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Use and trade of bitumen in antiquity and prehistory: molecular archaeology reveals secrets of past civilizations

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THE ROYAL SOCIETY

Use and trade of bitumen in antiquity and prehistory: molecular archaeology reveals secrets of past civilizations

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Natural asphalt (or bitumen) deposits, oil seepage and liquid oil shows are widespread in the Middle East, especially in the Zagros mountains of Iran. Ancient people from northern Iraq, south-west Iran and the Dead Sea area extensively used this ubiquitous natural resource until the Neolithic period (7000–6000 BC). Evidence of earlier use has been recently documented in the Syrian desert (Boëda *et al*. 1996) near El Kown, where bitumen-coated flint implements, dated to 40 000 BC (Mousterian period), have been unearthed. This discovery at least proves that bitumen was used by Neanderthal populations as hafting material to fix handles to their flint tools.

Numerous testimonies, proving the importance of this petroleum-based material in Ancient civilizations, were brought to light by the excavations conducted in the Near East as of the beginning of the century. Bitumen remains show a wide range of uses (Connan & Deschesne 1995) that can be classified under several headings.

First of all, bitumen was largely used in Mesopotamia and Elam as mortar in the construction of palaces (e.g. the Darius Palace in Susa), temples, ziggurats (e.g. the so-called 'Tower of Babel' in Babylon), terraces (e.g. the famous 'Hanging Gardens of Babylon') and exceptionally for roadway coating (e.g. the processional way of Babylon). Since the Neolithic, bitumen served to waterproof containers (baskets, earthenware jars, storage pits), wooden posts, palace grounds (e.g. in Mari and Haradum), reserves of lustral waters, bathrooms, palm roofs, etc. Mats, sarcophagi, coffins and jars, used for funeral practices, were often covered and sealed with bitumen. Reed and wood boats were also caulked with bitumen. Abundant lumps of bituminous mixtures used for that particular purpose have been found in storage rooms of houses at Ra's al-Junayz in Oman. Bitumen was also a widespread adhesive in antiquity and served to repair broken ceramics, fix eyes and horns on statues (e.g. at Tell al-Ubaid around 2500 BC). Beautiful decorations with stones, shells, mother of pearl, on palm trees, cups, ostrich eggs, musical instruments (e.g. the Queen's lyre) and other items, such as rings, jewellery and games, have been excavated from the Royal tombs in Ur. They are on view in the British Museum. With a special enigmatic material, commonly referred to as 'bitumen mastic', the inhabitants of Susa sculpted masterpieces of art which are today exhibited in the Louvre Museum in Paris. This unique collection is presented in a book by Connan & Deschesne (1996). Last, bitumen was also considered as a powerful remedy in medical practice, especially as a disinfectant and insecticide, and was used by the ancient Egyptians to prepare mixtures to embalm the corpses of their dead.

Modern analytical techniques, currently applied in the field of petroleum geochemistry, have been adapted to the study of numerous archaeological bituminous mixtures found in excavations. More than 700 bituminous samples have been analysed during the last decade, using gas chromatography alone and gas chromatography coupled with mass spectrometry and isotopic chemistry (carbon and hydrogen mainly). These powerful tools, focused on the detailed analysis of biomarkers in hydrocarbon fractions, were calibrated on various well-known natural sources of bitumen in Iraq, Syria, Iran, Bahrain and Kuwait. These reference studies have made it possible to establish the origins of bitumen from numerous archaeological sites and to document the bitumen trade routes in the Middle East and the Arabo-Persian Gulf.

Using a well-documented case history, Tell el 'Oueili (5800–3500 BC) in South Mesopotamia, we will illustrate in this paper how these new molecular and isotopic tools can help us to recognize different sources of bitumen and to trace the ancient trade routes through time. These import routes were found to vary with major cultural and political changes in the area under study.

A second example, referring to the prehistoric period, describes bitumen traces on flint implements, dated from Mousterian times. This discovery, from the Umm El Tlel excavations near El Kown in Syria, was reported in 1996 in Boëda *et al*. At that time, the origin of the bitumen had not been elucidated due to contamination problems. Last year, a ball of natural oil-stained sands, unearthed from the same archaeological layer, allowed us to determine the source of the bitumen used. This source is regional and located in the Jebel Bichri, nearly 40 km from the archaeological site.

The last case history was selected to illustrate another aspect of the investigations carried out. Recent geochemical studies on more than 20 balms from Egyptian mummies from the Intermediate, Ptolemaic and Roman periods have revealed that these balms are composed of various mixtures of bitumen, conifer resins, grease and beeswax. Bitumen occurs with the other ingredients and the balms studied show a great variety of molecular compositions (Connan 1998). Bitumen from the Dead Sea area is the most common source but some other sources (Hit in Iraq?) are also revealed by different molecular patterns. The absolute amount of bitumen in balms varies from almost zero to 30% per weight (Connan & Dessort 1991; Connan 1998).

Keywords: bitumen; antiquity; prehistory; biomarker; balms; Egyptian mummies

1. INTRODUCTION

Oil-stained rocks, i.e. oil reservoirs, solid bitumen deposits, oil and gas shows, are widespread at the surface in the Middle East, especially in the Zagros mountains of Iran (figure 1). Numerous testimonies proving the importance of these petroleum-based raw materials in ancient civilizations have been brought to light step-by-step by the various excavations conducted in the Near East since the beginning of the century. Bitumen remains show a wide range of uses, which were primarily listed by Forbes in 1954 and updated later in a second edition of his book (Forbes 1964). Prominent examples of bitumen use are cited in the Bible when referring to the 'Babel tower', the well-known ziggurat of Babylon (Genesis 11.3), Noah's ark (Genesis 6.14), Moses's (basket?) cradle on the Nile (Exodus 2.3).

Since the pioneering work by Forbes, summarized in his book (Forbes 1964), which is still a reliable reference today, attempts have been made to draw secrets from the available bituminous mixtures unearthed from many excavations. In the late 1970s, R. F. Marschner, a petroleum geochemist from Amoco, undertook a collaborative study with H. T. Wright on the bituminous materials found mainly in excavations from Iran. These studies, based on the geochemical techniques available at the time in most oil companies, incidentally paved the way to exploiting chemical data stemming from the bitumen itself as well as from other components in the mixture (vegetal debris, ash, minerals, etc.). These milestone papers (Marschner & Wright 1978; Marschner *et al.* 1978) have truly opened the era of modern investigations by new geochemical tools based on modern geochemistry, namely: detailed analysis of hydrocarbons (alkanes and aromatics) with an emphasis on biomarkers (or geochemical fossils) by gas chromatography (GC); computerized gas chromatography–mass spectrometry (GC/MS), and even more recently by determination of isotopic values (δ^{13}C in ‰ per PDB) in individual compounds by gas chromatography-combustion-isotope ratio–mass spectrometry (GC/C-IRMS).

Ten years ago, after having reviewed what was known through the available literature, we undertook our own investigation programme using updated knowledge and more efficient analytical techniques, upgraded to better serve oil exploration. Available analytical techniques were slightly adapted and refined to adjust for the particular constraints of archaeological materials, but basically the heart of the analytical tools and knowledge improved for applied purposes in the petroleum industry were successfully used to study archaeological bituminous materials.

The goal of this paper is not to review what we have already published on bitumens found in various excavations, but to present a comprehensive summary which provides 'the flavour of the subject'. Through selected examples we intend to show what kind of useful information can be brought through the study of bituminous objects from excavations and we would encourage readers to find more details in the published examples. Therefore, after two sections describing the general framework of the topic, demonstrative case histories, largely unpublished, will be summarized to document the historical information that may be deduced from the study of bituminous materials present on archaeological sites. When an archaeologist finds such a mixture, the most common questions that spring to his mind are:

1. Is it a real bituminous mixture? How much bitumen was used? What other additives were mixed with the bitumen? For what reason? Were any changes made to the recipe through time and in different areas? Is it possible to define significant changes in relation to variations in the use of the prepared mixtures?
2. Where did the bitumen come from? Were there any changes in sources of imported bitumen through time? Do these identified trade routes agree with other historical data, especially the geopolitical and cultural framework? Ultimately, can bitumen trade-routes be traced though time as has been done for other goods such as spices, silk, copper, lapis lazuli, steatite, pearls, etc.?

2. USE OF BITUMEN IN ANTIQUITY AND PREHISTORY

The diversified use of bitumen in antiquity has been documented in several papers and books published by Hansen (1975), Perrodon (1989), Moorey (1994), Connan & Deschesne (1995, 1996), and Bilkadi (1996). These uses have been classified under several headings in table 1.

It appears that the most frequent use of bitumen was as mortar in building construction. These mortars were sometimes used for ordinary constructions, i.e. dwellings for workers and farmers, but more frequently for prestigious buildings such as temples, palaces (e.g. the Ishtar Gate in Babylon), terraces and ziggurats (e.g. of Ur, Aqarquf, Tchoga Zanbil). This mortar was prepared by mixing bitumen with chopped straw, clay and sand.

Bitumen was also extensively appreciated as a waterproofing agent and is still used for that purpose today on terraces and roofs, as in the famous 'Hanging Gardens of Babylon'. Included in this category are bitumen-coated

