

## Asphalt in carbon-14-dated archaeological samples from Terqa, Syria

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The presence of fossil fuel compounds in archaeological samples giving ages much higher than expected has long been suspected but never proved by appropriate chemical analyses. An excessively high conventional  $^{14}\text{C}$  age was found in an archaeological charcoal sample from Terqa, Syria<sup>1</sup> (S313, Table 1). Its  $^{14}\text{C}$  age of 28,700 yr BP was at variance with the archaeological context, and with the  $^{14}\text{C}$  age of several other samples<sup>1</sup> (such as S283, Table 1) obtained from the same area and expected to date from -3000 BC or younger. The inconsistency can be explained by assuming contamination with geologically old material—either industrial petroleum products or ancient asphalt. We report here organic geochemical investigations of the sample S313 and of sample S267, which gave a  $^{14}\text{C}$  age -2,000 yr too old. A third charcoal sample (S283) from the same area, whose  $^{14}\text{C}$  age was consistent with its known historical age, and an asphalt sample found stuck to the bottom of a goblet from another site in the area dated at 1700 BC on typological grounds, were also analysed. Similar studies of used crankcase oils from motor vehicles, weathered 0-2 yr, and of hydraulic transmission fluid show that modern motor oil cannot be the contaminant at this excavation site. Our data clearly indicate that ancient asphalt must be the source of contamination. Caution should be exercised, therefore, in interpreting  $^{14}\text{C}$  dates of archaeological samples from areas containing asphalt or other fossil fuel deposits.

Fine charcoal samples were collected by D. Berry from and around an ancient dumpsite outside the ancient city wall of Terqa, Syria and stored in glass jars (see ref. 1 for details). Obvious extraneous matter, such as rootlets, was removed; the samples were converted to acetylene via lithium carbide<sup>2</sup> and counted in stainless-steel gas proportional @-detectors for  $^{14}\text{C}$  (Table 1).

The samples were Soxhlet-extracted successively with methanol and toluene/methanol (3:7 v/v) for 100 h. The extract was separated into hexane-insoluble (asphaltenes) and hexane-soluble (lipid or bitumen) fractions. The latter was fractionated into aliphatic and aromatic hydrocarbons and resins by silica gel column chromatography<sup>4</sup>. Samples S313 and S267 had asphaltenes and S267 also had traces of elemental

sulphur (Table 1). Sample S283 had no asphaltenes, but a considerable amount of elemental sulphur and resinous material characteristic of wood. The fractions were analysed by gas chromatography (GC) and GC-mass spectrometry. Sample S313 was  $^{14}\text{C}$  tested again after exhaustive extraction with toluene/methanol (3:7 v/v) and methylene chloride. After rinsing with 1 l of acetone to remove other organic solvents, the material was analysed for  $^{14}\text{C}$  measurements<sup>2</sup>. The  $^{14}\text{C}$  age determined was not significantly different from that found previously for the unextracted sample (Table 1).

The gravimetric (Table 1) and GC analyses revealed that the greater the discrepancy in age, the larger is the content of asphaltenes and hydrocarbons. The alkane profile of the control sample (S283) with correct  $^{14}\text{C}$  age was very different from those of the other two samples (Fig. 1, S267 not shown).

The normal alkanes in sample S283 ranged from  $\text{C}_{15}$  to  $\text{C}_{31}$  overlying a broad unresolved complex mixture (Fig. 1). Pristane and phytane are almost equally abundant. The carbon preference index (CPI) is -2.0, indicative of immature hydrocarbons derived from higher plant waxes. Triterpanes are present in minor amounts and are mainly  $17\alpha(\text{H})$ ,  $21\beta(\text{H})$ -hopanes. The lipids in this charcoal sample appear to be of mixed secondary origin from biogenic sources and traces of petroleum-like products seem to have been leached into the area by water over thousands of years. The presence of a few pyrolytic arenes<sup>6</sup> is consistent with such an input. The alkanes in samples S313 and S267 are predominantly cyclic triterpanes with minor amounts of steranes. Normal alkanes are found only in trace amounts (much less than in crude oils). The triterpanes consist mainly of a homologous series of  $17\alpha(\text{H})$ ,  $21\beta(\text{H})$ -hopanes and the extended hopanes ( $\geq\text{C}_{31}$ ) occur as their two diastereomers (R and S at position 22) in approximately equal abundance<sup>7</sup>. In fact, the ratio of the first eluting epimer (22S) to the second eluting epimer (22R) in the  $\text{C}_{31}$ - $\text{C}_{35}$  hopane series is -1.4 (measured with baseline GC resolution), consistent with mature ancient bitumen<sup>8</sup>. The aromatic fraction exhibits an unresolved hump over the entire boiling range, indicating heavy weathering of the lipid fraction. The low n-alkane content, such as that found in sample S283, could be masked in the other two samples which contain relatively higher concentrations of triterpanes from the presumed (fossil fuel) contamination.

