        | 301        | -16.8                        | 463        | -13.9                        | 43,639     | -40.0                        | 141,110    | -43.1                        | 102,295    | -58.5                        |
| 575           | 3487       | -2.9                         | 1561                  | -28.8                        | 122          | -17.0                        | 198                | -16.6                        | 286        | -16.5                        | 501        | -15.0                        | 6891       | -42.5                        |            |                              | 30,498     | -55.3                        |
| 600           | 643        | -11.4                        | 1249                  | -29.8                        | 150          | -15.3                        | 119                | -20.8                        | 387        | -11.4                        | 486        | -17.0                        | 183        | -25.2                        | 4440       | -24.5                        | 1516       | -23.7                        |
| 650           |            |                              | 982                   | -29.1                        |              |                              |                    |                              | 10,761     | 0.7                          | 452        | -16.3                        | 200        | -23.1                        | 2881       | -23.8                        | 1064       | -23.0                        |
| 700           | 388        | -22.2                        | 805                   | -27.8                        | 133          | -18.9                        | 140                | -20.6                        | 626        | -6.4                         | 451        | -25.0                        | 211        | -22.3                        | 2625       | -23.9                        | 1077       | -23.1                        |
| 750           |            |                              | 998                   | -27.1                        |              |                              |                    |                              |            |                              | 494        | -24.2                        |            |                              | 2154       | -22.2                        | 1105       | -23.3                        |
| 800           | 247        | -21.1                        | 1087                  | -28.8                        | 129          | -19.4                        | 131                | -20.3                        | 263        | -17.4                        | 544        | -27.5                        | 246        | -25.1                        | 2932       | -24.0                        | 1103       | -22.8                        |
| 850           |            |                              | 1220                  | -28.2                        |              |                              |                    |                              |            |                              | 600        | -29.4                        |            |                              | 2315       | -23.5                        | 1132       | -23.1                        |
| 900           | 217        | -21.6                        | 1432                  | -27.8                        | 87           | -21.6                        | 147                | -20.3                        | 184        | -22.0                        | 695        | -28.1                        | 294        | -28.3                        | 2429       | -23.2                        | 1187       | -22.5                        |
| 950           |            |                              | 2048                  | -28.1                        |              |                              |                    |                              |            |                              | 838        | -24.2                        |            |                              | 2631       | -23.6                        | 1277       | -23.0                        |
| 1000          |            |                              | 3883                  | -29.9                        |              |                              |                    |                              |            |                              | 1328       | -27.5                        |            |                              | 2894       | -23.8                        | 1368       | -24.1                        |
| 1100          |            |                              | 6890                  | -30.2                        |              |                              |                    |                              |            |                              | 3858       | -29.4                        |            |                              | 4160       | -23.9                        | 2039       | -24.8                        |
| 1200          |            |                              | 10,029                | -29.3                        |              |                              |                    |                              |            |                              | 6276       | -28.1                        |            |                              | 7125       | -24.8                        | 3019       | -25.5                        |
| 1300          |            |                              | 10,798                | -28.4                        |              |                              |                    |                              |            |                              | 7899       | -29.1                        |            |                              | 10,243     | -25.0                        | 4236       | -25.6                        |
| 1400          |            |                              | 9254                  | -27.7                        |              |                              |                    |                              |            |                              | 7956       | -28.7                        |            |                              | 10,004     | -24.3                        | 4042       | -25.7                        |
| Total         | 64,342     | -24.2                        | 916,075               | -30.9                        | 144,479      | -27.8                        | 359,439            | -36.7                        | 163,130    | -20.1                        | 565,955    | -14.0                        | 549,108    | -42.4                        | 732,026    | -44.8                        | 798,478    | -58.6                        |

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