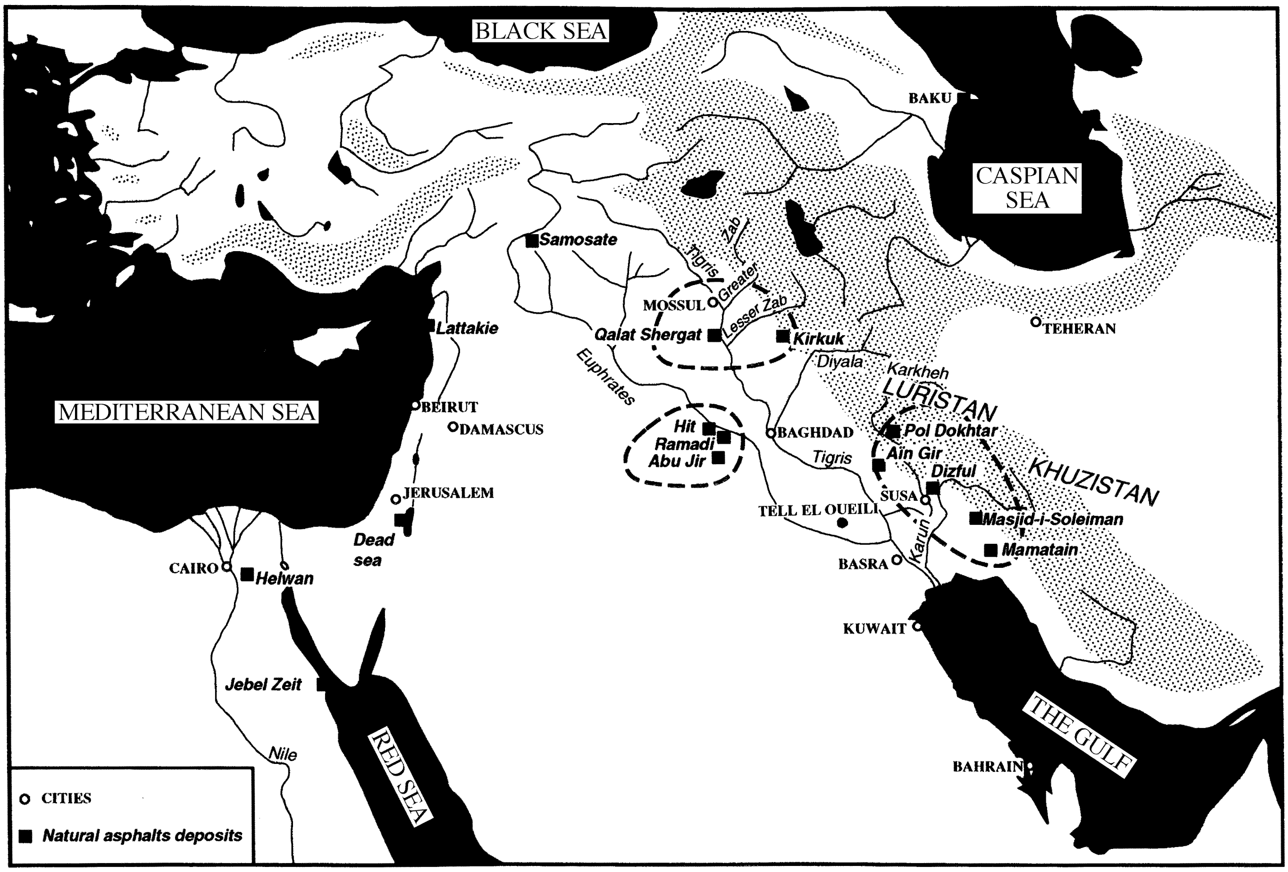

Figure 1. Map of the Near East showing the locations of the major natural asphalt deposits (e.g. Hit-Abu Jir, Dead Sea, Kirkuk, etc.).

Table 1. *Main use of bitumen in antiquity and prehistory*

use of bitumen	examples	excavations with examples studied
mortars in construction building	temples, palaces, terraces, floors, ziggurats, door threshold, courtyard	Mari, Babylon, Larsa, Haradum, Qal'at al-Bahrain, Mleiha, Failaka
waterproofing agent	mats, baskets, jars, water reserves, bathrooms, water pipes, cisterns, boats, sarcophagi	Tell es-Sawwan, Tell el'Oueili, Qal'at al-Bahrain, Saar, Baghdad, Ra's al-Junayz, Susa, Failaka, Tell Brak
adhesive and glue	sickles, tool handles, statues, jars, decoration (game, lyre, temple, pillar, ostrich egg)	Tell Atij, Netiv Hagdud, Umm El Tlel, Mari, Tell Halula, Ras Shamra, Susa
domestic artefacts	spindle whorls, balls, dice, wall cones	Tell el'Oueili, Failaka, Saar?, Qal'at al-Bahrain, Susa, Tell Brak
jewellery	bead, ring, gold badges on clothing or for horse harnesses	Umm al-Qaiwwain, Ulu Burun, Susa, Saar
sculpture	sculpture, cylinder and stamp seal of Susa in bitumen mastic	Susa
mummification	mixed with conifer resin, beeswax, grease to prepare mixtures for embalming	Egyptian mummies from the Queen valley and from several Museums (Lyon, Hannover, Paris)

mats, baskets, coffins, storage jars, sarcophagi, bathrooms, water pipes, cisterns, wooden poles, bridges and boats. Palm mats covered with bitumen are currently applied to waterproof roofs of houses or to shroud dead bodies. In basketry, combined effects may have been sought: for reinforcement, to preserve from decay and for waterproofing. A clay bathtub sarcophagus completely covered with bitumen, from the Assyrian period, is on exhibition in the Bahrain Museum. A famous example of bitumen mixture used as caulking agent on boats is given by the guffah, i.e. the small round boats which were used to cross the Euphrates and the Tigris rivers at the beginning of the century. An example of such boats may be seen in the Navy Museum in Paris, close to the Eiffel Tower.

Bitumen was the adhesive of antiquity. It was used extensively to repair broken statues or pottery; to fix flint implements on the wooden handles of sickles; to manufacture handles for small tools, such as chasing-chisels made

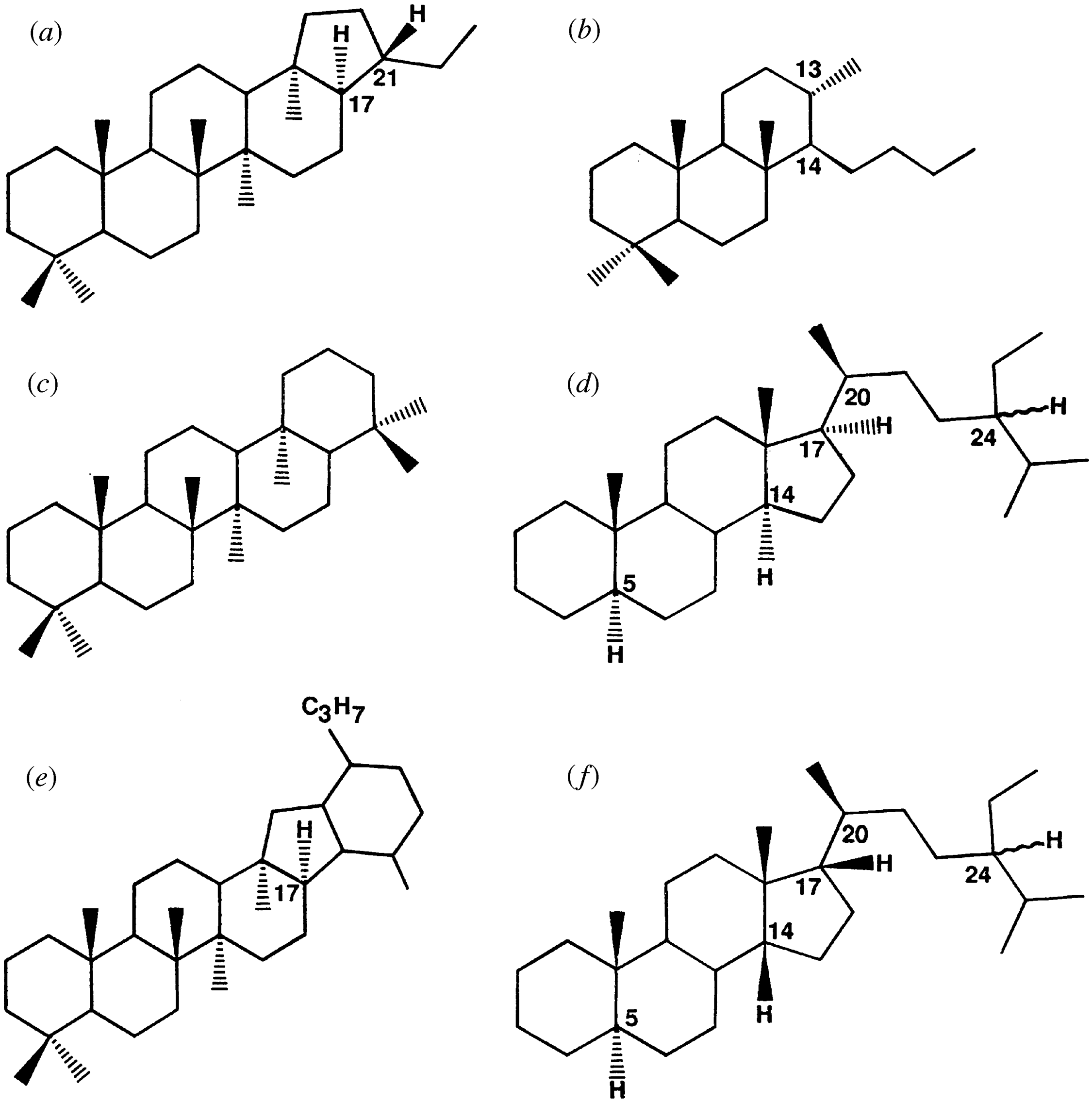

Figure 2. Molecular structures of some typical biomarkers found in the C_{15+} alkane fraction. Steranes are represented by (*d*) 5α(H), 14α(H), 17α(H)-20S-24-ethylcholestane (abbreviated to 29αααS) and (*f*) 5α(H), 14β(H), 17β(H)-20S-24-ethylcholestane (abbreviated to 29αββS). (*b*) C_{23}-13β(H), 14α(H)-tricyclopolyprenane (abbreviated to 23/3) is generally the dominant member of the tricyclopolyprenane family. (*a*,*c*,*e*) Other molecules belong to the terpane family.

of sharpened bones; to cover surfaces of artefacts subsequently decorated with mother-of-pearl, black shale, pink carbonate or lapis lazuli, as in the various artefacts discovered in the Ur graves dated around 2500 BC and on permanent exhibition at the British Museum. Among the most famous artefacts are the games and the royal lyres from Ur as well as the pillar from the temple at al-Ubaid in the same geographic area.

Bitumen mixtures used as an adhesive to stick flint implements to the handles of various tools were widespread until Neolithic times. We have studied several samples from Tell Atij in Syria dated 6800 BC and from Netiv Hagdud (8900–7800 BC) in Israel. Similar samples were also examined in Pakistan (Mehrgarhr, 3500 BC), in Syria (Mari, 2800 BC; Tell Halula), etc. Apparently, this use as an adhesive was prevalent at least from Mousterian times (Boëda *et al.* 1996) and perhaps earlier, for we now have evidence of its use from the Hummalian period (around 180 000 BC; Boëda *et al.* 1998). Hafting flint to handles and coating basketry are, up to now, the most commonly known uses of bitumen encountered during the prehistoric period.

Another section refers to the use of bitumen for jewellery. Asphaltite beads and dices are known in Susa. Beads of bitumen mixtures were found on necklaces in graves from the Ubaid period (Umm al Qaiwain, 5th millennium BC; Philips, personal communication). Rings manufactured from sea shells were decorated with beautiful inlays of precious stones encrusted in a bituminous glue. Some have been found in a boat sunk at Ulu Burun (Turkey), around 1500 BC. Decorative pieces of gold and silver, badges for clothing (a kind of fibula) or horse harnesses were prepared around a core of bitumen in Susa (Connan & Deschesne 1996). In some cases the gold and silver has been removed by robbers, but the former design is still visible as an imprint in the bitumen matrix.