Possible sources of oil contamination in the area are crankcase oil from motor vehicles, although the samples were retrieved from a depth of 2 m below the surface of an area with little or no traffic until a few years ago, and ancient asphalt. The area on the Euphrates in Syria contains asphalt<sup>9</sup>.

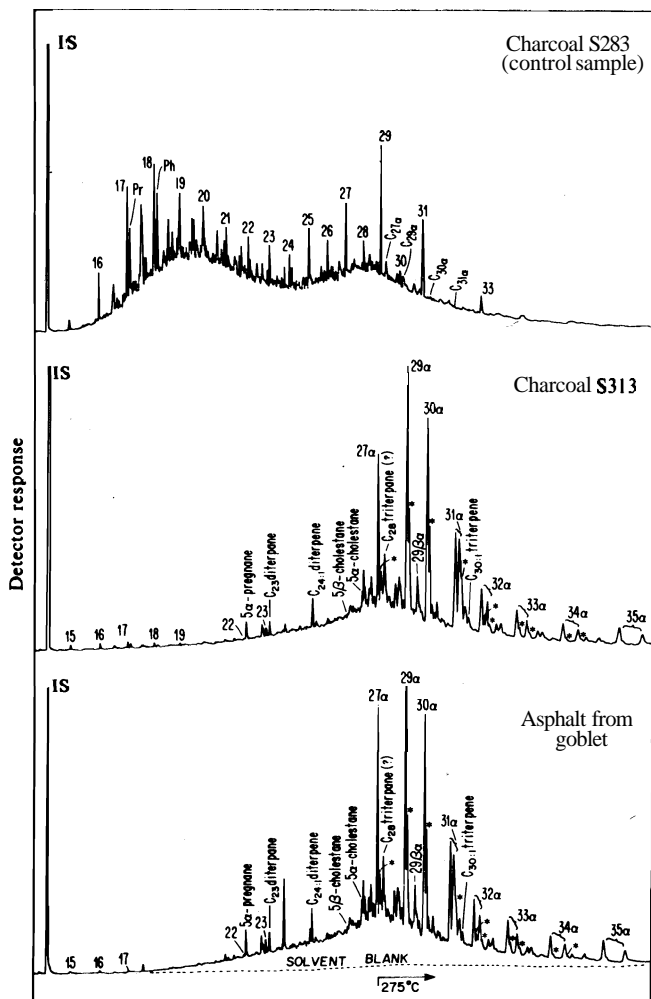
We analysed the hydrocarbon fractions of fresh hydraulic fluid and crankcase oil, fresh and weathered for -1 month to 2 yr. The crankcase oil was collected from underneath impounded cars and the period of weathering of the spilled oil from the cars is documented. The GC profiles of the hydrocarbons in the oils (Fig. 2) have a major unresolved hump at  $\text{C}_{20}$ - $\text{C}_{30}$  with a

Table 1 Organic geochemical results for archaeological samples from Terqa, Syria

Sample	Conventional $^{14}\text{C}$ age (BP)	Elemental sulphur* ( $\mu\text{g per g}$ )	Asphaltenes* ( $\mu\text{g per g}$ )	Hexane-soluble lipids* ( $\mu\text{g per g}$ )	Aliphatic fraction* ( $\mu\text{g per g}$ )	Aromatic fraction* ( $\mu\text{g per g}$ )	Asphaltenes			
							H/C	$\delta^{13}\text{C}$ (% PDB)	$\text{S}^{18}\text{O}$ PDB	SD (% SMOW)
Charcoal S283	4,110 ± 70	-15	—	144	41	53	—	—	—	
Charcoal S267	5,700 ± 100	Trace	900	1,440	260	86	1.27	-27.61	-15.58	-60.9
Charcoal S313	28,700 ± 1,100 28,200 ± 1,300†	—	5,300	14,560	2,790	1,820	1.03	-27.61	-15.88	Lost
Asphalt from goblet	—	—	104,000	43,000	4,860	2,410	1.23	-27.95	-15.58	-60.0