Special mention should be made of the so-called ‘bitumen mastic’, which was extensively carved by the chisels of Susian sculptors until the fourth millennium to manufacture masterpieces of art which constitute the

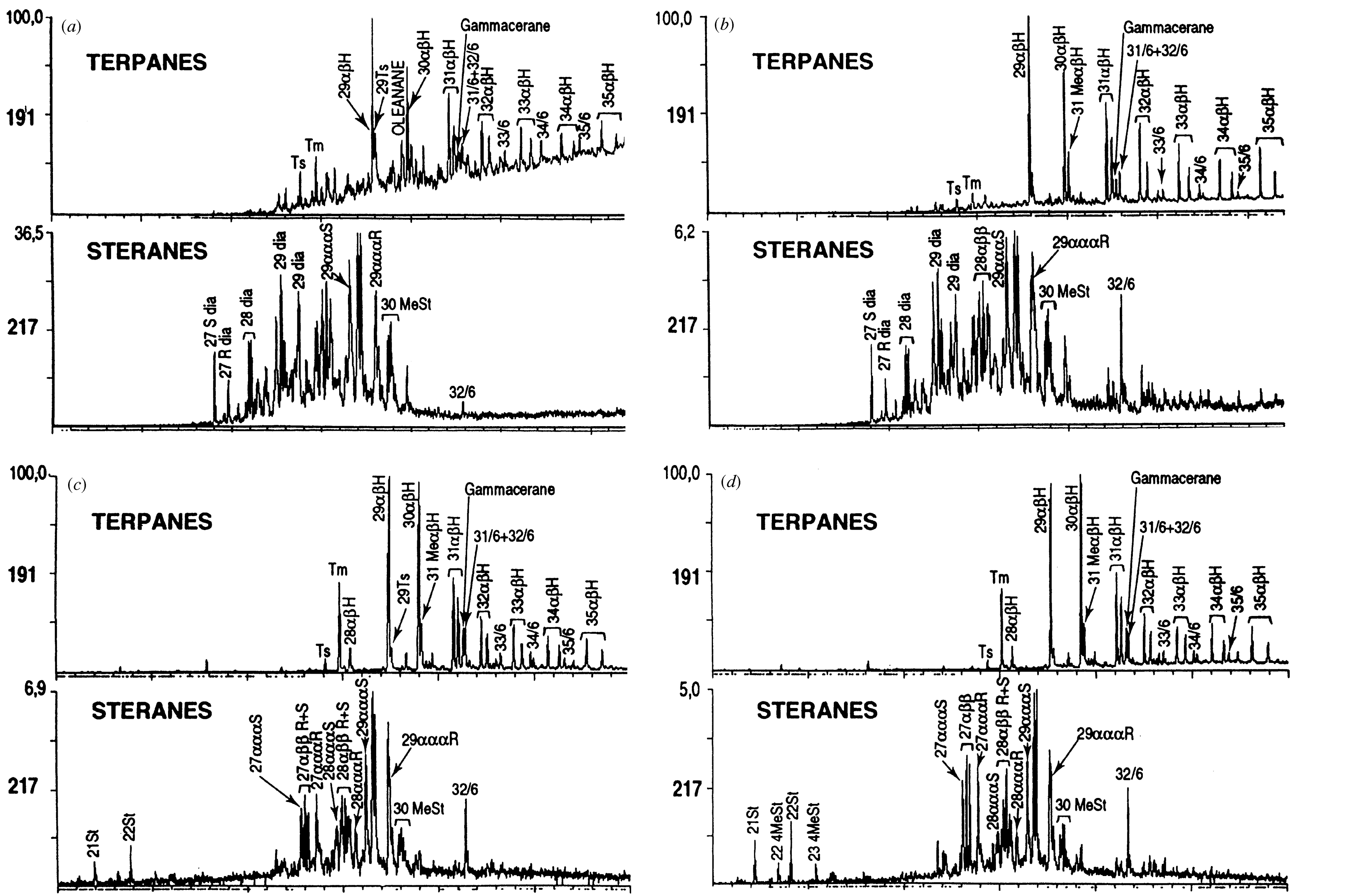

Figure 3. Distribution patterns of steranes and terpanes from some samples from Tell el'Oueili in southern Mesopotamia (Iraq). (*a*) 132-mats?-Ubaid 1—5400–4800 BC; (*b*) 134-bituminous cone-Ubaid 1—5400–4800 BC; (*c*) 26-spindle whorl-Ubaid 1—5400–4800 BC; (*d*) 60a-potsherd-Uruk—3500–3200 BC.

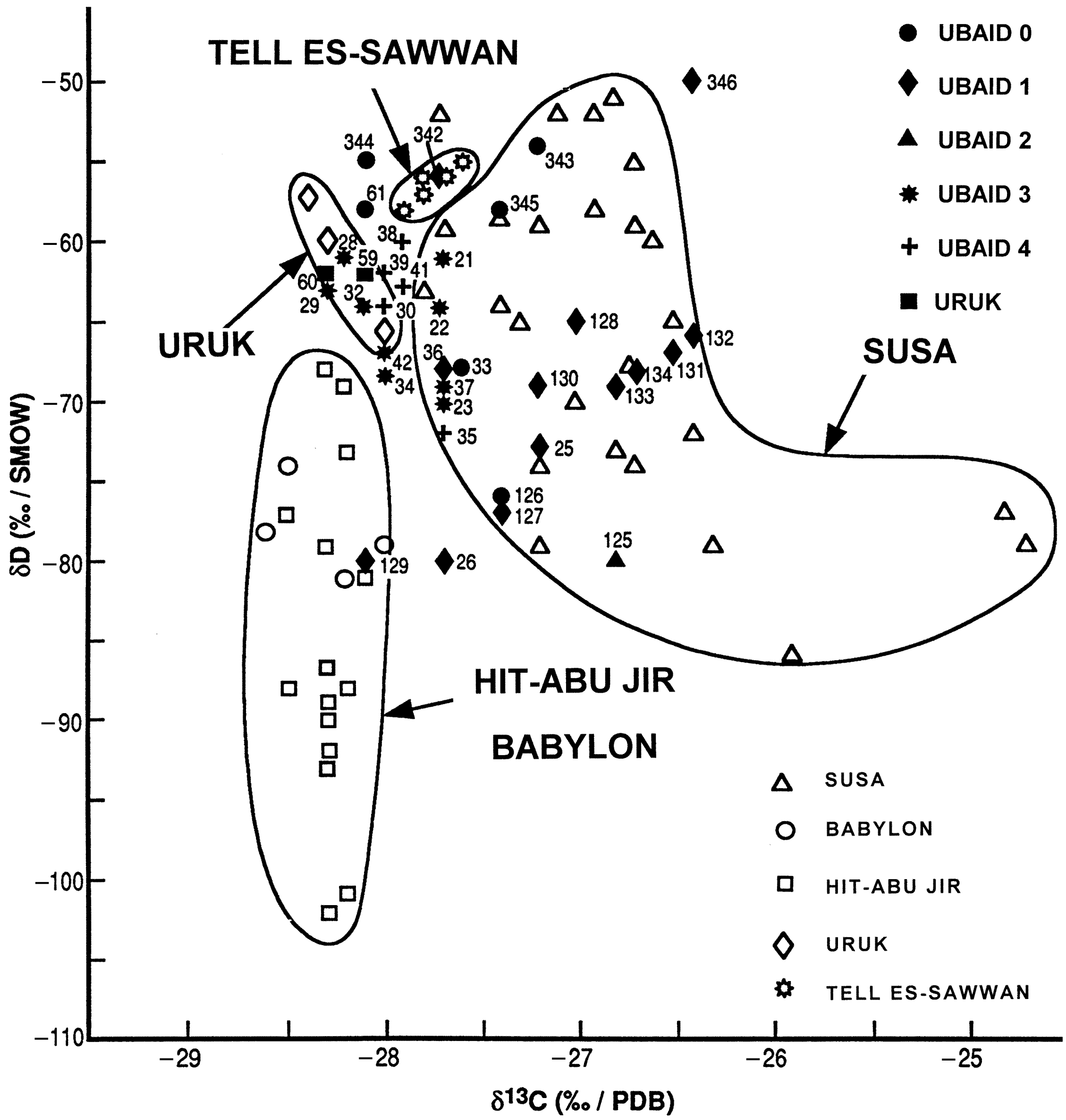

Figure 4. Plot of δ^{13}C vs δD in asphaltenes of Tell el'Oueili and some references from other archaeological sites (Susa in Iran, Babylon, Tell es-Sawwan and Uruk in Iraq) and natural asphalt deposits (Hit-Abu Jir in Iraq). Samples of Tell el'Oueili (i.e. with numbers) are presented according to their dates: Ubaid 0 (5800–5400 BC), Ubaid 1 (5400–4800 BC), Ubaid 2 (4800–4550 BC), Ubaid 3 (4550–4000 BC), Ubaid 4 (4000–3700 BC), Late Uruk (3500–3200 BC).

Louvre Museum's collection. Two years ago, when the book *Le bitume à Suse* (Connan & Deschesne 1996) was published, our conclusion leaned in favour of an artificial material, obtained through moderate thermal treatment of a bitumen-based mixture. Recent geochemical analyses of a carbonate source rock sequence from Iran have obliged us to reconsider our previous view and to announce that our book's conclusions may be modified in future (Connan & Deschesne 1998*b*). If this new hypothesis is confirmed at the end of the ongoing study, the material of Susian artefacts, referred to as 'bitumen mastic', will be defined differently, i.e. as a source rock within the glossary of petroleum geochemical terms. In that respect, the term 'bitumen mastic' will be no longer valid, for it refers to a preparation made by human beings, of an artificial bitumen-based mixture. The new hypothesis under study, which refers to a sedimentary rock, easily explains why the raw material was sculpted as a stone and not moulded, and why the presumed human discovery is mainly restricted to the Susian area.

Last, bitumen was used by embalmers in Ancient Egypt to prepare mixtures allowing the preservation of the dead bodies. Examples of the so-called 'black mummies' are currently visible in the British Museum.

3. FROM LIVING ORGANISMS TO PETROLEUM: BIOMARKERS AS TOOLS IN MOLECULAR ARCHAEOLOGY

All remains of living organic matter and its by-products (fat, wood, oil, pigments, pitch, wax) or fossil organic matter (coal, crude oil, amber, bitumen, asphaltite) provide the analytical chemist with diagnostic molecular features. Difficulties in archaeological artefacts are due to a constant evolution of the primary molecular spectrum through weathering processes (oxidation, photo-oxidation, water washing, biodegradation, evaporation, etc.). This step-by-step change can seriously alter the original molecular pattern, and the role of the geochemist is to establish what molecules are the most reliable for tracing