10 statistical counting errors are given for the conventional BP dates. The calibrated dates in centuries can be obtained using the table in ref 3. The age of the charcoal samples expected from stratigraphy is 3000 BC. PDB, Peedee belemnite. SMOW, standard mean ocean water. La Jolla Laboratory numbers in sequence of increasing  $^{14}\text{C}$  are: LJ 5052, LJ 4823 and LJ 5031.

\* Gravimetric determination. † After exhaustive extraction with organic solvents



**Fig. 1** Gas chromatograms of aliphatic fraction from charcoal and asphalt samples from Terqa, Syria. A Hewlett-Packard 5840A gas chromatograph equipped with a fused silica capillary column (SP-2100, 25 m, 0.2 mm i.d.) was used. The column was temperature-programmed for 35–275°C<sub>iso</sub> at 4°C per min. A 30 m, SE-54 (J&W) column of the same specifications was used for GC-MS analysis on a Finnigan model 4000 quadrupole mass spectrometer interfaced with a Finnigan Model 9610 gas chromatograph. The mass spectra data were processed with a Finnigan Incos Model 2300 data system. n-Alkanes were identified by their retention times. Di- and triterpenoids were identified from *m/z* 191 mass chromatograms. Triterpanes  $\geq C_{31}$  occur as R and S diastereomers. IS, internal standard (hexamethylbenzene); numbers (except when followed by a or  $\beta$ ) refer to n-alkanes; Pr, pristane; 27 $\alpha$ , 29 $\alpha$ , and so on refer to 17 $\alpha$ (H), 21 $\beta$ (H)-hopanes with the designated carbon numbers; 29 $\beta\alpha$  is a C<sub>29</sub> moretane (17 $\beta$ (H), 21 $\alpha$ (H)). \*Refers to the homologous series of methylated hopanes. Charcoal sample S267 had the same GC profile as S313 and therefore is not shown here.

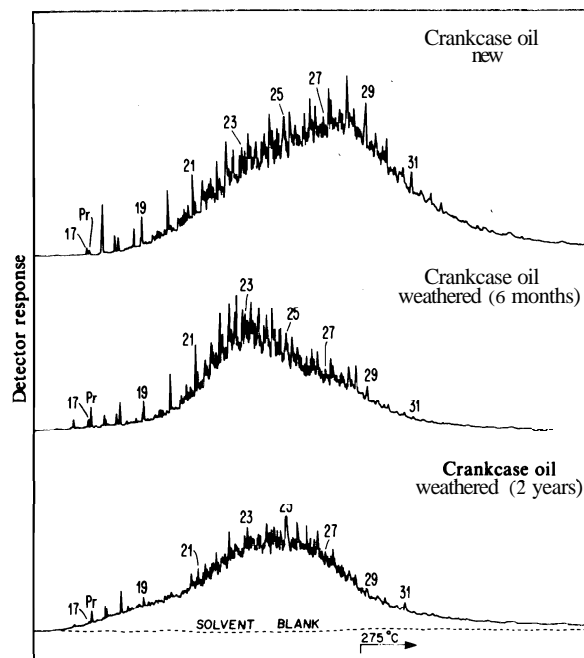
homologous series of n-alkanes and branched and cyclic hydrocarbons, in contrast to the contaminated charcoal samples which are depleted in n-alkanes. If the contaminant were crankcase oil weathered only since cars began operating in this region (20–40 yr), then almost total degradation of n-alkanes would be impossible. This can be surmised if we compare the fresh oil to the one weathered over two years (also heated to a certain extent in the car). The maximum temperature to which crankcase oil is normally heated is –205°C (250°C in diesel engines, D. Godfrey, personal communication), which may not be high enough to pyrolyse all the n-alkanes<sup>10,11</sup> in the time during which the oil is heated in the car. Also, the stratigraphy at the sample locations showed no streaks of spilled oil from the surface to the 2 m depth of the samples. These observations preclude automobile

oil from being the contaminant.