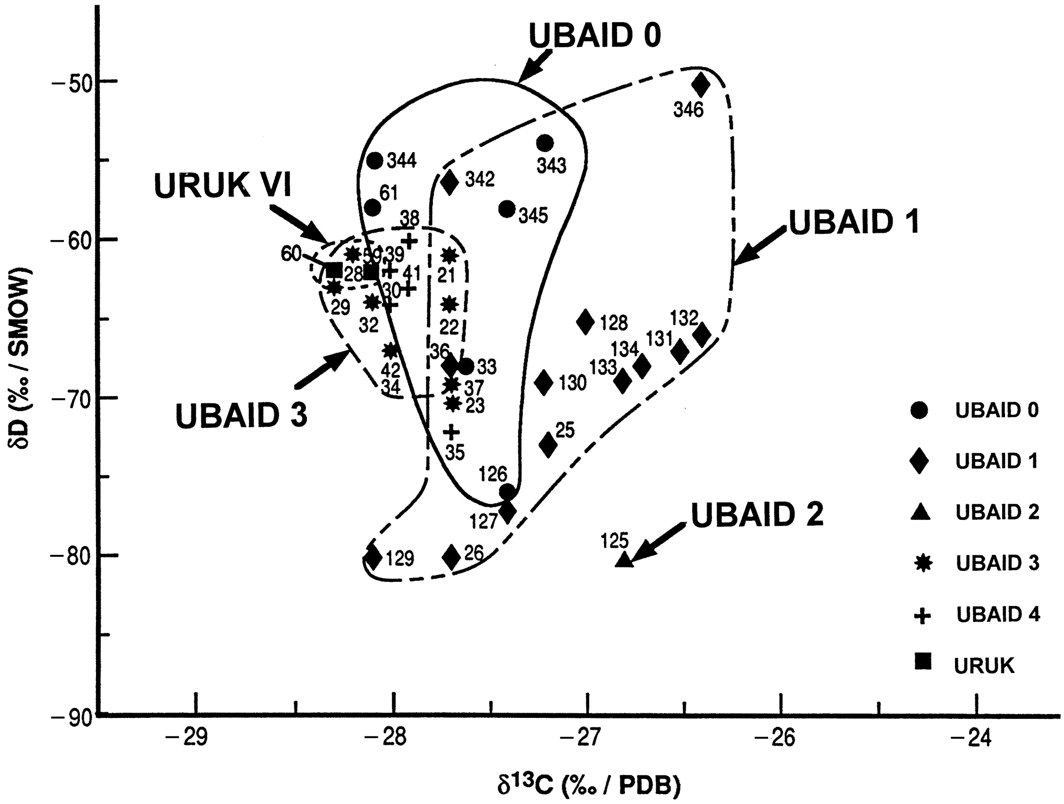

Figure 5. Plot of $\delta^{13}C$ vs δD in asphaltenes of Tell el'Oueili: comparison of data as a function of sample dates: Ubaid 0 (5800–5400 BC), Ubaid 1 (5400–4800 BC), Ubaid 2 (4800–4550 BC), Ubaid 3 (4550–4000 BC), Ubaid 4 (4000–3700 BC), Late Uruk (3500–3200 BC).

back to the source and what transformation pathways have evolved to generate the by-products identified.

Fossil fuels contain many so-called biomarkers or geochemical fossils (Eglinton & Calvin 1967) which are analysed by GC/MS to establish the genetic fingerprint of petroleum-derived products. Among the most commonly used classes of biomarkers (Peters & Moldowan 1993) are steranes and the terpanes, which occur in the C_{15+} alkane fractions. Other biomarkers can also be recorded in the C_{15+} aromatic fractions. Steranes (figure 2) are a class of polycyclic alkanes derived from steroids by moderate rearrangement. They contain between 21 and 30 carbon atoms. Cholesterol is a well-known member of the steroid family. Steroids are present in eukaryotic membranes in which they improve mechanical strength and impermeability to water. The second group of petroleum biomarkers are terpanes (figure 2). The most important family are the geohopanoids, which are thought to be derived from cholesterol surrogates (bacteriohopanoids) in bacterial membranes (Ourisson & Rohmer 1992).

In aromatic hydrocarbons various categories of molecular structure are currently found in archaeological bitumens. Specific biomarkers (aromatic steroids, secohopanoids, benzohopanes, etc.) are clearly brought to the mixture by the bitumen itself. Polyaromatic hydrocarbons of pyrolytic origin, such as fluoranthene and pyrene, are indicative of thermal treatment of the bitumen or of significant contribution of charred material, e.g. soot or ash (White 1986).

Archaeological samples are generally mixtures of bitumen (less than 30% as the most common composition) with mineral (clay, sand, carbonate, ash, baked bricks, etc.) and organic materials (chopped straw, rushes, palm leaves, reeds, etc.). All these compounds, especially the organic ones, provide molecular information which must be decoded and interpreted to understand the composition of the complex mixture. The major aim of studying the molecular information carried by the petroleum-based phase is to identify the source of the bitumen, and by calibration with known geological occurrences, to identify its importation to a site and study the trade routes through time.

4. CASE HISTORIES

(a) *Bituminous mixtures from Tell el'Oueili in Iraq: Mesopotamian trade routes through time*

Tell el'Oueili (figure 1) is a small tell, 10 m high, close to Larsa in southern Mesopotamia which was excavated by a French team, headed by J.-L. Huot from the Paris I University (Panthéon-Sorbonne) until 1989. According to Huot, who conducted the excavation programme, this tell is one of the first villages of a settled population in southern Mesopotamia. This excavation was particularly interesting because the explored layers brought to light several levels of settlements ranging from the Ubaid 0 (5800–5400 BC) to the Late Uruk (3500–3200 BC). Three millennia of history, with some serious gaps, are covered in a single location. Spindle whorls, mats, baskets, potsherds, balls and shapeless bituminous pieces were found from all excavated levels. Natural bitumen seepage is not found in that alluvial plain area (figure 1)

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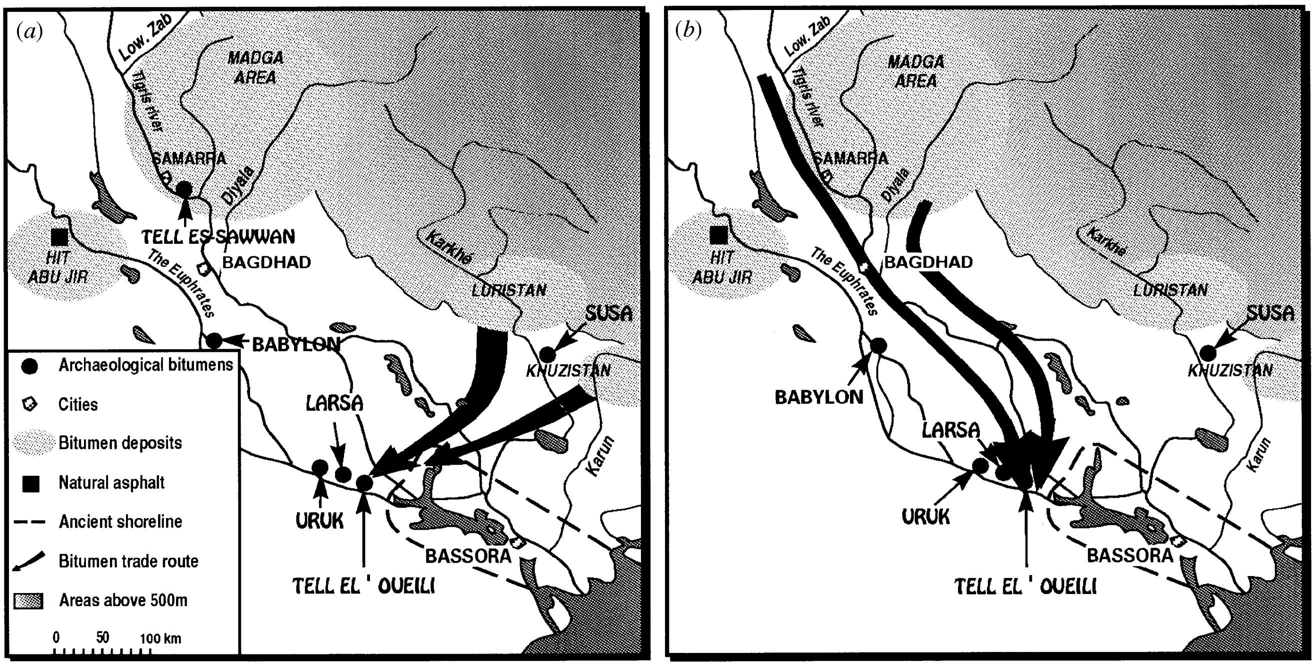

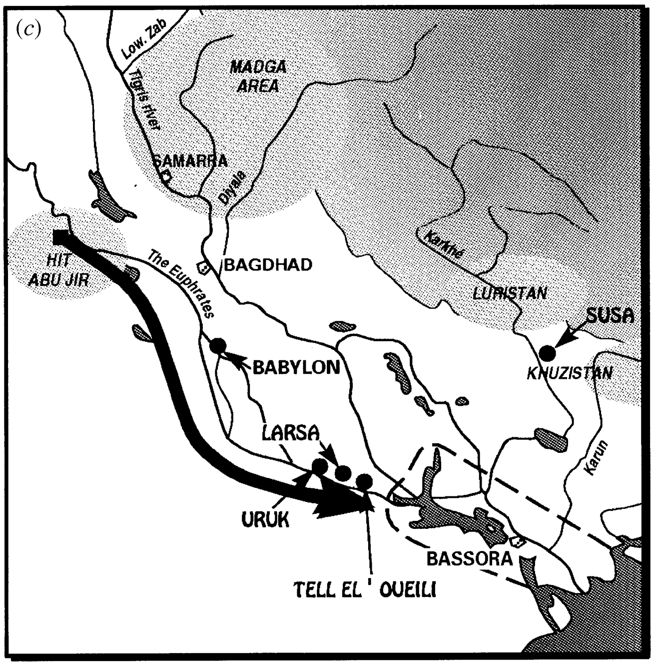

Figure 6. Changes in bitumen import routes to Tell el'Oueili through time. (*a*) Ubaid 0-1-2, 5800–4550 BC; (*b*) Ubaid 3-4, 4550–3700 BC; (*c*) Uruk, 3500–3200 BC.

signifying that the raw material was imported to Tell el'Oueili.

Fifty samples of bituminous material were analysed for biomarker patterns (steranes and terpanes) and isotopic values of asphaltenes ($\delta^{13}C$ in ‰ per PDB). The extraction of the samples with chloroform confirmed the presence of bitumen. The results of the detailed study were published in Connan *et al.* (1996). The bitumen extracted by chloroform displays different molecular and isotopic characteristics. Terpane patterns show significant molecular differences which are presented in figure 3. In some terpanes, including those of the bituminous mat (no. 132, figure 3), the oleanane molecule is observed, whereas in others (e.g. nos 134, 26, 60a, figure 3), no oleanane is detected. This molecule constitutes a unique genuine chronostratigraphic biomarker because it provides key information to trace an oil type back to a specific geological period. Oleanane, present in small quantities at the end of the Cretaceous (65 million years ago), is widespread among more recent Tertiary rocks and associated oils. This plant-derived molecule has never been observed in oil-stained reservoirs or surface oils in Iraq and Syria. However, this particular molecular structure is well known among many oils in Iran, in particular those from the Khuzestan and Fars provinces. All these oils received a contribution from the Pabdeh formation (Palaeocene–Oligocene), i.e. the famous Tertiary source rock in Iran (Bordenave & Burwood 1990; Connan & Deschesne 1996). Other samples possess very different terpane and sterane patterns, including bitumen from Luristan in Iran (Sargelu source rock), from northern Iraq (Magda region in antiquity, i.e. present-day Kirkuk area) and the very famous Hit-Abu Jir region (figure 1). Examination of isotope values on asphaltenes confirmed the different suspected sources of bitumen (figures 4 and 5).

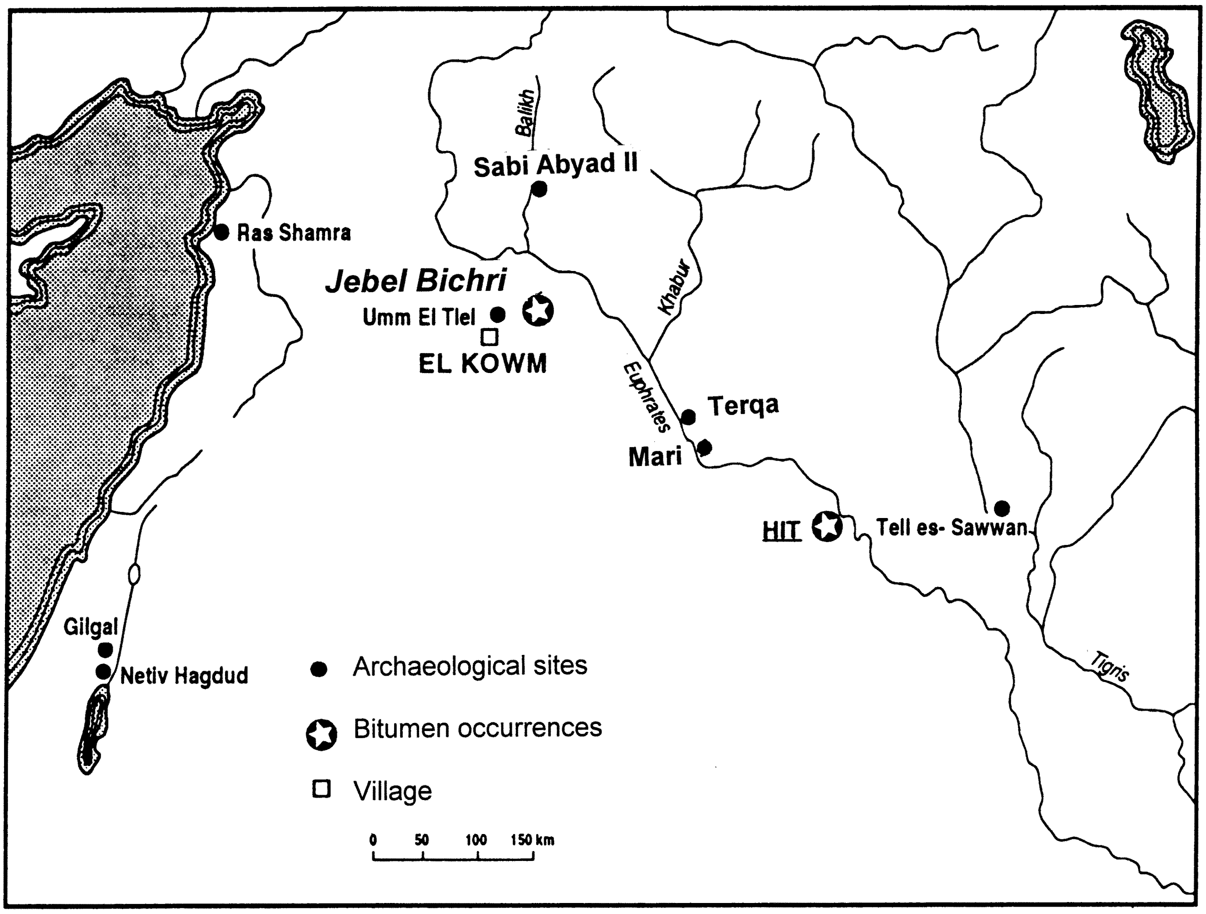

Figure 7. Map of Syria showing the location of Umm El Tlel; Jebel Bichri, Hit, Terqa and some other archaeological sites (Netiv Hagdud, Gilgal, Ras Shamra, Sabi Abyad II, Tell es-Sawwan). Mari is located close to Terqa.

The mat bitumen came from the Khuzestan province, whereas the spindle-whorl bitumen originates from Luristan (figure 6).

Between the Ubaid 0 and the Ubaid 2 periods (5800–4550 BC; figure 6), the bitumen at Tell el'Oueili was imported mainly from Iran: Luristan (Ubaid 0), or Khuzestan and Luristan (Ubaid 1 and 2). Amiet (1988) and Huot (1994) emphasized that during that period the Susian and Mesopotamian cultures lived in a kind of symbiotic relationship as a result of frequent contacts due to trade links. Bitumen was evidently part of the exchange between both civilizations.

In the Ubaid 3 period (4550–4000 BC), the Ubaid culture in Lower Mesopotamia began to expand step-by-step towards the north and pervaded the northern Halafian settlements. As this south–north current developed, the village of Tell el'Oueili began importing its bitumen from northern Iraq (perhaps the Kirkuk region, figure 6). The Iranian source was abandoned in favour of the new south–north axis.

Finally, in the last period exposed by excavations, i.e. the Late Uruk period (3500–3200 BC), a new change took place. Tell el'Oueili now obtained its bitumen essentially from Hit-Abu Jir, in Iraq (figure 6). From then on, into the third and the second millennium, Hit-Abu Jir was the main source of bitumen supply along the Euphrates (Connan & Deschesne 1998*a*), both downstream (Aqarquf, Babylon, Uruk, Larsa, Tello) and upstream (Haradum, Mari, Terqa, Habuba Kabira, Tell Sheikh Hassan, Jerablus Tahtani, Hacinebi). On his visit to the locality of Hit, the Assyrian king Tukulti Ninurta II (890–884 BC) wrote in his annals relating to one of his military campaigns: 'In front of Hit, by the bitumen (kupru) springs, the place of Usmeta stone, in which the gods speak, I spent the night' (Bilkadi 1996). Apparently the people of antiquity considered bitumen as a gift of gods, like the gems in ancient Egypt (Aufrerère 1991).

The study of bituminous substances from Tell el'Oueili revealed successive changes in the source of imported bitumen in the course of time. These variations are directly related to other major, known cultural changes recorded in those civilizations settled at the site. This example demonstrates that archaeometry of bitumen can help to reveal substantial exchanges of organic substances through trade. In the present case, the conclusions, drawn from chemical study of bitumen lumps, are in good agreement with the geopolitical changes in the area, as known from other archaeological data.

Another demonstrative example in the Gulf area, using information from several archaeological sites on Bahrain, was reported recently (Connan *et al.* 1998). It illustrates significant changes in bitumen trade routes between the Dilmun period (around 2000 BC) through the 16th century AD. Bitumen in Bahrain does not have a local source, as commonly thought, but was imported from Iraq and Iran (Luristan and Khuzestan provinces).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

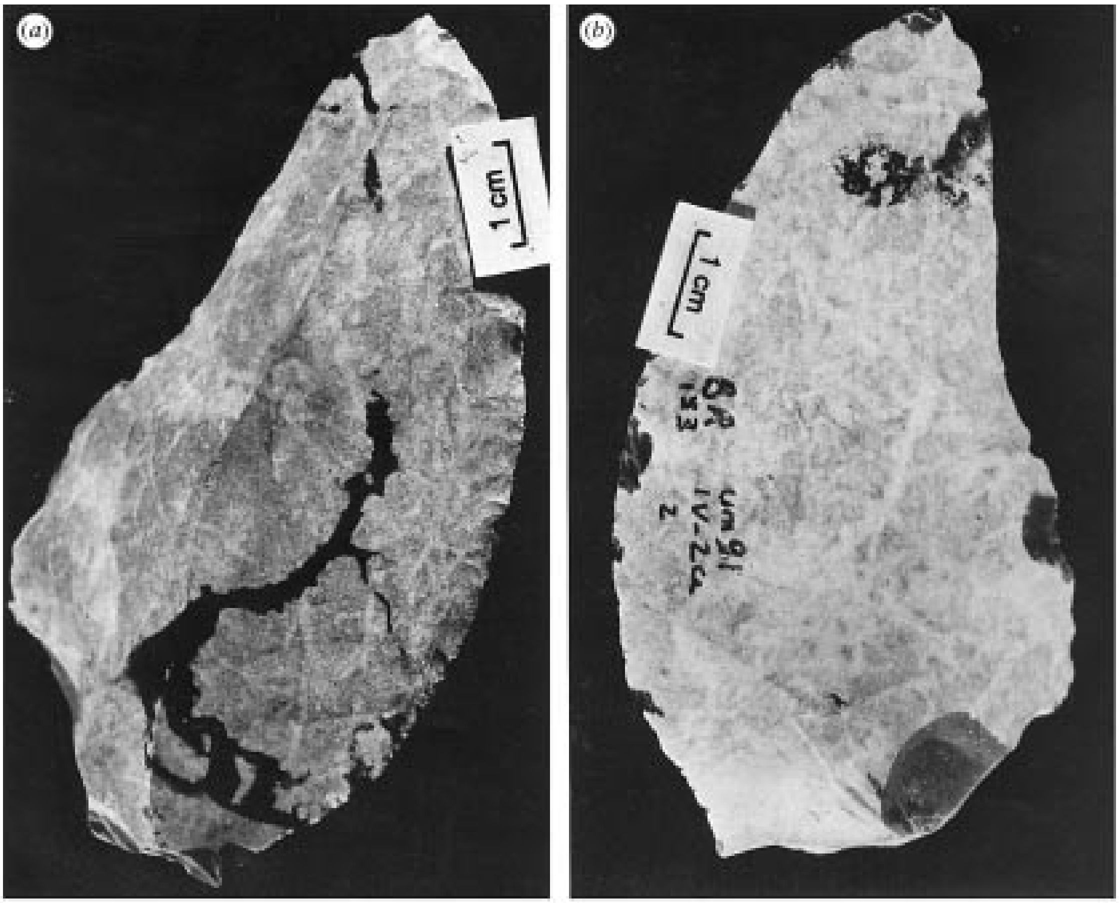

Figure 8. Photograph of a convergent scraper (*a* and *b*) from Umm el Tlel showing bitumen traces and of a lump of oil-stained sands (*c*), found in the Mousterian archaeological levels.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

(b) *Origin of bitumen used as a hafting material on Middle Palaeolithic artefacts from Umm El Tlel (Syria)*

Two Middle Palaeolithic sites, Hummal and Umm El Tlel, situated in the neighbourhood of the El Kown village in Syria (figure 7), have revealed 16 artefacts with black traces which were identified as likely bitumen (Boëda *et al*. 1996). In Umm El Tlel, only 15 pieces with black traces (figure 8) were found among 30 000 pieces uncovered in the excavations of this site since 1991. Unfortunately, the origin of the presumed bitumen could not be determined from the geochemical study of the artefacts, for several reasons (Boëda *et al*. 1996). First, the available amount of extractable bitumen was too low to obtain any isotopic data on asphaltenes. Moreover, this chloroform extract was highly depleted in hydrocarbons due to biodegradation and oxidation phenomena (Lemoine 1996) and the result gave only minute amounts of hydrocarbons for analysis. In addition, in many cases the original fossil molecular spectrum related to bitumen was obscured by contamination due to hydrocarbons in paste used for taking pictures of the implements. Lastly, SEM investigation and X-ray analysis have established that the black traces were not exclusively organic residue but also precipitated manganese oxide.