The only other possible source seems to be ancient, indigenous asphalt. Modern asphalt seems an unlikely candidate as there were no paved roads near the excavation site. An asphalt sample from a goblet in the area had the same n-alkane (trace amounts) and triterpenoidal distributions as did the two contaminated samples (Fig. 1). The H/C ratio and  $\delta^{13}C$  data of the asphaltenes from the samples (Table 1) are typical of data reported for asphalt<sup>12–14</sup>. The close agreement in the stable isotopic data (of carbon, oxygen and hydrogen obtained according to ref. 15) of the asphaltenes also suggests a common source of asphalt in the contaminated samples and the asphalt from the goblet, that is, indigenous asphalt.

The nonextractable residue, after exhaustive solvent extraction, gave almost the same <sup>14</sup>C age as the original sample (Table 1), suggesting that the unusually old age is largely due to the insoluble pyrobitumen<sup>16</sup> that could have originated from the asphalt. (Modern motor oil would probably be completely extracted by organic solvents used on sample S313, in which case the residue should have given a comparable age to that of other syngenetic samples in the area.)

In the third millennium in Syria, the asphalt used for sealing cracks in ceramic vessels<sup>17</sup> and fastening tool heads onto wooden handles<sup>9</sup> was probably melted by heating<sup>18,19</sup>. Frequent reheating, coupled with weathering, might have altered most of the asphalt into pyrobitumen. The residual asphalt which did not undergo complete thermal alteration could contain a triterpenoidal profile similar to the one reported here. At elevated temperatures (–375°C) straight-chain alkanes decompose<sup>10</sup>, whereas tricyclic diterpanes and pentacyclic triterpanes survive<sup>20</sup>. Indeed, the triterpenoidal distribution in the contaminated samples and asphalt are very similar to those of pyrolysates from kerogen matrices<sup>20</sup>. These pyrolysates have lesser amounts of steranes and moretanes compared with triterpanes and the C<sub>29</sub> $\alpha$  hopane is more abundant than the C<sub>30</sub> $\alpha$  homologue, as is observed here (Fig. 1). A minor series with *m/z* 205, analogous to the major hopane series, is also present, indicating an extra methyl group in the A or B ring. 3-Methylhopanes have been detected in bacteria<sup>21</sup> and the presence of the methylated hopanes implies microbial residues probably involved in the synthesis of petroleum hopanes<sup>22</sup>. Water washing and biodegradation of crude oil in reservoirs also could



**Fig. 2** Gas chromatograms of aliphatic fraction from crankcase oils. Experimental details as for Fig. 1. Numbers refer to n-alkanes; Pr, pristane.

remove n-alkanes and isoprenoids and lead to a similar distribution of triterpenoids in the resultant asphalt<sup>23</sup> as these compounds do not seem to be significantly affected by bacterial degradation<sup>23,24</sup>. It is not surprising, therefore, to see the biomarker steranes and di- and triterpanes (derived from the thermally altered and probably biodegraded indigenous asphalt) in the charcoal samples.

A broken storage pot of asphalt dumped in refuse could easily have contaminated some of the charcoal samples excavated from the ancient dumpsite. It is also feasible, that some of the native asphalt might have undergone thermal alteration by its proximity to the fireplace from which the charcoal samples could have originated. It is not known whether the asphalt was used as a fuel.

According to the <sup>14</sup>C data, pyrobitumen from ancient asphalt has contributed as much as 95.5% and 18% to the total carbon in samples S313 and S267 respectively. This large amount explains why, after removing the solvent solubles, a younger <sup>14</sup>C age was not observed for S313. The extractable material was much lower in concentration relative to the non-extractables.

This is the first organic geochemical study to verify contamination in <sup>14</sup>C dated archaeological samples, which could account for much older apparent ages than expected. Chronologies based on <sup>14</sup>C dates of archaeological materials containing fossil organic carbon in the absence of confirmatory molecular analysis should be accepted with caution. Similar organic geochemical analyses of a few samples (<sup>14</sup>C dated) from Jericho and Jarmo (northern Iraq) where traces of asphalt have been found on ancient stone tools<sup>18</sup> are in progress.

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