Contamination problems encountered in the first studies have initiated a more careful sampling procedure to avoid any post-sampling contamination problems. The 1996 excavation campaign on Umm El Tlel served as a test to gather representative fingerprints by chloroform extraction of flint implements. Artefacts with their surrounding soils were gathered and analysed separately.

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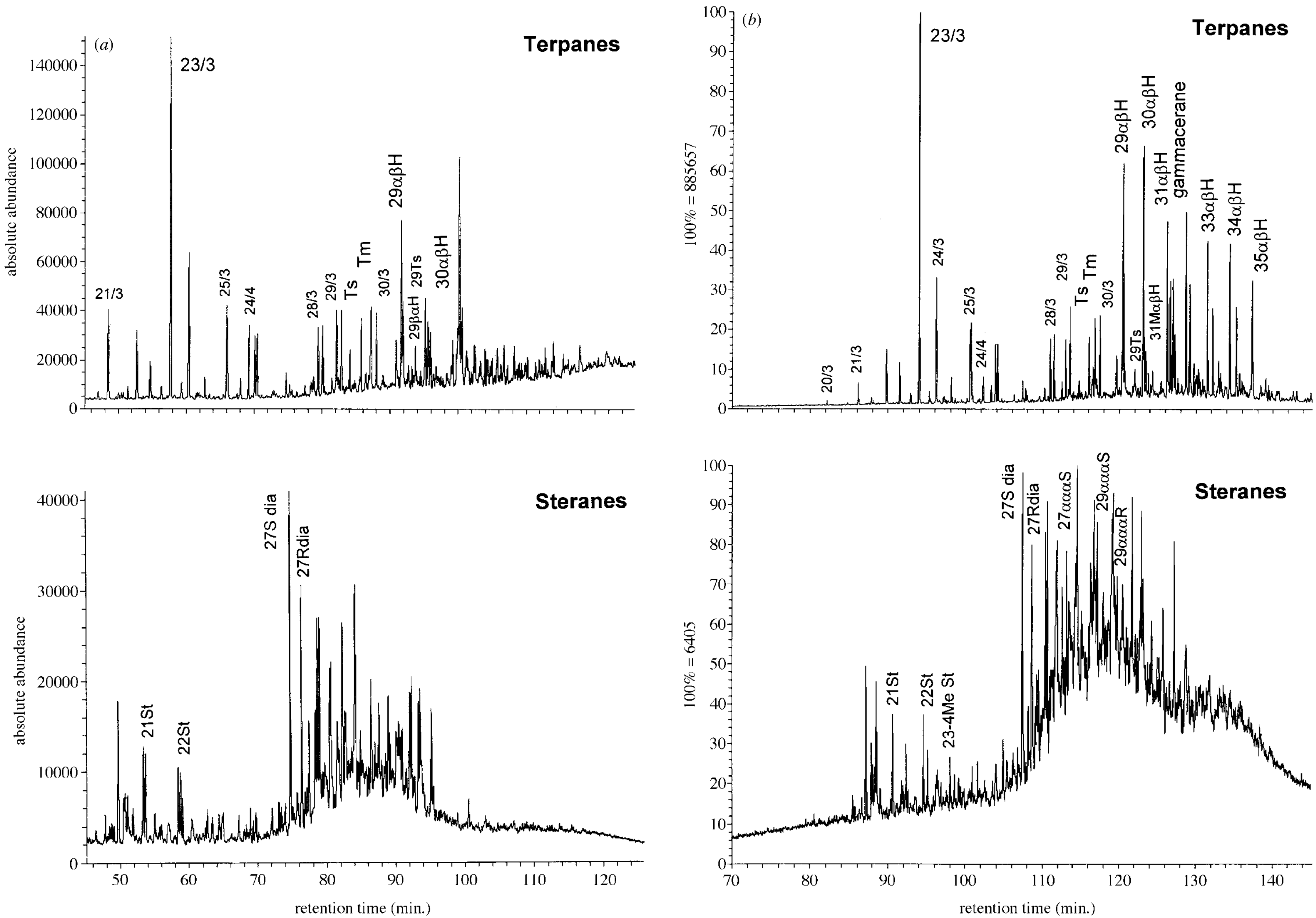

Figure 9. Comparison of the sterane and terpane patterns of an oil-stained sand (no. 1033) from the archaeological level of Umm El Tlel (*b*), and from an oil-stained rock (no. 170) at surface in the Jebel Bichri (*a*).

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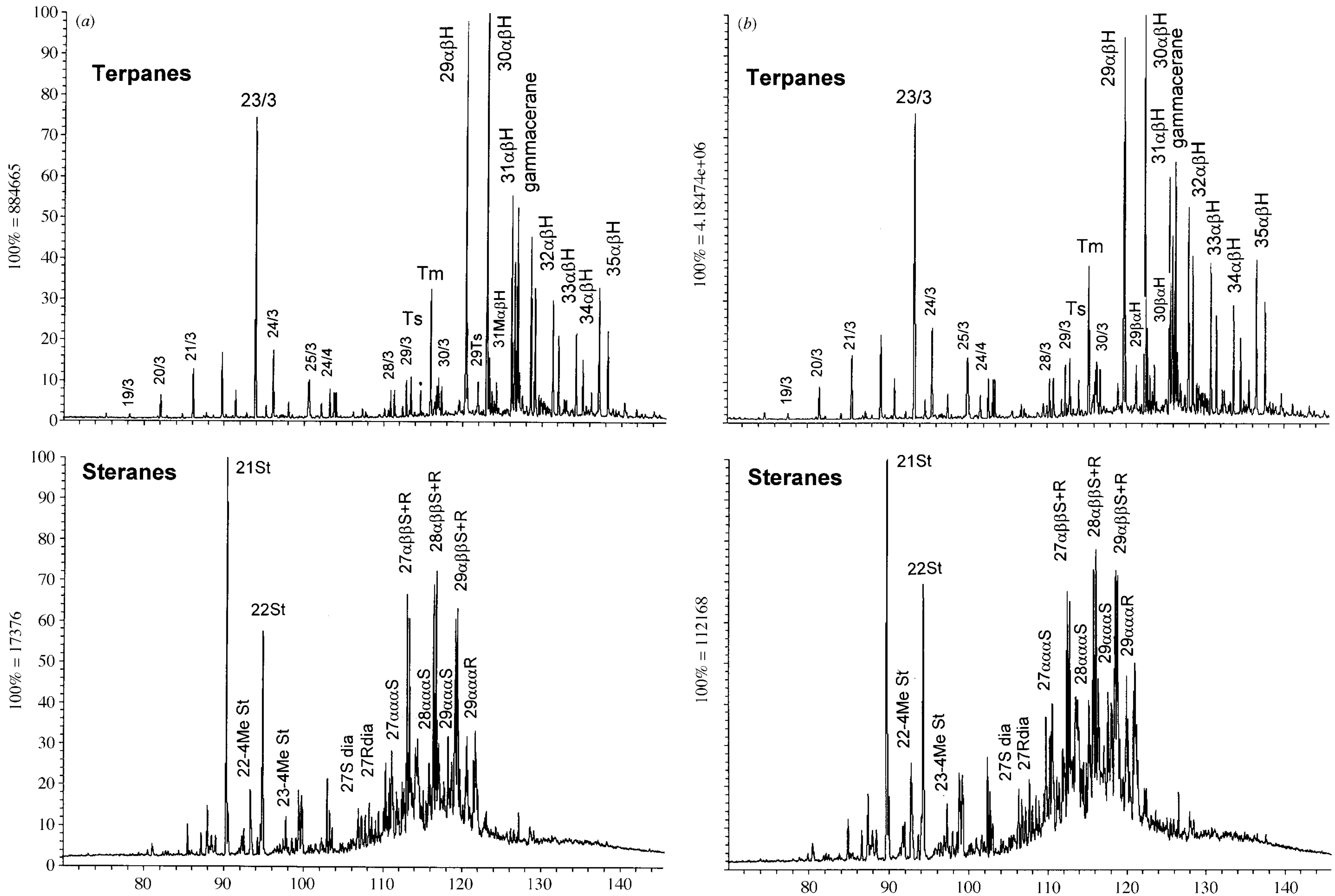

Figure 10. Comparison of the sterane and terpane patterns of an oil-stained rock (no. 1031) found 15 km north of Umm El Tlel (*b*), and of an oil-stained rock (no. 429) from the Jebel Bichri (*a*).

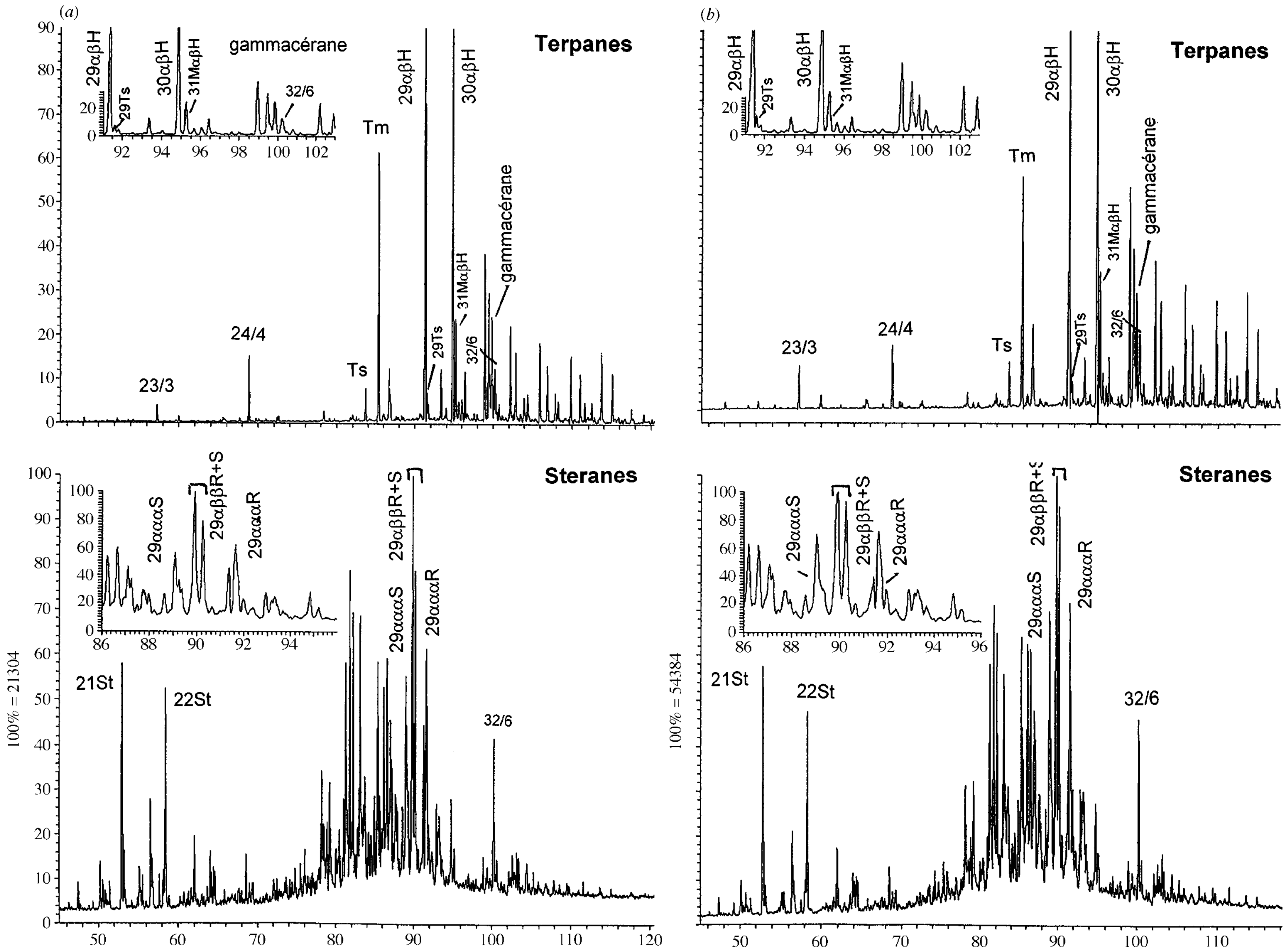

Figure 11. Comparison of sterane and terpane patterns of Mari (*a*), an archaeological site along the Euphrates and Hit (*b*), the most famous natural source of bitumen in the area.

Table 2. *Origin and quantity of bitumen found in balms of some Egyptian mummies, dated 1000 BC–400 AD with a summary of other constituents identified in the mixtures analysed*

Elf number	archaeological reference (after Macke)	date range	quantity of bitumen in % of balm/weight)	bitumen origin	ingredients identified in balm mixtures in significant concentration
255	M31-P-2	1100–800 BC	12.0	Dead Sea	4 constituents: **bitumen**, **beeswax**, **fat**?, conifer resin?
320	M39-1	750–400 BC	3.0	Dead Sea?	4 constituents: bitumen, beeswax, **fat**? conifer resin?
321	M39-3	750–400 BC	0.2	unknown—Iraq?	1 major constituent: **conifer resin**
322	M39-39	750–400 BC	0.7	Dead Sea	2 constituents: fat? conifer resin?
323	M21-1	750–400 BC	4.5	Dead Sea	3 constituents: **bitumen**, beeswax, **conifer resin**
237	M33-10	50–400 AD	18.0	Dead Sea	4 constituents: **bitumen**, beeswax, fat? **conifer resin**
238	M73-3	50–400 AD	3.0	unknown—Hit in Iraq?	3 constituents: bitumen, beeswax, **conifer resin**
249	M23-51	50–400 AD	32.0	unknown—Iraq?	4 constituents: **bitumen**, beeswax, fat? conifer resin?
250	M23-47	50–400 AD	0.2	unknown—Iraq?	2 constituents: fat? conifer resin
251	M23-47	50–400 AD	1.9	unknown—Iraq	3 constituents: bitumen, fat? conifer resin?
252	C23-4	50–400 AD	0.7	Dead Sea?	2 constituents: fat? conifer resin?
253	M16-70	50–400 AD	0.1	unknown—Dead Sea?	2 constituents: fat? conifer resin
254	M31-1	50–400 AD	11.0	Dead Sea	3 constituents: **bitumen**, **fat**? conifer resin?

Each sample gave a characteristic signature which validated the sampling and analytical procedure. Unfortunately, no flint implements with potential bitumen traces were unearthed and the study was mainly a methodology which provided blank references on soils and flint pieces. However, a lump of bituminous sand (no. 1033, figure 8), very much like the oil-stained sands outcropping in several places in the Jebel Bichri, was unearthed from the layer PM 2d of Umm El Tlel, close to layer IVa, where the black-stained artefacts were discovered. Another oil-stained sand sample (no. 1031) gathered in a wadi, 15 km north of Umm El Tlel, was also analysed as reference.

$\delta^{13}C$ (28.4 and 28.5 in ‰ per PDB) and δD (98 and 89 in ‰ per SMOW) in asphaltenes from the two oil-stained sands, namely nos 1033 and 1031, match current values known in the Jebel Bichri oil impregnations—the $\delta^{13}C$ in the asphaltenes of the latter range from −28.5 to −28.9‰ per PDB. Complementary analysis of alkanes by computerized GC/MS confirms the presumed origin of the bitumen. Both samples show striking molecular similarities with natural oil-stained sands collected from several outcrops in the Jebel Bichri, as seen in figures 9 and 10. Several diagnostic molecular parameters can be highlighted: high amounts of tricyclopolyprenanes from C_{19} to C_{30} (19/3 to 30/3) and of gammacerane with a particular Tm to Ts ratio and a relatively high concentration of C_{27}–C_{29} αββsteranes. These molecular characteristics have not been observed in the other famous bitumen occurrence of the area, namely Hit-Abu Jir. For instance, tricyclopolyprenanes are almost lacking in the Hit bitumen, the Tm to Ts ratio is much higher and C_{27}–C_{29} steranes exhibit a very different pattern (figure 11). During the third millennium, the Hit bitumen (figure 7) was exported all along the Euphrates, especially in Mari, close to Terqa (figure 7), as illustrated in figure 11.

To summarize, although the bitumen from Hit was extensively exported in antiquity, especially by boat, this bitumen source has not been found in the Palaeolithic excavation of Umm El Tlel. In a wadi 15 km north of Umm El Tlel, as well as in Umm El Tlel layer PM 2d, oil-stained sands from the Jebel Bichri have been clearly identified. This discovery indicates that the bitumen used in Umm El Tlel in Mousterian times was from a regional source, located nearly 50 km from the Umm El Tlel settlement. This conclusion is consistent, since at that prehistoric time, bitumen was necessarily transported in low quantities (several kilograms). The sample, found in the wadi where no oil-stained outcrops occur, may have been lost on the transport path. No direct evidence of occurrence of this bitumen in Palaeolithic artefacts has been obtained so far, due to the lack of suitable samples. However, what is undoubtedly established is that the bitumen from the Jebel Bichri was brought to Umm El Tlel during Palaeolithic times. We are hopeful that forthcoming excavation campaigns will provide suitable material to complete the story.

(c) *Geochemical analysis of balms from Egyptian mummies (1000 BC–400 AD): occurrence of bitumen, conifer resins and beeswax*

The origin of the black colour on mummies has always been a subject of debate. Some years ago, chemical studies were undertaken to find a solution to this controversial problem. Several studies (Rullkötter & Nissenbaum 1988; Connan & Dessort 1989, 1991) using molecular tools, and especially sterane and terpane fingerprints, have definitely

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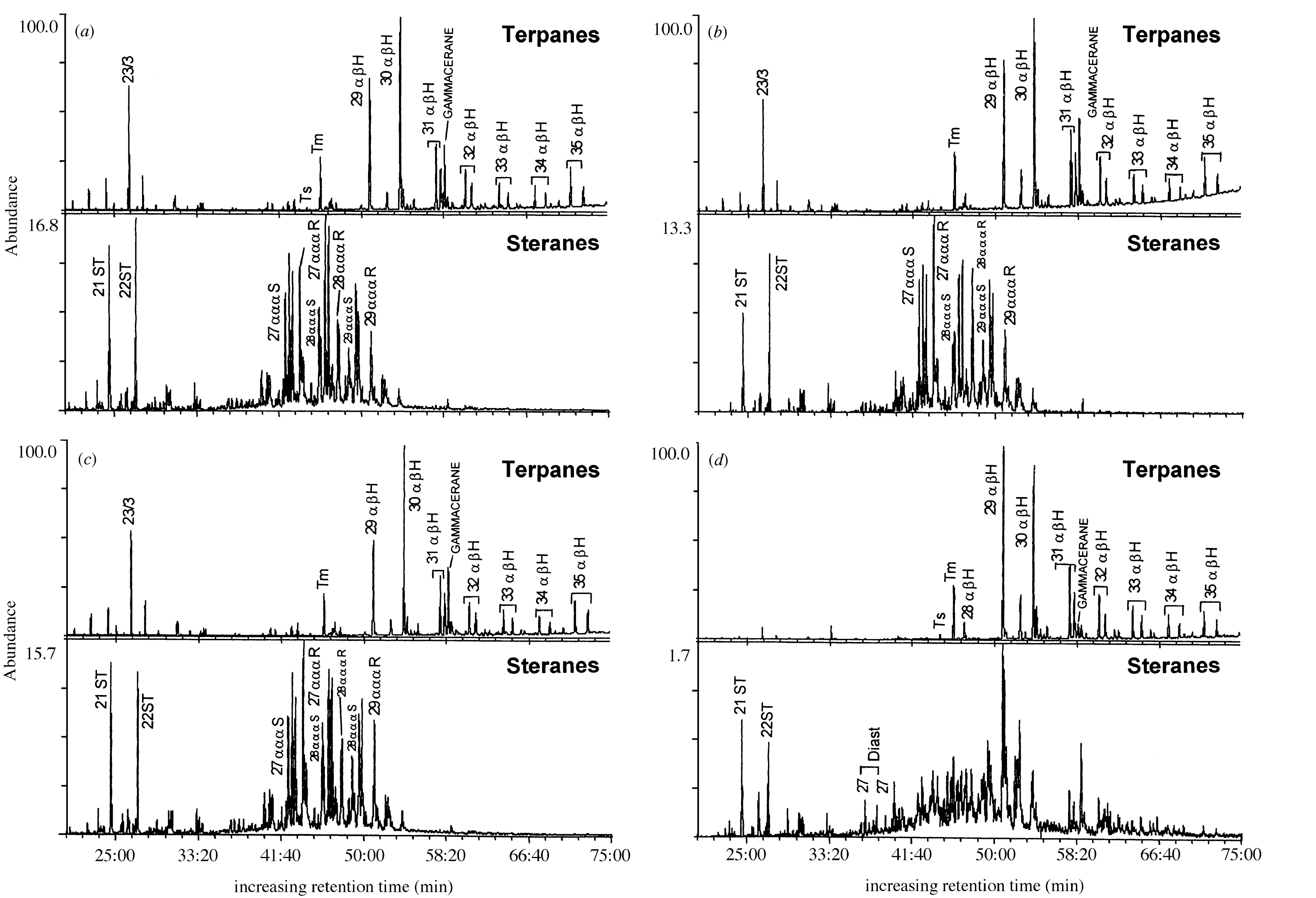

Figure 12. Sterane and terpane patterns of some balms of Egyptian mummies: comparison to the very famous source, namely the Dead Sea (*a*). Samples 255 (*b*) and 254 (*c*) show the typical molecular pattern of the Dead Sea bitumen, whereas sample 249 (*d*) contains a bitumen, from a different source.

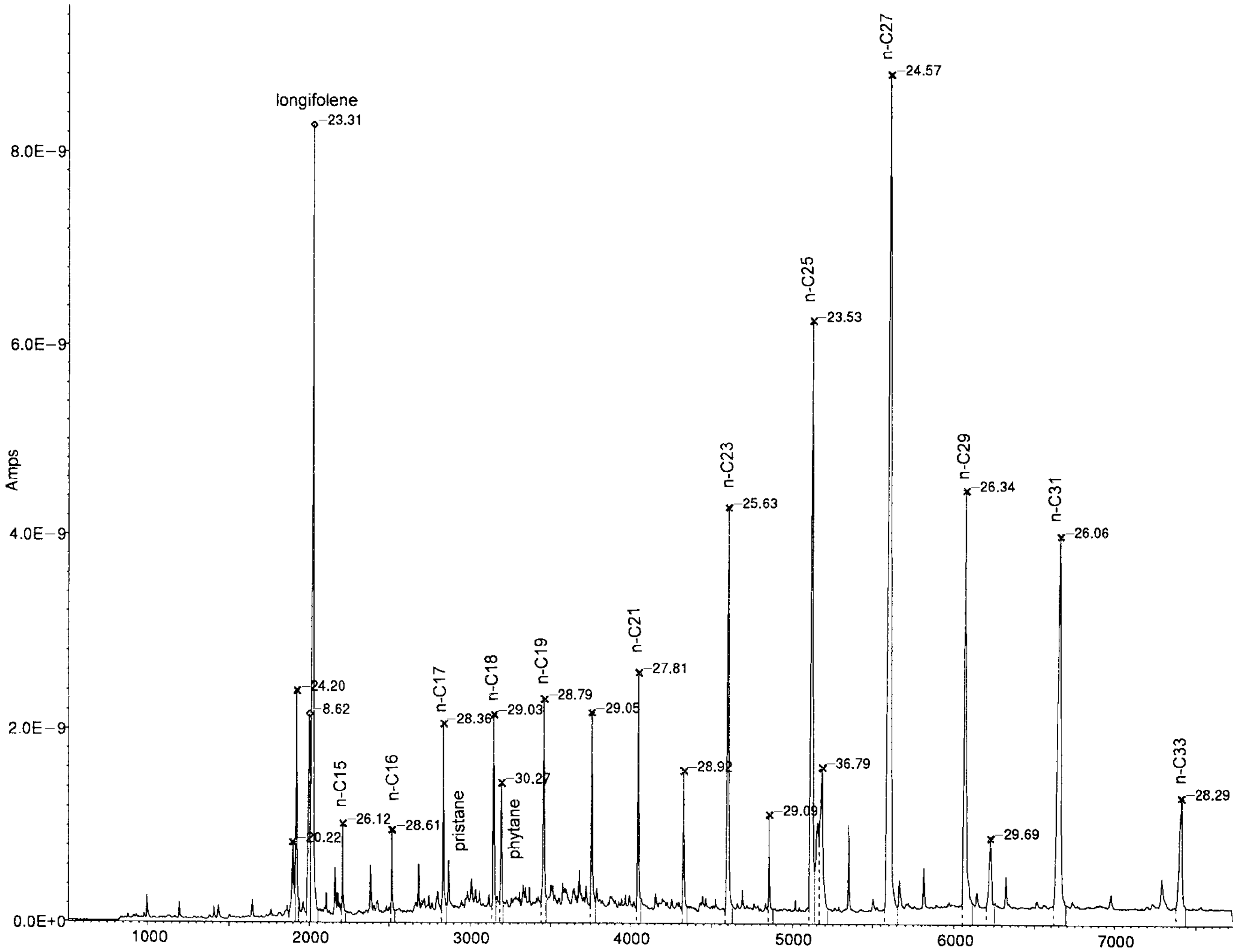

Figure 13. Example of GC/C-IRMS analysis of the C_{15+} alkanes from the balm of a mummy, dated 750–400 BC.

proven that bitumen occurs in variable quantities in balms prepared by ancient Egyptians. Quantities of bitumen range from 30% to almost zero (Connan & Dessort 1991; Connan 1998) in balms from mummies dating from 1000 BC to 400 AD. Presently little data is available on older mummies as it is difficult to collect samples for analysis. As a result of our recent study (Connan 1998) on 20 balms from Egyptian mummies, mainly from the Valley of the Queens and not older than 1000 BC, it appears that bitumen from the Dead Sea is the most common bitumen found in balms. Bitumen from the Dead Sea was exported to Egypt from the fourth–third millennium BC (Connan *et al.* 1992). Obviously, this fossil product was still strategic for Egypt at the end of the Ptolemaic period. For example, in 30 BC Cleopatra lost her entire fleet in Alexandria during conflict with the Nabataeans from Petra (Frain 1998). They were extremely angry with the Queen of Egypt who had put an end to their monopoly on the exploitation of Dead Sea bitumen and consequently one of their sources of prosperity. They organized a raid on Alexandria and set fire to Cleopatra's fleet, which was completely burnt. However, even if the bitumen of the Dead Sea is the most common bitumen identified in balms (table 2), other sources which have not been definitely identified were also used (Rullkötter & Nissenbaum 1988; and also sample no. 249 in figure 12). As suggested by molecular criteria, namely sterane and terpane patterns, a likely candidate may again be the bitumen from Hit in Iraq, but other potential sources must also be considered: in Egypt (Mons Petrolus in Jebel Zeit close to the Red Sea), in Sinai and also far away, maybe in Yemen (the country of Punt for the ancient Egyptians?). The last quoted possibilities have not yet been cross-checked due to the lack of reference samples.

The analysis of balms from Egyptian mummies reveals complex molecular mixtures which are diagnostic of other classes of products mixed with bitumen to prepare each balm. Gas chromatography, GC/MS analysis and GC/C-IRMS (Evershed *et al.* 1994, this issue; Rieley *et al.* 1993) of C_{15+} alkanes and C_{15+} aromatics, have made it possible to differentiate diagnostic molecular structures originating from different sources. Figure 13 shows an example of GC/C-IRMS on the C_{15+} alkanes from the mummy M21-1, dated to the Intermediate period (750–400 BC). $\delta^{13}C$ values of individual compounds clearly reflect two major contributions: plant-derived products (longifolene and associated terpenes with $\delta^{13}C$ between −20.2 and −24.3‰ per PDB, odd *n*-alkanes between *n*-C_{23} and *n*-C_{31} with $\delta^{13}C$ between −23.5 and −26.1‰ per PDB) and petroleum-related structures (pristane and phytane with $\delta^{13}C$

around 30.0‰ per PDB, *n*-alkanes between *n*-C_{16} and *n*-C_{19} with $\delta^{13}C$ between −28.4 and −29.0‰ per PDB). The latter values are typical of the Dead Sea bitumen.

A discussion of these results, presented elsewhere (Connan 1998), is out of the scope of the present paper focused on bitumen. Nevertheless, some outstanding results are summarized in table 2. These results show that the composition of the mixtures prepared to produce various balms is highly variable and that no well-defined recipe was systematically applied. One of the major conclusions of the study, restricted to mummies dated between 1000 BC and 400 AD, is that the molecular signatures are extremely diverse from one sample to another and that conifer resin is the key ingredient from which most balms were prepared. In our study, no turpentine resin has been identified so far in the balms analysed. In fact, the most common resin appears to be conifer resins, which were widespread in the ancient world especially around the Mediterranean Sea and were, in addition, the cheapest of all the available resins (Faure 1987).

5. CONCLUSION

Bitumen use, currently recorded in excavations from the Near East and the Gulf, dates back to Palaeolithic times. An example from the Mousterian of Umm El Tlel in the Syrian desert has been discovered and studied.

Molecular typology of bitumens, based on detailed patterns of biomarkers, permits identification of their origin and subsequently to trace their trade routes. Bitumen is a raw material which has been exported over long distances (e.g. from Iran to Bahrain).

Bitumen was used by Egyptian embalmers for mummification. This material, used to blacken the mummy, was mixed with other ingredients such as conifer resin and beeswax. These data are only valid for mummies dating from 1000 BC to 400 AD. Older mummies have not been analysed so far and consequently this information should not be extrapolated to them.

I thank E. Boëda, C. Philips, S. Ashkan, J.-L. Huot, M. Macke, A. Caubet and O. Deschesne for providing samples and archaeological information for the examples quoted. I am also indebted to D. Dessort for his help in identifying some molecular structures, especially in the balms of ancient Egyptian mummies. My thanks are also due to all the analysts of Elf EP's Technical Division who have contributed to the analytical work. The final version of the manuscript has largely benefited from the critical comments of G. Eglinton and P. Farrimond. The unknown archaeologist who reviewed the archaeological aspects of my paper is also acknowledged for his helpful comments.

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Discussion

R. P. Evershed (*University of Bristol, UK*). In your studies of archaeological bitumens of petroleum origin, you are clearly relying on databases of likely sources compiled for the purpose of petroleum exploration. Could you indicate any allowances you have to make for complications that might arise from the operation of degradative processes (such as oxidation), arising in the bitumens due to long-term exposure at archaeological sites?

J. Connan. Weathering processes including water-washing, biodegradation, photo-oxidation and oxidation are indeed modifying the gross composition of the bitumen, entailing a marked increase of polar fractions, namely resins, asphaltenes and insoluble residues. During that alteration process, C_{15+} aromatics tend to disappear and polar by-products are generated. Fortunately, C_{15+} alkanes are much less affected by these weathering processes; consequently steranes and terpanes may be used to correlate bitumen from archaeological samples to their geological sources, namely natural asphalts. According to our experience, this class of biomarkers provides reliable genetic fingerprints which may be used to find the source of the archaeological bitumen.

L. Biek (*London*). It is difficult to understand how structures built with bitumen mortars (e.g. the Ishtar Gate) have been able to survive the high temperatures of the region without movement and loss of stability. Have you found any differences, at molecular level, between the bitumen in the state in which it would have been applied and the state in which it is now found?

J. Connan. Your question refers to weathering processes that alter the original bitumen which has been used to prepare the archaeological mixtures. In fact, these alteration processes, which include biodegradation, water-washing and oxidation, modify the gross composition (neogenesis of resin sand asphaltenes) and the molecular spectrum of aromatics. These alterations are less effective on alkanes which are much more resistant. This fraction is preferentially used as a reference fingerprint to establish archaeological bitumen–natural asphalt correlations and trace back the source of the bitumen used to prepare the archaeological mixture. In fact, secondary effects, linked to weathering, are of limited extent with the alkanes. This fraction is therefore the most suitable as a characteristic genetic tracer.

G. Eglinton (*University of Bristol, UK*). Have you been able to extend your type of approach to bitumens outside of the Middle East—there surely must have been trading of bitumen over vast distances along trader routes within Asia, the Far East, etc.—even in very early times?

J. Connan. Most of my work has been related to typing of archaeological bitumen in the Middle East (Iraq, Iran, Syria, Israel), the Gulf (Kuwait, Bahrain, the Emirates), Oman (South of Mascate) and Pakistan (Mehrgart). Within these studies, no evidence of import of bitumen from Asia and the Far East has been found. In particular, we were expecting some bitumen from Pakistan in localities along the coast south of Mascate, but our study turns out to prove that the bitumen found there came from Iraq. Other goods are known to have been brought from Asia: for instance Ming pottery (celadon) may be collected on the surface of the Tell of Qal'at al-Bahrain on Bahrain Island.